1963

Autoxidation of carbanions: occurrence of electron-transfer reactions

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Recommended Citation

Janzen, Edward George, "Autoxidation of carbanions: occurrence of electron-transfer reactions " (1963). *Retrospective Theses and Dissertations*. 2509.
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JANZEN, Edward George, 1932-
AUTOXIDATION OF CARBANIONS. OCCURRENCE
OF ELECTRON-TRANSFER REACTIONS.

Iowa State University of Science and Technology
Ph.D., 1963
Chemistry, organic

AUTOXIDATION OF CARBANIONS.
OCCURRENCE OF ELECTRON-TRANSFER REACTIONS

by

Edward George Janzen

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1963

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"How is bread made?"

"I know *that*!" Alice cried eagerly. "You take some flour"

"Where do you pick the flower?" the White Queen asked. "In a garden, or in the hedges?"

"Well, it isn't *picked* at all," Alice explained; "it's ground -"

"How many acres of ground?" said the White Queen. "You mustn't leave out so many things."

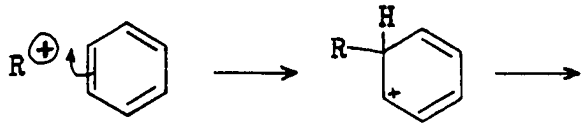
Lewis Carroll

I. INTRODUCTION

Chemistry of today is becoming the practice of electron mechanics. Whereas it sufficed for the Fathers of Chemistry to be sure of the atomic and molecular constitution of the products of a small number of reactions the emphasis has swung to puzzling out electronic mechanisms of as many transformations as possible sometimes merely to allow classification. The largest part of organic chemistry has been mechanistically classified into electrophilic or nucleophilic reactions.

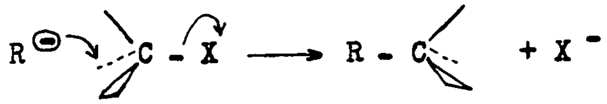
Electrophilic attack:

(1)



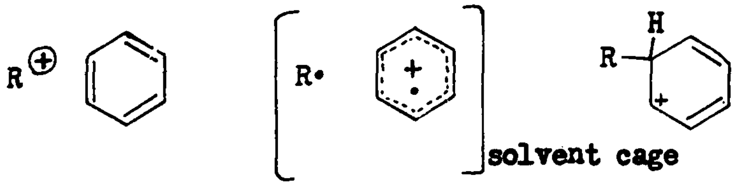
Nucleophilic attack:

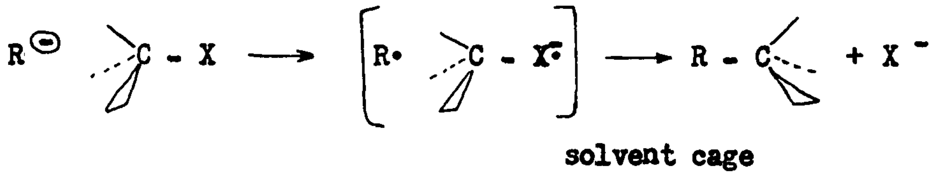
(2)



The net result is the very popular curved arrow-directing two-electron transfer. It would appear that one-electron transfer mechanisms have not been given equal consideration. Feasible mechanisms for electrophilic and nucleophilic reactions should include

(3)



(4) 

Evidence suggesting that free radical intermediates are produced via the above formulation is the discovery of free radical species in solutions of aluminum trichloride under Friedal Crafts conditions (1) and the isolation of 2,3-dimethyl-2,3-diphenylbutane from certain Wurtz reactions run in cumene (2).

This study is concerned with the reaction of oxygen with carbanions sometimes considered a two-electron transfer process.

(5) $$R^{\ominus} + \overset{+}{\ddot{\underset{\cdot\cdot}{O}}} - \overset{-}{\ddot{\underset{\cdot\cdot}{O}}}: \longrightarrow R - \ddot{\underset{\cdot\cdot}{O}} - \ddot{\underset{\cdot\cdot}{O}}:^{-}$$

The mechanism most consistent with the results in this thesis involves one-electron transfer steps:

(6) $$\begin{tikzcd} R^{\ominus} + \cdot\ddot{\underset{\cdot\cdot}{O}} - \ddot{\underset{\cdot\cdot}{O}}\cdot \arrow[r] & \left[R\cdot + :\ddot{\underset{\cdot\cdot}{O}} - \ddot{\underset{\cdot\cdot}{O}}\cdot^{-}\right]_{\text{solvent cage}} \arrow[d] \\ & R\cdot \xrightarrow{O_2} ROO\cdot \xrightarrow{R^{\ominus}} ROO^{-} \end{tikzcd}$$

The occurrence of one-electron transfer from carbanions to common charge-transfer acceptors has been discovered and the wide generality of the reaction investigated.

(7) $$R^{\ominus} + A \longrightarrow R\cdot + A^{\overline{\cdot}}$$ A = <u>e.g.</u>, nitrobenzene

(8) $$R^{\ominus} + A \longrightarrow R^{\overline{\cdot}} + A^{\overline{\cdot}}$$

II. LITERATURE

A. Carbanion Reactions

A detailed literature review of the reactions of oxygen with carbanions was made by A. J. Moye in 1961 (3). Of necessity the literature discussed in this section will contain only selected topics concerning recent oxidation studies in various solvents, stable free radicals and electron-transfer processes. In part the choice in subject matter will reflect the author's past and present interests during the course of this study.

The classic solvents for carbanion reactions of organometallics have been ethers which suitably solvate the reagents made *in situ* from the free metal and an organohalide. A more highly ionizing medium is required to produce carbanions from their conjugate acids. Although sodium ethoxide in absolute ethanol is a suitable solvent system for the production of many enolate anions in alkylation reactions (4), sodamide in liquid ammonia (5), *t*-butyl alcohol containing potassium *t*-butoxide (6), or benzyltrimethylammonium methoxide (Triton B) in pyridine (7) have been used to ionize more weakly acidic compounds. The most useful solvents for ionic organic reactions including carbanion formation are dipolar aprotic solvents such as dimethyl sulfoxide, dimethylformamide and sulfolane (8).

Zaugg and co-workers studied the effect of the addition of small quantities of polar substances on the rate of alkylation of the sodium enolates of malonic esters in benzene (9). They found rate enhancement to be large when dipolar aprotic solvents were used, *e.g.*, rates for hexamethylphosphoramide, pyridine-N-oxide, dimethyl sulfoxide and dimethylformamide were 21, 13, 6.3 and 5.8 times faster than the same reaction in benzene.

Cram et al. (10) reported rate enhancement in potassium methoxide catalyzed racemization reactions to be of the order of 10^9 in dimethyl sulfoxide as compared to the same reaction in methanol. Since the appearance of Cram's early observations numerous reactions involving anions have been found to proceed at faster rates and produce better yields in dipolar aprotic solvents than in previously used solvents. A review on the topic of solvation in dipolar aprotic solvents by Parker (8) contains a list of reactions which can be run to advantage in these solvents.

It is thought that the higher reactivity of anions in dipolar aprotic solvents is due to a lower degree of solvation in these solvents. As a result of this effect anions are oxidized at a mercury electrode at lower potentials in aprotic dipolar solvents than in water. Only one series of examples is mentioned by Parker (8) studied by Kolthoff and Coetzee (11) who made a comparison of the potentials observed in water or acetonitrile for hydroxide, halides and thiocyanide.

The base-catalyzed autoxidation of mercaptans has been studied in alcohol, ethers and dimethylformamide (DMF) by Wallace and Schriesheim (12). The rate was found to be first order in mercaptan and increased in solvent mixtures containing DMF. Stronger bases also increased the rate (sodium t-butoxide $>$ ethoxide $>$ methoxide and sodium $>$ potassium $>$ rubidium $>$ cesium t-butoxide). An electron transfer mechanism was suggested involving dimerization of thiyl radicals (12, 13),

(9) $RSH + B^- \longrightarrow RS^- + BH$

(10) $RS^- + O_2 \longrightarrow RS\cdot + \cdot O_2^-$

(11) $RS^- + \cdot O_2^- \longrightarrow RS\cdot + O_2^=$

(12) $2RS\cdot \longrightarrow R\text{-}SSR$

(13) $O_2^= + BH \longrightarrow OH^- + B^- + \frac{1}{2}O_2$
$(HO_2^- + B^-)$?

which agreed with the overall stoichiometry observed.

(14) $2RSH + \frac{1}{2}O_2 + B^- \longrightarrow R\text{-}S\text{-}S\text{-}R + OH^- + BH$

The assumption was made that the mercaptan was completely ionized and that $\cdot O_2^-$ and $O_2^=$ existed only at steady state concentrations. From these assumptions first order kinetics could be derived.

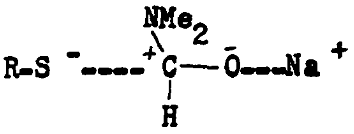
(15) $$\ln\left[(RSH) / (RSH)_o\right] = kt$$

The rates of oxidation of various mercaptans in methanol were approximately in the order of the expected stabilities of the anion, although benzylmercaptan oxidized almost twice as fast as n-butyl mercaptan in spite of the fact that the former is more acidic than the latter by 2 pK_a units; in methanol, benzyl mercaptan $>$ n-butyl mercaptan $>$ p-aminothiophenol $>$ cyclohexyl mercaptan $>$ thiophenol $\gg$ p-nitrothiophenol. p-Nitrothiophenol was stable to oxygen but its attempted oxidation in DMF was not reported.

A mechanism involving electron-transfer from mercaptide ion to oxygen seems reasonable (Equation 9). However, there seems to be no justification for the assumption that a rapid electron transfer occurs between mercaptide anion and superoxide anion (both negatively charged species) or that base cleavage of peroxide is fast to yield hydroxide and oxygen, except that these steps produce the correct stoichiometry.

In a further study of autoxidation in DMF the picolines were oxidized in the presence of potassium t-butoxide under 4 atm. oxygen pressure and at ambient temperatures to produce 59%, 70% and 80% yields of α-, β- and γ-picolinic acids after 10 min. (14). No dimeric products were found. The oxidation of pyrrole was observed in t-butyl alcohol containing potassium t-butoxide but products could not be identified.

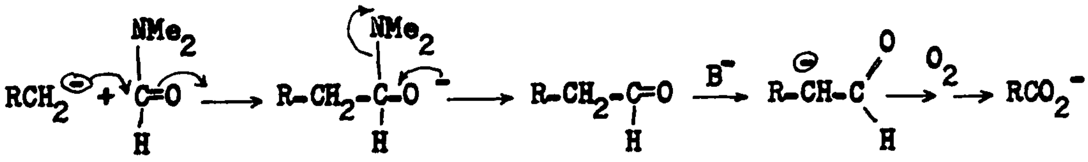
In discussing the effect of solvent on the rate of autoxidation of mercaptide ions the following solvated anion was drawn (13).



$$R\text{-}S^{-}\text{----}{}^{+}\overset{NMe_2}{\underset{H}{C}}\text{—}\bar{O}\text{---}Na^{+}$$

I

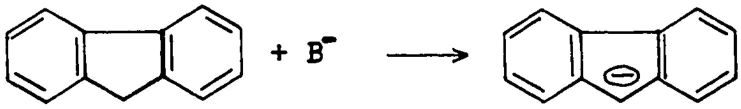
The possibility exists in the oxidation of carbanions in DMF that a direct nucleophilic displacement occurs, which yields a new carbanion much more vulnerable to oxidation. This reaction would also account for the selectivity in product formation in DMF in oxidation of picolines.

(16) 

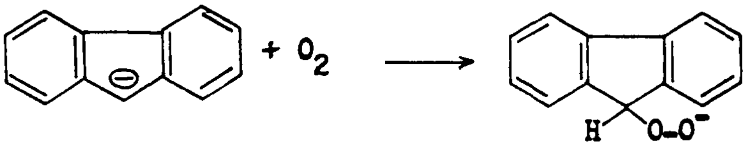
(picolines)

In a series of papers on the reactions of active methylene compounds in pyridine Sprinzak has described the isolation of various hydroperoxides from base-catalyzed autoxidation reactions (7). Whereas ring substituted fluorene derivatives gave high yields of substituted fluorenones in the presence of benzyltrimethylammonium hydroxide (Triton B) absorbing approximately 1 mole of oxygen per mole of fluorene, 9-substituted fluorenes produced good yields of hydroperoxides at 0° under the same conditions. At 40° only 0.5 mole of oxygen was absorbed and the carbinols were isolated. These observations prompted Sprinzak to suggest the following mechanism:

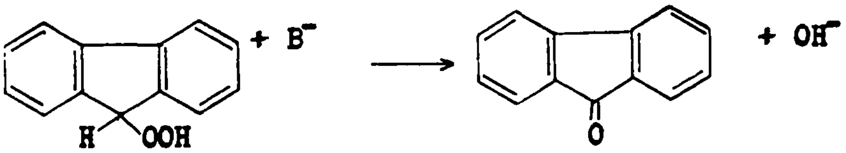
(17)



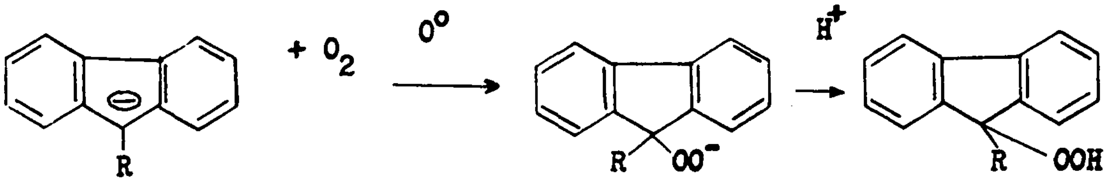
(18)



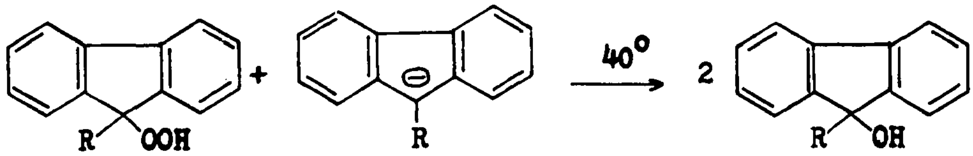
(19)



(20)



(21)



It was found that the rate of the latter reaction decreased according to the sequence R = phenyl $>$ benzyl $>$ alkyl. Since the overall rate of reaction was not altered by the addition of ferric chloride, manganese dioxide, arsenic trioxide, quinone or picric acid, the conclusion was made that the reaction of carbanion with oxygen was ionic. However it was also shown that the hydroperoxide reaction product decreased the rate of oxidation of the hydrocarbon. A 9:1 mixture of 9-hydroperoxy-9-benzylfluorene to 9-benzylfluorene oxidized slower than the same concentration of hydrocarbon in the absence of the hydroperoxide.

Evidence for an electron transfer mechanism in base-catalyzed oxidations will be presented in this thesis. The proposed oxidation steps will be:

$$(22) \qquad R^{\ominus} + O_2 \longrightarrow R\cdot + \cdot O_2^{-}$$

$$(23) \qquad R\cdot + O_2 \longrightarrow R\text{-}OO\cdot$$

$$\begin{array}{lll} (24) \qquad & ROO\cdot + R^{\ominus} \longrightarrow & ROO^{-} + R\cdot \\ & & \downarrow \\ & & \text{products} \\ & & \uparrow \\ (25) \qquad & ROO\cdot + \cdot O_2^{-} \longrightarrow & ROO^{-} + O_2 \end{array}$$

The observations made by Sprinzak (7) are in accord with this mechanism if radical initiation is very fast and if inorganic ions can not hinder the reaction of fluorenyl free radicals with oxygen. The rate retarding effect of added peroxide suggests an interesting feature in accord with a free radical mechanism. In the basic solution the hydroperoxide undoubtedly is ionized and the following chain breaking steps may be important:

$$(22)\qquad R^{\ominus} + O_2 \longrightarrow R\cdot + \cdot O_2^{-}$$

$$(26)\qquad R\cdot + ROO^{-} \longrightarrow R^{\ominus} + ROO\cdot$$

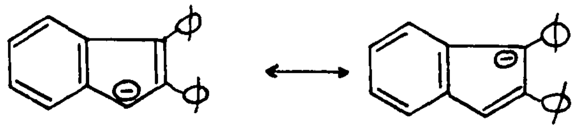
$$(25)\qquad ROO\cdot + \cdot O_2^{-} \longrightarrow ROO^{-} + O_2$$

The crucial step is the reversible electron transfer between radical and hydroperoxide anion. In low concentrations of peroxide electron transfer from carbanion to peroxy radical to yield peroxide anion (Equation 24) may be favored but the reverse may be true at high concentrations of peroxide anion (Equation 26). The electron affinities of HOO· and $(C_6H_5)_3C\cdot$ have been reported as 70 and 48 kcal. (15). It might be expected that the electron affinity of 9-benzylfluorenyl would be greater than that for triphenylmethyl and possibly the electron affinity of 9-benzylfluorenylperoxy is less than for hydroperoxy.

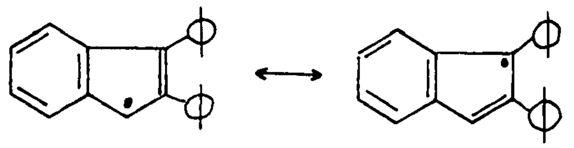
Then:

$$\begin{array}{lll} ROO\cdot + e \longrightarrow ROO^{-} & & < 70 \text{ kcal.} \\ R^{\ominus} + \;>48 \longrightarrow R\cdot + e & & \\ \hline ROO\cdot + R^{-} \longrightarrow ROO^{-} + R\cdot & \ll 22 & \end{array}$$

2,3-Diphenylindene gave approximately equal amounts of products as a result of reaction at both carbon 1 and 3.



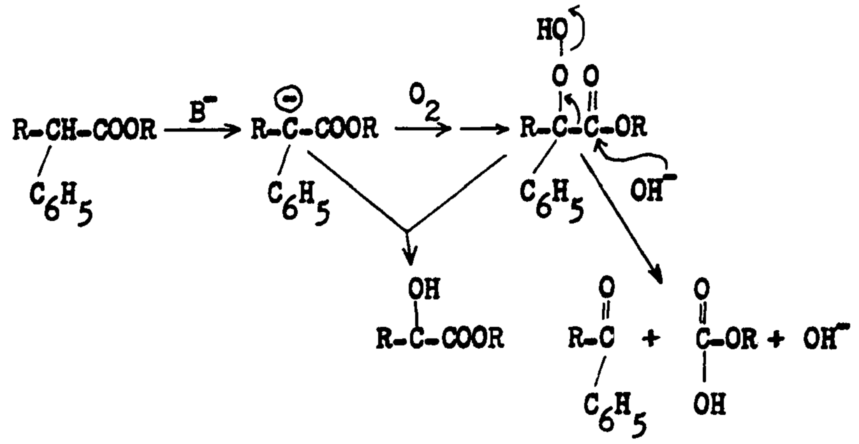
In predicting the products via a free radical pathway the tertiary carbanionic site might be expected to react exclusively, because of the accepted greater stability of free radicals at a tertiary than at a secondary carbon atom.



Reasoning after the fact, this reaction can be considered an example of a free radical reacting at the more reactive of two possible sites (an "ambident" radical), *i.e.*, although the 3-position may have a higher odd electron density than the 1-position, the reaction at the 1-position with oxygen has the lower activation energy and competes favorably with the reaction at the 3-position. Addition and co-oxidation reactions of thiols with substituted hexadienes yield products in accord with these interpretations (16).

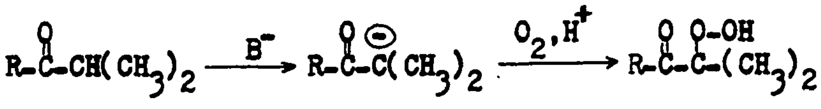
The base-catalyzed oxidation of the esters of diarylacetic and 2,3-diarylpropionic acids gave *α*-hydroperoxyesters, *α*-hydroxyesters and ketones (17).

(27)



In this study Sprinzak (17) concluded that an α-aryl group was necessary for peroxide formation since a purely aliphatic ester, ethyl isobutyrate, failed to react under the conditions used. This is in agreement with the observation made by Russell, Moye and Nagpal (18) that carbanions stabilized by phenyl groups usually oxidized faster than the same carbanions not similary substituted.

However Gersmann *et al.* (19) reported the preparation of α-hydroperoxides of ketones and esters by the use of solid potassium *t*-butoxide suspended in aprotic solvents, *e.g.*, toluene. Isolated yields of approximately 50% were obtained from compounds such as di-isopropyl ketone, *p*-methoxyisobutyrophenone and *t*-butyl phenylacetate.

(28) 

$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH(CH_3)_2 \xrightarrow{B^-} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{\ominus}{C}(CH_3)_2 \xrightarrow{O_2,H^+} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O\text{-}OH}{\overset{|}{C}}\text{-}(CH_3)_2$$

(29) 

$$C_6H_5\text{-}CH_2\text{-}COOC(CH_3)_3 \longrightarrow C_6H_5\text{-}\overset{O\text{-}OH}{\overset{|}{C}H}\text{-}COOC(CH_3)_3$$

A detailed study of the mechanism of the base-catalyzed autoxidation of *p*-nitrotoluene and derivatives was made by Moye (3). *p*-Nitrotoluene oxidized in *t*-butyl alchol containing potassium *t*-butoxide to yield only *p*,*p*'-dinitrobibenzyl and *p*-nitrobenzoic acid in varying proportions depending on oxygen pressure, rates of agitation, and concentration of reactants. The stoichiometry was best described by the following equations:

$$(30)\quad 2NO_2\text{-}C_6H_4\text{-}CH_2K + O_2 \longrightarrow NO_2\text{-}C_6H_4\text{-}CH_2\text{-}CH_2\text{-}C_6H_4\text{-}NO_2 + K_2O_2$$

$$(31)\quad NO_2\text{-}C_6H_4\text{-}CH_2K + 3/2O_2 \longrightarrow NO_2\text{-}C_6H_4\text{-}COOK + H_2O$$

Metal ions had little effect on the rate of oxidation. The dimerization reaction was interpreted as a radical coupling reaction in the presence of oxygen.

Derivatives of p-nitrotoluene oxidized at rates in accord with the expected pK_a values of the compounds. Very weakly acidic compounds showed rates of oxidation in the order of primary $>$ secondary $>$ tertiary although stable carbanions formed from very acidic compounds were found to be unreactive towards oxygen. The reactivity of a large number of common carbanions towards oxygen has been shown to follow the order tertiary $>$ secondary $>$ primary by Russell, Moye and Nagpal (18). This sequence is in accord with the mechanistic interpretation that the more unstable tertiary carbanion will undergo electron-transfer to oxygen with greater ease to yield a more stable tertiary radical.

p-Nitrotoluene was the only compound found which produced dimeric products in autoxidation reactions. p-Nitrobenzoic acid was isolated from the oxidation of p-nitroethylbenzene, p-nitrobenzyl alcohol, p-nitroacetophenone and p-nitrobenzaldehyde. Ketones were obtained from the oxidation of 4-nitrodiphenylmethane, bis-(4-nitrophenyl)-methane, fluorene, diphenylacetonitrile, fluorenol and benzhydrol. The corresponding alcohol was obtained from the oxidation of mono-p-nitrotriphenylmethane. The oxidation of benzhydrol also produced a yellow solid thought to be potassium superoxide. No products could be determined from the oxidation of ortho-alkyl nitroaromatic derivatives and nitrofluorene.

The effect of added metal ions, e.g., ferric chloride, was most dramatic in the oxidation of alcohols where almost complete inhibition was observed for benzhydrol and benzyl alcohol. Tris-(p-nitrophenyl)-methane oxidized at a faster rate in potassium hydroxide - ethanol than in potassium t-butoxide - t-butyl alcohol.

The dimerization mechanism of p-nitrotoluene in the presence and absence of oxygen is still a disputed question. In view of Williamson's work (20) on the copolymerization of p-nitrostyrene in the presence of oxygen the mechanism involving radical dimerization in p-nitrotoluene oxidation becomes untenable. A dimerization mechanism within a charge-transfer complex is most consistent with the work to be presented on this topic in this thesis. This route would be relatively insensitive to usual oxidation catalysts or inhibitors but very sensitive to changes in solvent media as was found to be the case.

The strongest case for an electron transfer pathway was found for the oxidation of alcohols. Although the rate-limiting step for fluorenol and p-nitrobenzyl was undoubtedly the ionization step:

$$(32) \qquad R_2CH\text{-}O^{\ominus} \longrightarrow R_2\text{-}\overset{\ominus}{C}\text{-}\overset{\ominus}{O} \xrightarrow{O_2}$$

this probably was not true for the oxidation of benzhydrol and benzyl alcohol. Russell and Geels[1] have made a comparison of rates of oxidations of fluorenol, xanthydrol and benzhydrol in dimethyl sulfoxide, pyridine and t-butyl alcohol and have found large amounts of potassium superoxide formed in the faster oxidations in the more polar solvents. A number of interesting conclusions can be drawn from these observations. In cases where it seems reasonable to assume that no organic peroxy radical is

---

[1] G. A. Russell and E. J. Geels, Dept. of Chemistry, Iowa State University, Ames, Iowa. Private communication concerning oxidation of alcohols, 1962.

formed potassium superoxide will be a major oxidation product.

(33) $$R_2\overset{\ominus}{C}-\overset{\ominus}{O} + O_2 \xrightarrow{\text{fast}} R_2-\overset{\bullet}{C}-\overset{-}{O} + \cdot O_2^-$$

(34) $$R_2\overset{\bullet}{C}-O^- + O_2 \xrightarrow{\text{fast}} R_2-C{=}O + \cdot O_2^-$$

(35) $$R_2\overset{\ominus}{C}-\overset{\ominus}{O} + \cdot O_2^- \xrightarrow{\text{v. slow}} R_2\overset{\bullet}{C}-\overset{-}{O} + O_2^{=}$$

(36) $$R_2\overset{\bullet}{C}-\overset{-}{O} + \cdot O_2^- \xrightarrow{\text{v. slow}} R_2C{=}O + O_2^{=}$$

(37) $$KO_2^- + B^- \xrightarrow{\text{v. slow}}$$

The latter three steps might be expected to be slow because the reaction of two negatively charged species is involved. These considerations can be extended to conclude that in reactions which certainly involve organic peroxy radicals superoxide can transfer an electron to the peroxide.

(25) $$R-OO\cdot + \cdot O_2^- \longrightarrow ROO^- + O_2$$

This step is consistent with the stoichiometry found in many oxidations and with the observation that no superoxide is found in the oxidation of secondary or tertiary carbanions.

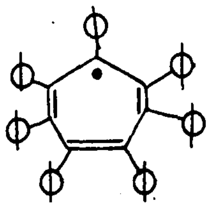
B. Stable Free Radicals

The interesting question of what free radicals are stable received extensive consideration during the course of this study since an interest had developed in uncovering new, efficient and stable electron acceptors for the study of electron transfer reactions. The most obvious factor involved in the stabilization of a free radical is a retarded rate of dimerization or disproportionation. Aromatic resonance stabilization coupled with a low bond strength in the dimer accounts for the stability of most free radicals.

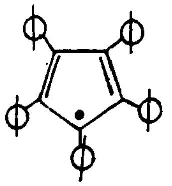
One of the classic free radical examples is the triphenylmethyl radical which received early attention when the technique of electron spin resonance spectroscopy (E.S.R.) became available. Other examples are the ketyl radical anions and the semiquinones. The early E.S.R. literature is the subject of numerous review articles (21, 22, 23, 24, 25) and a book by Ingram (26). Selected references and more recent studies of stable free radicals will be described. The closely related topic of electron transfer will be included.

Numerous free radicals are known which are either completely dimerized or are in equilibrium with the dimer at room temperature, *e.g.*, hexaphenylethane. An interesting series of free radicals in the order of their stability towards dimerization is heptaphenyltropylium (27), pentaphenylcyclopentadienyl (28), triphenylcyclopropenyl (29) and tetraphenylpyrryl (30), 2,4,5-triphenylimidazole (31), tetraphenylhydrazine (32).

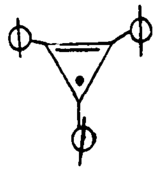
At room temperature



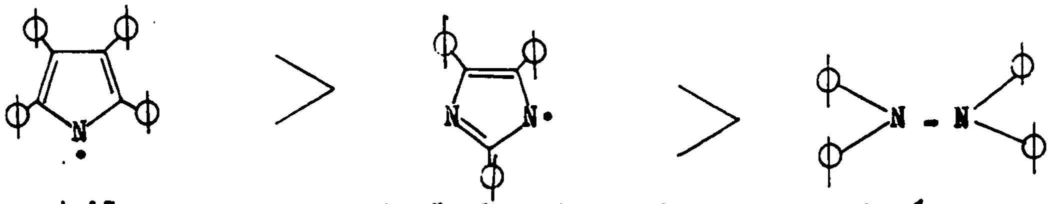
100% radical



100% radical

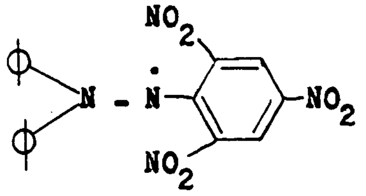


100% dimer

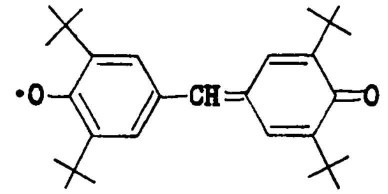


stable $t_{\frac{1}{2}}$ "a few minutes" 100% dimer

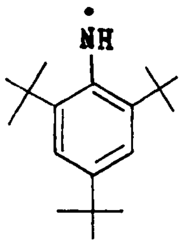
Other radicals which undoubtedly gain stability because of steric hindrance to dimerization are the diphenylpicrylhydrazyl series (26, 33), 2,6-di-t-butylphenoxy derivatives (34, 35), 2,4,6-tri-t-butyl anilino (36).



DPPH



galvinoxyl

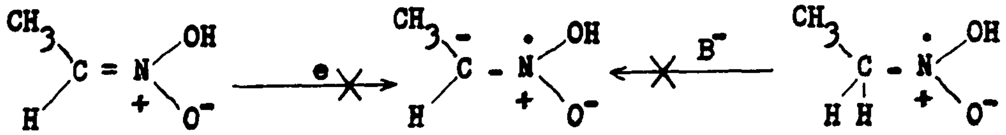


The nitrogen-oxygen bond in a variety of forms seems to furnish free radicals more stable than either the nitrogen-carbon, oxygen-carbon or the carbon-carbon bond. The nitro and nitrogen oxide radicals have been studied most extensively. In what has now become a classic reference Geske and Maki reported the synthesis by electrolytic reduction of the nitrobenzene radical anion and its derivatives (37, 38, 39). The technique is now widely used for the generation of free radicals. Nitrobenzene radical anion and most of its derivatives are remarkably stable and react with oxygen relatively slowly. The ease of reduction to the radical ion increases with electron-withdrawing substituents. A correlation was drawn between the half-wave reduction potential and Hammett's sigma constant. The best fit was obtained for meta substituents, *p*-amino and *p*-nitro groups falling farthest from the best straight line for all the points (38).

The alkali metal reductions in ether solvents of nitroaromatic derivatives to yield radical anions have been studied by Ward (40, 41). In general similar results were obtained except for a difference in association of metal ion with the radical resulting for example in the *m*-dinitrobenzene radical anion spectrum indicating interactions from two equivalent nitrogen atoms in acetonitrile (39) but only from one in dimethoxyethane (40).

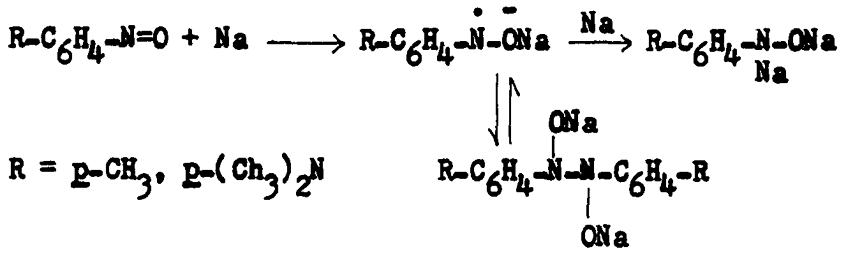
Piette, Ludwig and Adams (42) have succeeded in generating nitroaromatic and nitroaliphatic radical ions in aqueous media. The nitrogen splitting constants showed a marked solvent effect (a_N = 13.87 gauss in aqueous solution as compared to 10.32 in acetonitrile for nitrobenzene) which apparently also minimized the difference in the splitting constants for the ortho and para protons. *p*-Nitrophenol and *p*-nitrobenzoic acid could only be reduced to their radical ions in basic solution. Whether the radical was a mono- or dianion was not ascertained. The aliphatic radical anions had half-lives of approximately 0.5 sec. No evidence of an aci form for the radical was observed although reduction took place in an alkaline solution.

(38)



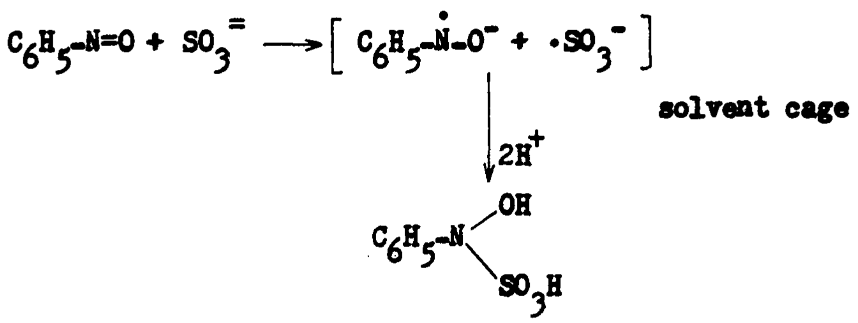
Although nitrosobenzene radical anion has not been reported two derivatives have been synthesized by Kauffmann and Hage (43).

(39)



Russell and Geels[1] have been able to obtain the radical anion from electron exchange between nitrosobenzene and phenylhydroxylamine in ethanol and ethoxide in a rapid flow system but the radical does not appear to be stable. Apparently the polarographic reduction of nitrosobenzene to phenylhydroxylamine occurs normally in the pH range 1-10 (44) and the radical anion has been suggested as the primary product of a rate-determining electron-transfer step in the sodium bisulfite reduction of nitrosobenzene (45).

(40)



The first of two stable liquid free radicals isolated in a pure form reported to date was the di-t-butylnitroxide synthesized by Hoffmann *et al.* (46).

$$\left[(CH_3)_3C\right]_2N\text{-}O\cdot \longleftrightarrow \left[(CH_3)_3C\right]_2\underset{\bullet}{\overset{+}{N}}\text{-}\overset{-}{O} \qquad \text{II}$$

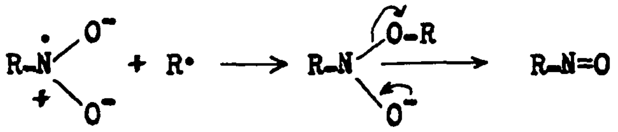
---

[1] G. A. Russell and E. J. Geels, Dept. of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Private communication regarding nitrosobenzene radical anion, June, 1963.

It was suggested that the reduction of t-nitrobutane produced an unstable radical which decomposed via the following reactions:

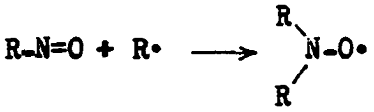
(41) $$R-NO_2 \xrightarrow{e} R-NO_2^{\overset{\cdot}{-}} \longrightarrow R\cdot + NO_2^-$$

(42)



$$R-\overset{\cdot}{N}{}^{+}(O^-)(O^-) + R\cdot \longrightarrow R-N(O-R)(O^-) \longrightarrow R-N=O$$

(43)



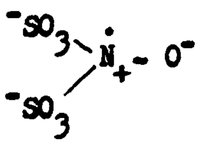
$$R-N=O + R\cdot \longrightarrow R_2N-O\cdot$$

A number of workers have studied the stable diphenyl nitric oxide radical formed by the reaction of various peroxides in diphenylamine (32, 47). It is interesting to note that the presence of the diphenylamino radical has also been detected by Pannell in oxidation of diphenylamine and t-butyl hydroperoxide (32). The mechanism suggested is:

(44) $$ROOH \xrightarrow{h\nu} RO\cdot + \cdot OH \qquad (X\cdot = RO\cdot, \cdot OH)$$

$$\begin{tikzcd}
(45) & (C_6H_5)_2NH \arrow[r, "X\cdot"] & (C_6H_5)_2N\cdot \arrow[d, "\cdot OH"] & \\
(46) & (C_6H_5)_2NH \arrow[r, "ROOH"] & (C_6H_5)_2NOH \arrow[r, "X\cdot"] & (C_6H_5)_2N-O\cdot
\end{tikzcd}$$

The inorganic stable nitric oxide radical ion finds use in line width calibration (48).



$$({}^{-}SO_3)_2\overset{\cdot}{N}{}^{+}-O^-$$

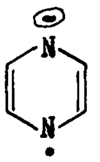
III

Baird and Thomas (47) reported the E.S.R. observation of numerous nitric oxide radicals formed from the *α,α'*-azo-*bis*-isobutyronitrile initiated oxidation of primary and secondary amines. Diphenylamine, aniline, N-ethylaniline, di-*n*-hexylamine, *t*-butylamine, dibenzylamine and phenothiazine apparently all gave the corresponding nitric oxide radicals under the conditions described. In a study of the mechanism of inhibition of oxidation of hydrocarbons by diphenylamine, the diphenylamine oxide radical was found present in solution and shown to be an effective radical trap (49). The interesting statement was made that diphenylamine radical did not react with oxygen to give diphenylamine oxide.

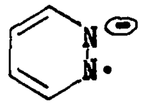
$$(47)\qquad (C_6H_5)_2N\cdot \longrightarrow \overset{O_2}{\nrightarrow} (C_6H_5)_2N\text{-}\dot{O}$$

Similar amine oxides were reported by Coppinger and Swalen (48) in the reaction of secondary amines with *t*-butyl hydroperoxide.

A number of stable free radicals formed by the reduction of carbon-nitrogen and nitrogen-nitrogen double bonds have been reported. Simple diazine molecules reduce readily to form radical anions. Ward (50) reduced pyrazine and pyridazine with potassium to obtain:

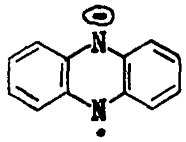


IV



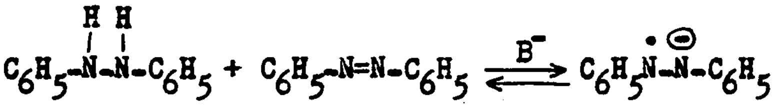
V

Phenazine radical anion has also been synthesized (51).

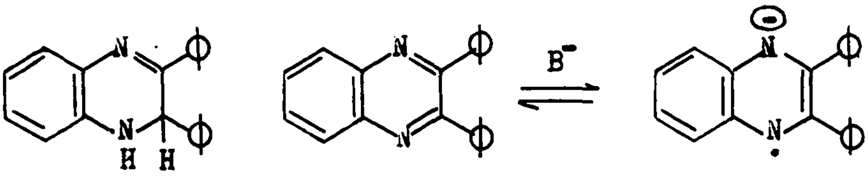


VI

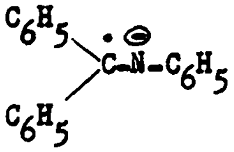
Russell *et al.* (52) has reported the ready formation of azobenzene and diphenylquinoxaline radical anions *via* an electron exchange between the dihydro derivatives and their saturated analogues in strong base.

(48) 

$$C_6H_5-\overset{H}{N}-\overset{H}{N}-C_6H_5 + C_6H_5-N=N-C_6H_5 \overset{B^-}{\rightleftharpoons} C_6H_5\overset{\bullet\ominus}{N-N}-C_6H_5$$

(49) 

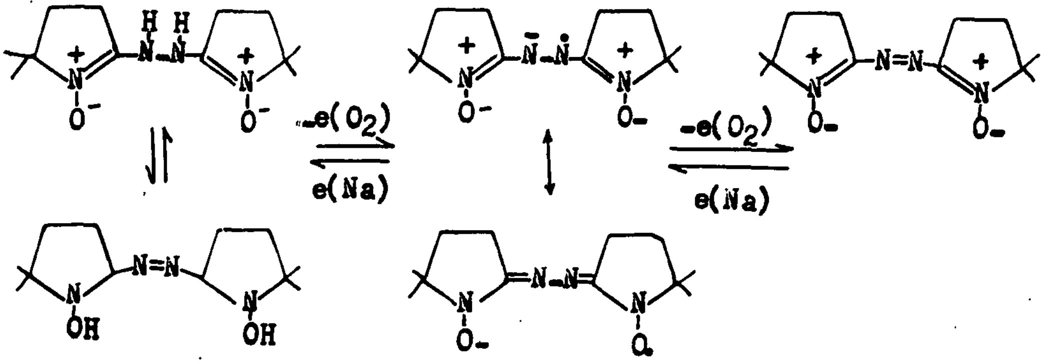
It is interesting that radical anions of isolated carbon-nitrogen double bonds have not received equal attention. Only the radical anion from benzophenone anil has been reported (53) but its spectrum has not been studied.



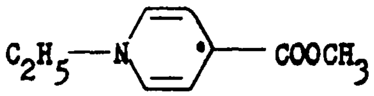
A combination of the azobenzene and semiquinone features serve to stabilize the following radical anion observed by Forrester and Thomson (54).

(50)

(51)

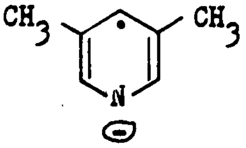


Quarternary amines can be reduced to stable free radicals. 1-Ethyl-4-carbomethoxypyridinium iodide can be reduced by zinc in acetonitrile at 0° to produce a dark emerald-green oil, 1-ethyl-4-carbomethoxypyridinyl,



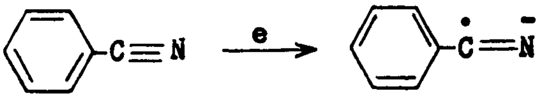
VII

which can be isolated by vacuum distillation at 40° (55). The polarographic reduction potentials of the substituted pyridinium salt was found to be -0.93 v. (vs. standard calomel-electrode) (56). The early literature on the alkali metal reductions of pyridinium salts has been reviewed by Weitz (57). The reduction of pyridine and pyrimidine (a m-diazine) leads to dimerization (50, 58) as in the case of unsubstituted pyridinium salts (57). However, 3,5-lutidine radical anion has been made with potassium in dimethoxyethane (59).

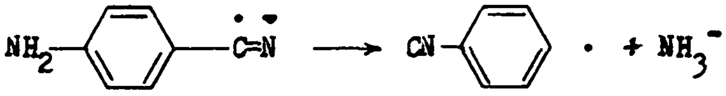


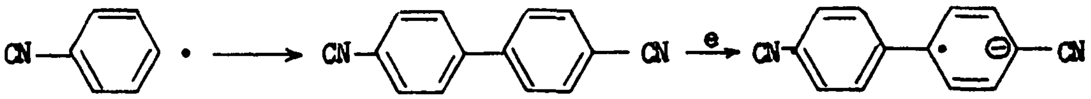
VIII

The E.S.R. spectra of substituted benzonitriles have been obtained by Rieger *et al.* by electrolytic reduction in dimethylformamide (60).

(52) 

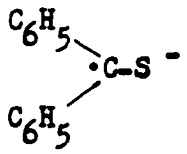
The *o*-, *m*- and *p*-dicyanobenzene radical anions appeared to be very stable radicals as well as the *p*-nitro, 3,5-dinitro and *p*-carboxy derivatives. The *p*-amino and *p*-fluoro substituents were presumably lost from the radical anion to yield a cyanophenyl radical. The spectrum of *p*,*p*'-dicyanobiphenyl was obtained in these cases.

(53) 

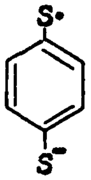
(54) 

Stable radicals could not be obtained from *p*-methoxy-, *p*-hydroxy- and *p*-chlorobenzonitrile.

The very well known ketyl and semiquinone radical anions seem to have no stable analogues in the sulfur family.

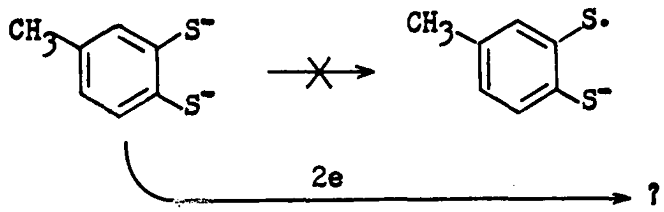


IX

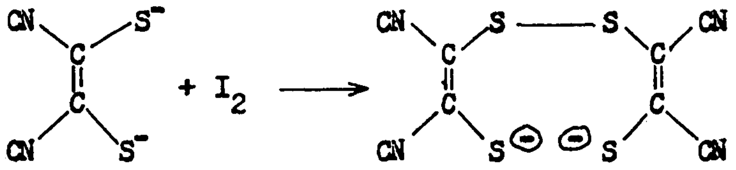


X

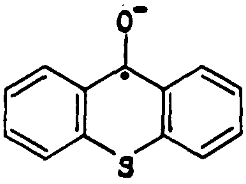
In electron transfer experiments from anions we were unable to detect an intermediate sulfur *o*-semiquinone from 3,4-dimercaptotoluene.

(55) 

Simmons et al. (61) did not report the existence of an intermediate sulfur radical in the reaction.

(56)


The E.S.R. spectra of thiaxanthone, thiaxanthone-5-dioxide and thianthrene-5,10-tetroxide (62) radical anions have been reported recently. The radicals were synthesized by potassium reduction in 1,2-dimethoxyethane and were stable over extended periods of time. The spectra of the sulfones were remarkable in their narrow line width. The free electron density apparently is considerably lower in the aromatic rings of the anion radical than on the sulfur functions. The line width of the thiaxanthone radical,

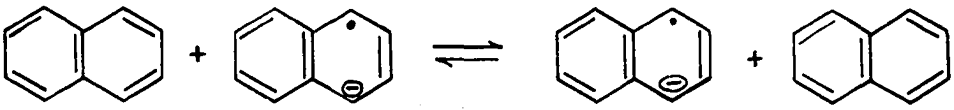


XI

was 17.3 gauss; 5 groups of lines (separated by 3.5 gauss) further split into 18 lines were observed. The colors of the radicals were reported to be pale blue.

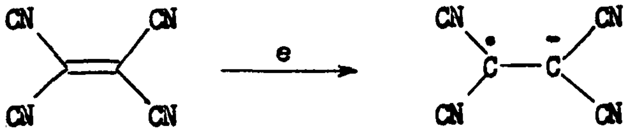
C. Electron Transfer

Electron transfer reactions of inorganic ions are described in early literature but interest in the mechanism and rates of these reactions has developed relatively recently. Electron transfer reactions between the same organic molecules have been investigated by Weissman (63) with the advent of electron spin resonance (E.S.R.). The rates of electron exchange are fast enough to cause line broadening of hyperfine splitting components of the observed spectrum (63, 64). In the symmetrical case of the electron exchange between naphthalene and naphthalene radical anion the rate was found to be 10^6 1. mole^{-1} sec.$^{-1}$ in dimethoxyethane (65).

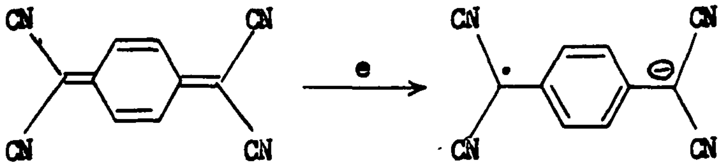
(57) 

The electron exchange from anion to neutral radical has been studied for _tris_-(_p_-nitrophenyl)-methide ion and found to occur at a rate of the order of the rate of diffusion (66). The unsymmetrical electron transfer between unsaturated hydrocarbons has also been studied (67, 68). Paul, Lipkin and Weissman (69) showed that the electron affinities of aromatic hydrocarbons followed the order: naphthacene, anthracene > naphthalene > phenanthrene > benzene and a coulometric titration procedure has been developed for the analysis of anthracene, nitrobenzene, nitromethane, benzophenone and azobenzene by electron transfer from the biphenyl radical anion (70). A number of examples of radical formation _via_ symmetrical electron exchange between dihydro derivatives and their unsaturated analogues in the presence of strong base were reported by Russell _et_ _al_. (52).

Electron transfer between a given pair of compounds of widely varying nature especially those which contain electron-rich and electron-deficient carbon-carbon double bonds may in all cases involve prior charge-transfer complex formation[1]. The use of charge-transfer complexes to make solid derivatives for identification, e.g., picrates, dates back to early chemical knowledge. Lately it has been found that many charge-transfer complexes are paramagnetic in the crystal state (76). A well studied example is the electron and charge-transfer acceptor 7,7,8,8-tetracyanoquinodimethan (77), a vinylogue of tetracyanoethylene of similar properties (78).

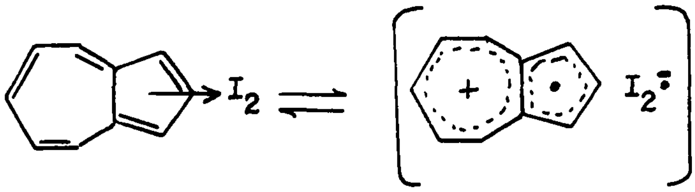
(58)


$E_{\frac{1}{2}} = 0.152$

(59)


$E_{\frac{1}{2}} = 0.127$

A number of iodine complexes with electron-donar aromatic hydrocarbons have also been shown to be paramagnetic (79).

(60)


?

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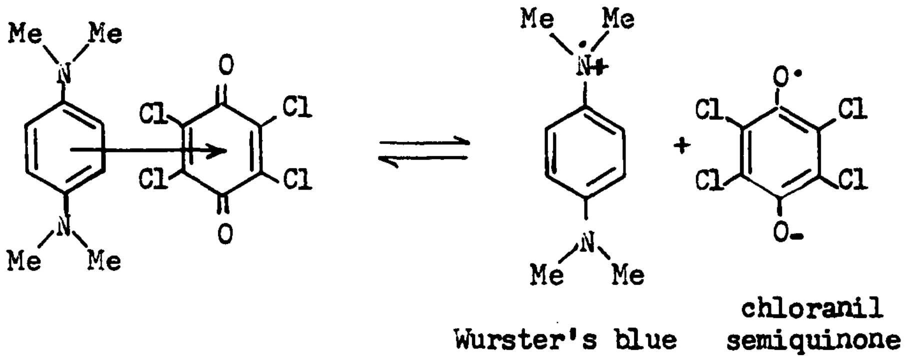
[1] Reviews on charge-transfer complexes appear in articles by Mulliken and Person (71), Briegleb and Czekalla (72), Briegleb (73), McGlynn (74) and Murrell (75).

The dissociation into free radicals of a donar-acceptor complex is very strongly influenced by solvents. The solid complex consisting of N,N,N',N'-tetramethyl-p-phenylenediamine and chloranil dissociates into radicals in acetonitrile, ethanol or 1,2-dichloroethane but not in dioxane, chloroform or benzene (80, 81, 82).

(61)



A solvent effect has been observed in the formation of a radical cation from tetrakis-(p-dimethylaminophenyl)-ethylene diiodide by potassium iodide, the radical formation occurring in water but not in ethylene chloride (83). In general more polar solvents aid the charge-separating free radical formation. A marked solvent effect was observed in the tetraphenylethylene radical anion formation by Garst and Cole (84) the equilibrium favoring the radical in dimethoxyethane but not in diethyl ether.

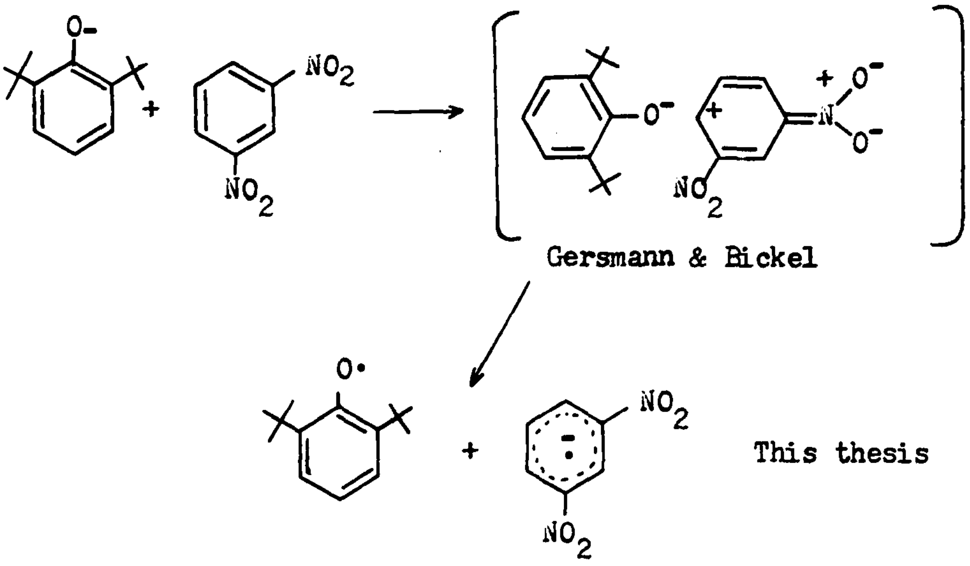
$$(62)\quad (C_6H_5)_2\overset{\ominus}{C}-\overset{\ominus}{C}(C_6H_5)_2 + (C_6H_5)_2C{=}C(C_6H_5)_2 \rightleftharpoons (C_6H_5)_2\overset{\ominus}{C}-\overset{\bullet}{C}(C_6H_5)_2$$

The spectral properties of the charge-transfer compexes and products from polynitroaromatic compounds in basic solutions are still the subject of extensive study (85, 86, 87) and the observation of free radicals has been reported in solutions of trinitrobenzene containing donators (88).

The formation of a weak charge-transfer complex between oxygen and polynuclear aromatic hydrocarbons has been found (89) and described as an intermediate in the electron transfer reaction producing perylene cation radical and superoxide anion from perylene and oxygen (90). Complexing of an aromatic carbanion and oxygen prior to electron transfer is an interesting possibility.

Faster rates of oxidation of 2,6-di-t-butyl phenol in basic solution in the presence of dinitrobenzene has been attributed to charge-transfer complexing by Gersmann and Bickel (91) although in the light of the studies to be presented in this thesis it would seem an increased rate of initiation *via* direct electron transfer would be the better explanation.

(63)



The rate of acetolysis of 2,4,7-trinitro-9-fluorenyl-p-toluenesulfonate is enhanced in the presence of charge-transfer donars, e.g., phenanthrene and anthracene (92). This observation was consistent with stabilization of the electron-deficient transition state in the reaction.

(64) $$\text{R-OTOS} \xrightarrow{k_1} \overset{\delta+}{\text{R}} - - - \overset{\delta-}{\text{OTOS}}$$

(65) $$\text{D} \longrightarrow \text{R-OTOS} \xrightarrow{k_2} \text{D} \longrightarrow \overset{\delta+}{\text{R}} - - - \overset{\delta-}{\text{OTOS}} \qquad k_2 > k_1$$

Russell et al. (93) reported the rate enhancement of the base-catalyzed autoxidation of fluorene in *t*-butyl alcohol. A free radical mechanism involving electron transfer was suggested.

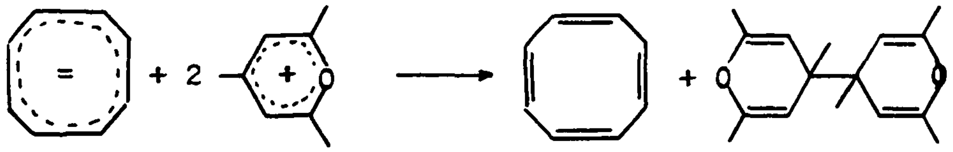
(22) $$\text{R}^{\ominus} + \text{O}_2 \longrightarrow \text{R}\cdot + \cdot\text{O}_2^{-}$$

(66) $$\text{R}^{\ominus} + \text{C}_6\text{H}_5\text{NO}_2 \longrightarrow \text{R}\cdot + \text{C}_6\text{H}_5\text{NO}_2^{\overset{\cdot}{-}}$$

It might be argued that charge transfer complexing of fluorenyl anion could have a similar effect.

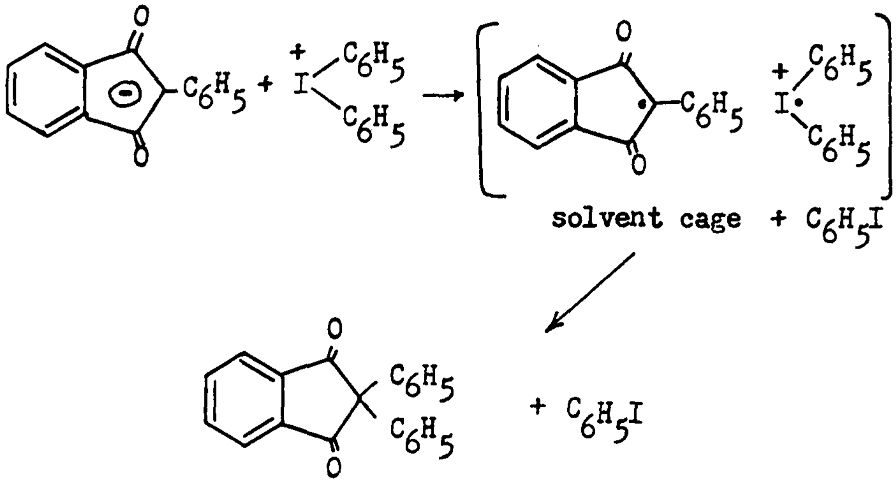
(67) $$\begin{tikzcd}[column sep=small] \text{R}^{\ominus}\rightarrow\text{A} + \text{O}_2 \arrow[r] & {[\text{R}\cdot\rightarrow\text{A}]} + \cdot\text{O}_2^{-} \arrow[d] & & \\ & \text{A} + \text{R}\cdot \arrow[r, "\text{O}_2"] & \text{ROO}\cdot \arrow[r] & {} \end{tikzcd}$$

Species with a formal positive charge should serve as good charge-transfer acceptors and lead to electron transfer. Examples of these are the formation of the heptaphenyltropylium radical from heptaphenyltropylium anion (27), the production of the dimer of trimethylpyrylium from cyclooctatetraene dianion and trimethylpyrylium cation (94)

(68) 

and the phenylation of indandiones by diphenyliodonium salts (95).

(69)



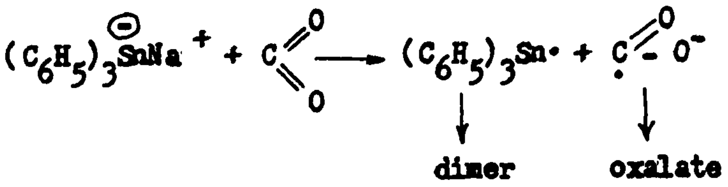
Free radical products of one-electron transfer reactions have been reported which show no obvious relationship to charge-transfer complexes. Electron-transfer to benzophenone to produce the benzophenone ketyl has been observed for triphenyl methyl sodium (96) and sodium triphenyltin (97).

$$(70)\quad (C_6H_5)_3\overset{\ominus}{C}Na^{+} + (C_6H_5)_2C{=}O \longrightarrow (C_6H_5)_3C\cdot + (C_6H_5)_2\dot{C}{-}O^{\ominus}$$

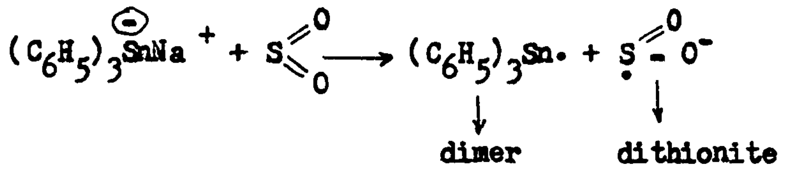
$$(71)\quad (C_6H_5)_3\overset{\ominus}{Sn}Na^{+} + (C_6H_5)_2C{=}O \longrightarrow (C_6H_5)_3SnSn(C_6H_5)_3 + (C_6H_5)_2\dot{C}{-}O^{\ominus}$$

In the presence of sodium or lithium triphenyltin, carbon dioxide and sulfur dioxide act as electron acceptors to produce 98% and 96% yields of sodium oxalate and sodium dithionite (97, 98).

(72)

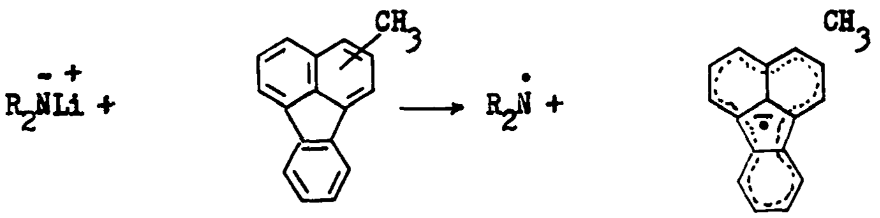


$$(C_6H_5)_3\overset{\ominus}{Sn}Na^{+} + O{=}C{=}O \longrightarrow \underset{\substack{\downarrow\\ \text{dimer}}}{(C_6H_5)_3Sn\cdot} + \underset{\substack{\downarrow\\ \text{oxalate}}}{\dot{C}(=O){-}O^{-}}$$

(73) 

$$(C_6H_5)_3\overset{\ominus}{\text{Sn}}\text{Na}^{+} + \text{S}\genfrac{}{}{0pt}{}{\nearrow \text{O}}{\searrow \text{O}} \longrightarrow \underset{\text{dimer}}{\underset{\downarrow}{(C_6H_5)_3\text{Sn}\cdot}} + \underset{\text{dithionite}}{\underset{\downarrow}{\underset{\bullet}{\text{S}}\overset{\nearrow \text{O}}{-}\text{O}^{-}}}$$

In a recent publication Streitweiser and Langworthy (99) reported the observation of free radicals in solutions of methyl polynuclear aromatic hydrocarbons in cyclohexylamine containing lithium cyclohexylamide, e.g., 3- and 8-methylfluoranthene. These results were interpreted as an electron transfer reaction from the lithium amide to the polynuclear aromatic.

(74) 

It would seem a spontaneous radical formation reaction similar to that found for p-nitrotoluene in base by Russell and Janzen (100) would be energetically more favorable.

(75)

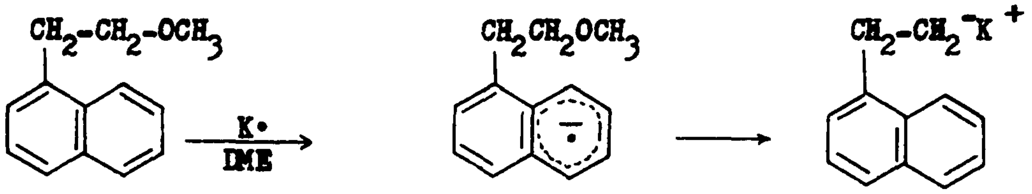
$$RCH_2^{\ominus} + RCH_3 \longrightarrow R\text{-}CH_2\cdot + R\text{-}CH_3^{\dot{-}}$$

where R = fluoranthene

Further results are to be published.

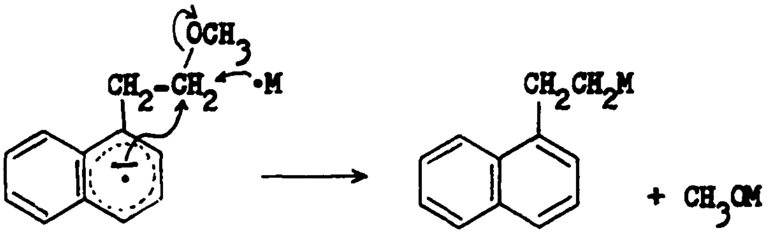
Radical anions have been shown to serve as effective neighboring groups via electron transfer in substitution-reduction reactions. Cram and Dalton (101) found that 1-methoxy-2-(1-naphthyl)-ethane reacted rapidly with potassium in 1,2-dimethoxyethane to yield α-ethylnaphthalene.

(76)



Since deteurium in the 1-position was not scrambled in the reaction with potassium as was observed in the acetolysis of the tosylate, a symmetrical cyclopropyl intermediate was ruled out and an electron transfer without bond formation was postulated as the mechanism of the substitution-reduction reaction.

(77)

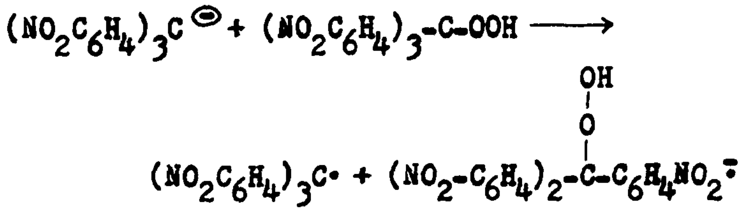


In this connection the reaction reported by Hawthorne and Hammond (102) between the tris-(p-nitrophenyl)-methide ion and tris-(p-nitrophenyl)-methyl hydroperoxide deserves reconsideration. The reaction produced tris-(p-nitrophenyl)-carbinol and tris-(p-nitrophenyl)-methyl radical. The process was formulated as a one-electron transfer reaction in close analogy to hydroperoxide cleavage by ferrous ion to give alkoxy radicals, hydroxide and ferric ion (103).

(78) $R_3C^{\ominus} + R_3C\text{-}O\text{-}OH \longrightarrow R_3C\cdot + R_3CO\cdot + OH^-$

The relatively slow oxidation of the *tris*-(*p*-nitrophenyl)-methide anion by oxygen and the oxidation catalysis observed in the presence of nitrobenzene (to be presented) suggest that the anion does not transfer an electron easily and that an electron acceptor like nitrobenzene could facilitate this transfer. The decomposition of *tris*-(*p*-nitrophenyl)-methyl hydroperoxide may involve electron transfer from the carbanion yielding the stable *tris*-(*p*-nitrophenyl)-methyl radical and a derivative of a nitrobenzene radical anion.

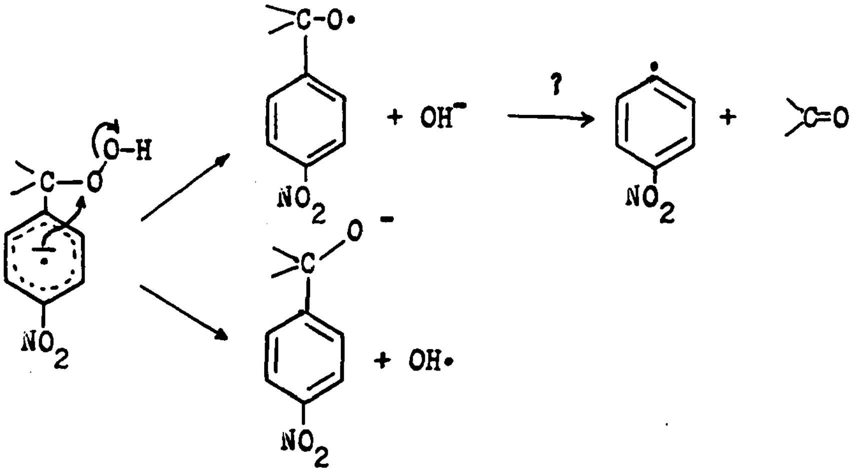
(79)



$$(NO_2C_6H_4)_3C^{\ominus} + (NO_2C_6H_4)_3\text{-C-OOH} \longrightarrow (NO_2C_6H_4)_3C\cdot + (NO_2\text{-}C_6H_4)_2\text{-}\overset{\substack{OH\\|\\O\\|}}{C}\text{-}C_6H_4NO_2^{\overline{\cdot}}$$

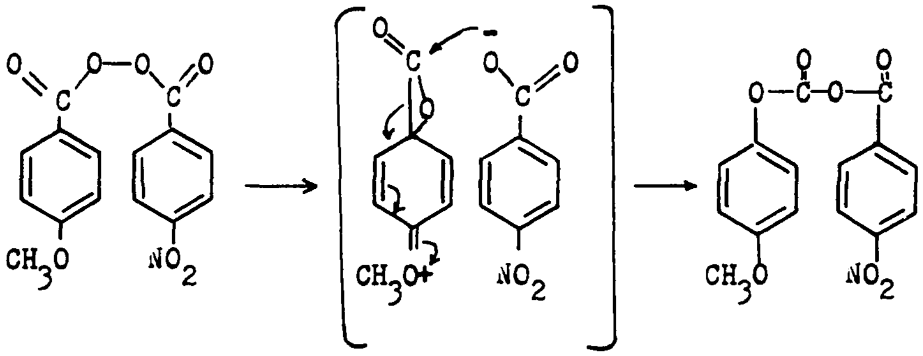
The hydroperoxide nitrophenyl radical anion should decompose spontaneously in an analogous fashion to the neighboring group reaction to yield a radical and an anion, either an alkoxy radical and hydroxide ion or the hydroxy radical and alkoxide ion.

(80)



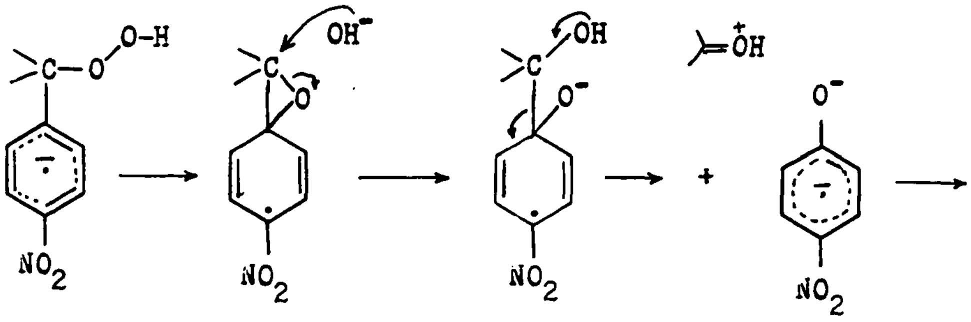
Traces of p-nitrophenol and p,p'-dinitrobenzophenone were known to form as well in the reaction. By analogy to the mechanism suggested for the rearrangement of p-methoxy-p'-nitrobenzoylperoxide (104)

(81)



it could be possible that an epoxide is also formed as an intermediate in the decomposition of the radical anion of the hydroperoxide derivative.

(82)



The electron transfer reactions between organic and inorganic molecules involved in oxidative and reductive synthetic pathways are being studied and their mechanisms elucidated. A detailed study of the electron transfer reactions of cupric salts has been made by Kochi (105). The mechanism of permanganate oxidation received attention during the 1960 discussion of the Faraday Society on "Oxidation-Reduction Reactions in Ionizing Solvents" as well as in a number of reviews

(106, 107). The mechanisms of chromic acid (107) and ferricyanide (108) oxidations have also been discussed.

III. RESULTS AND DISCUSSION

A. Introduction

Since the triplet ground state configuration of oxygen has been established

$$\uparrow\cdot\underset{\cdot\cdot}{\ddot{O}} - \underset{\cdot\cdot}{\ddot{O}}\cdot\uparrow$$

it would seem that one-electron transfer mechanisms in the reactions of oxygen with electron-rich molecular sites would be demanded

(83) $$Z{:}\uparrow\downarrow + \uparrow\cdot\underset{\cdot\cdot}{\ddot{O}} - \underset{\cdot\cdot}{\ddot{O}}\cdot\uparrow \longrightarrow Z\cdot\uparrow + \downarrow\uparrow{:}\underset{\cdot\cdot}{\ddot{O}} - \underset{\cdot\cdot}{\ddot{O}}\cdot\uparrow$$

where Z: = $>C{:}^{\ominus}$, $>N{:}$, $>P{:}$, etc.

because direct ionic reactions with electrophilic oxygen would violate conservation of spin.

(84) $$Z{:}\uparrow\downarrow \quad \uparrow\cdot O - O\cdot\uparrow \longrightarrow Z - \underset{\cdot\cdot}{\ddot{O}} - \underset{\cdot\cdot}{\ddot{O}}{:}\uparrow\downarrow$$

Autoxidation of the 2-nitropropyl carbanion was shown to be a free radical chain reaction in aqueous sodium hydroxide (109) and the dimerization of p-nitrotoluene and derivatives in basic solution in the presence of air was suggestive of a free radical process (3). It was our objective in part to shed light on the mechanism of autoxidation in basic solution of numerous carbanions some of which had received considerable attention prior to the start of this work. Our study involved the measurement of the rate of absorption of oxygen by a solution containing a weak acid and a strong base. Since the carbanions studied were formed in situ and reacted with oxygen in solution, a consideration of the rates of oxidation should include the consideration of both the ionization step to produce carbanions as well as the initiation step to produce radicals. In general the rate of oxidation should be faster with an increase in carbanion concentration (i.e., rapid and extensive ionization of substrate) as well as with an increase in rate of electron transfer yielding a high steady state concentration of free radicals.

A free radical chain reaction would involve some or all of the following steps:

	Steps	
ionization	1	$RH + B^{-} \longrightarrow R^{\ominus} + BH$
initiation	2	$R^{\ominus} + O_2 \longrightarrow R\cdot + O_2^{\cdot-}$
	3	$ROOH + R^{\ominus} \longrightarrow RO\cdot + R\cdot + OH^{-}$
propagation	4	$R\cdot + O_2 \longrightarrow ROO\cdot$
	4a	$R'-CH_2-\overset{\bullet}{C}H-R' + B^{-},O_2 \longrightarrow R'-CH{=}CH-R' + O_2^{\cdot-} + BH$
	5	$ROO\cdot + R^{\ominus} \longrightarrow ROO^{-} + R\cdot$
	6	$RO\cdot + R^{\ominus} \longrightarrow RO^{-} + R\cdot$
	7	$2ROO\cdot \longrightarrow 2RO\cdot + O_2$
termination (radical)	8	$ROO\cdot + O_2^{\cdot-} \longrightarrow ROO^{-} + O_2$
	9	$2R\cdot \longrightarrow R{-}R$

Steps

10 $R\cdot + ROO\cdot \longrightarrow ROOR$

secondary (reactions) 11 $ROO^- + H^+ \longrightarrow ROOH$

12 $ROOH + B^-, R^\ominus \longrightarrow$ products (non-radical)

13 $ROOR + B^-, R^\ominus \longrightarrow$ products (non-radical)

It could be argued that the following steps should be included:

Steps

14 $R^\ominus + O_2^{\overset{-}{\cdot}} \longrightarrow R\cdot + O_2^=$

15 $O_2^{\overset{-}{\cdot}} + H^+ \longrightarrow HOO\cdot$

16 $R^\ominus + \cdot OOH \longrightarrow R\cdot + HOO^-$

Step 14 which involves reaction of two negatively charged species might be an equilibrium step well on the left side of the equation. Step 16 also seems unlikely on the basis of known electron affinities of hydroperoxy and carbon radicals (see page 9).

For very weakly acidic compounds the rate-limiting step might be ionization to yield carbanion. If all oxidation steps subsequent to ionization were much faster than ionization the rate of absorption of oxygen should be first order in base and substrate.

$$-dO/dt = k_1 \left[RH \right] \left[B^- \right] \tag{85}$$

The initial rates of oxidations as a function of base (or substrate) concentration should be linear at constant substrate (or base) concentrations. The rate of oxidation should not be increased by electron transfer reagents but stronger bases or aprotic solvents should strongly increase the oxidation rates. For ionization to be rate-limiting the following steps must be unimportant:

Steps

17 $ROO\cdot + RH \longrightarrow ROOH + R\cdot$

18 $RO\cdot + RH \longrightarrow ROH + R\cdot$

Electron transfer reactions between anions and radicals have been found to be extremely fast and of the order of the rate of diffusion (65, 66) (10^6-10^8 1. mole^{-1} sec.$^{-1}$). On this basis it seems reasonable to consider Steps 17 and 18 unimportant relative to Steps 5, 6 and 16 in oxidation reactions of carbanions.

In the case of very acidic compounds the rate of ionization is very rapid and essentially complete ionization of the substrate would occur. The rate of oxidation would be limited by the rate of electron transfer from the carbanion (Steps 2, 5 and 6). Such reactions should be insensitive to increase in base strength of the medium but catalysis by electron transfer reagents should be possible and rates should be increased by the use of aprotic dipolar solvents which leave the carbanion unsolvated and more reactive.

For the intermediate case where the substrate is ionized fairly rapidly and electron transfer reactions with oxygen also occur rapidly a steady state concentration of numerous radical and ionic intermediates must exist. Electron transfer agents, stronger bases and aprotic dipolar solvents should all have a large rate-increasing effect on the reaction, although due to the complexity of the reaction it would be difficult to establish what phase of the reaction had been affected. The majority of cases studied undoubtedly fall into this class of compounds and kinetic analysis of the rates of oxidation was not attempted.

B. Solvent Effects

Base-catalyzed autoxidation in solution had been studied in water (109), alcohols (3, 6) and pyridine (7) previous to this work. These solvents limited the choice of compounds for study to those of relatively high acidity. It was our objective to attempt to extend the scope of carbanion autoxidation to compounds that had pK_a values greater than 25 (see Appendix, Table 26). Our efforts were directed towards experimenting with various solvent systems which would be stable ionizing solvents for carbanion formation and oxidation. Dimethyl sulfoxide and hexamethylphosphoramide containing potassium t-butoxide were found to be the most suitable systems studied.

In the extensive study of the autoxidation of p-nitrotoluene and derivatives Moye (3) confined himself to solutions of potassium t-butoxide in t-butyl alcohol. This system was stable towards both oxygen and oxidation intermediates but would ionize extensively only those acids which had pK_a's of less than 25. Although o- and p-nitrotoluenes ionized appreciably in this solvent, p-nitrocumene did not (the rate of oxidation of p-nitrotoluene was 25 times faster than p-nitrocumene). The use of pyridine as an oxidation medium increased the rates of oxidation of both p-nitrotoluene and p-nitrocumene (Figures 1 and 2). In 80% pyridine -

Figure 1. A comparison of the rates of oxidation of *p*-nitrotoluene in *t*-butyl alcohol and pyridine (25 ml. solvent)

Curve 1	3.7 mmoles *p*-nitrotoluene, 4.5 mmoles lithium *t*-butoxide in pyridine
Curve 2	3.6 mmoles *p*-nitrotoluene, 9.7 mmoles potassium *t*-butoxide in *t*-butyl alcohol
Curve 3	4.0 mmoles *p*-nitrotoluene, 4.85 mmoles potassium *t*-butoxide in 80% pyridine - 20% *t*-butyl alcohol

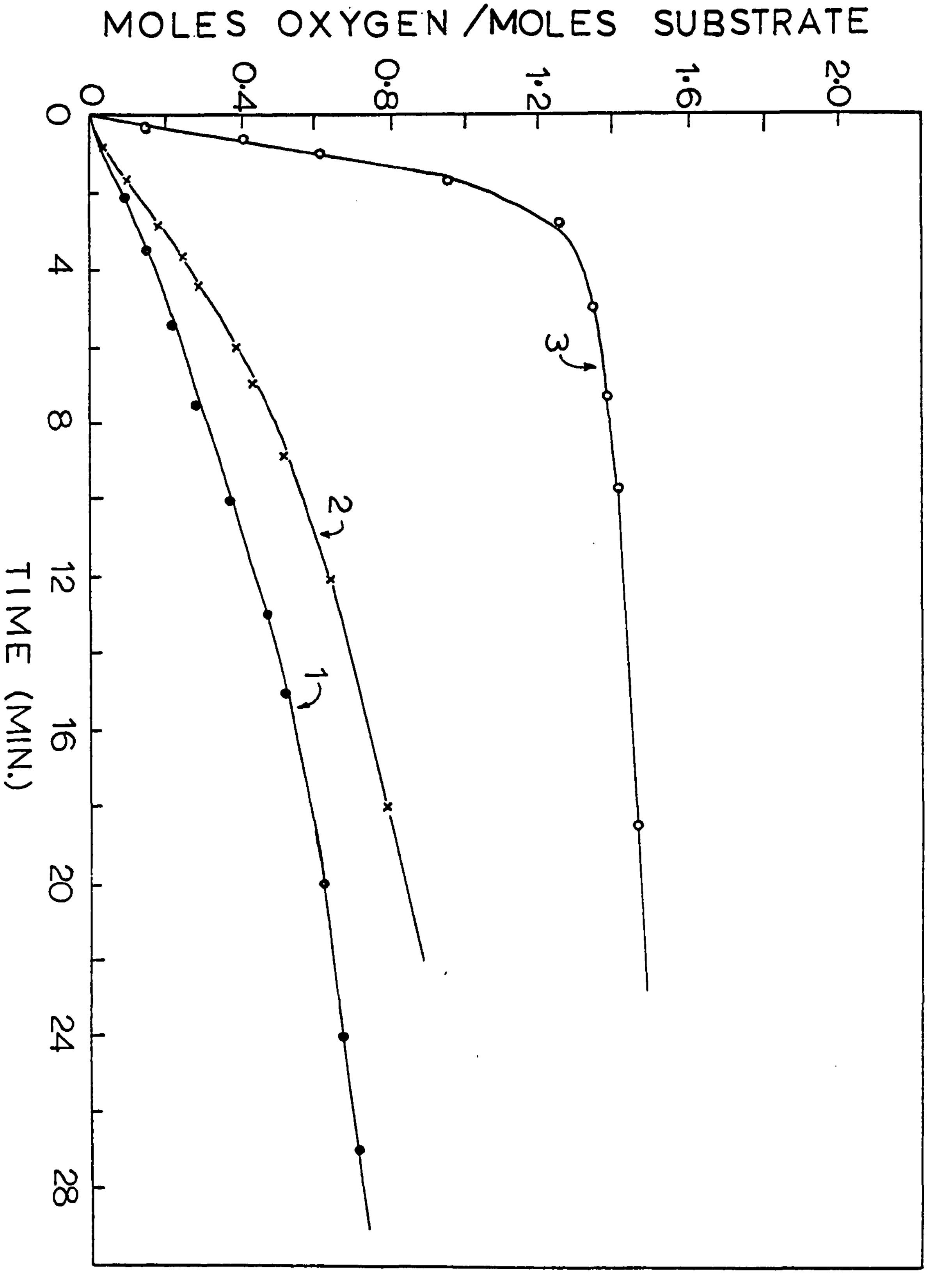
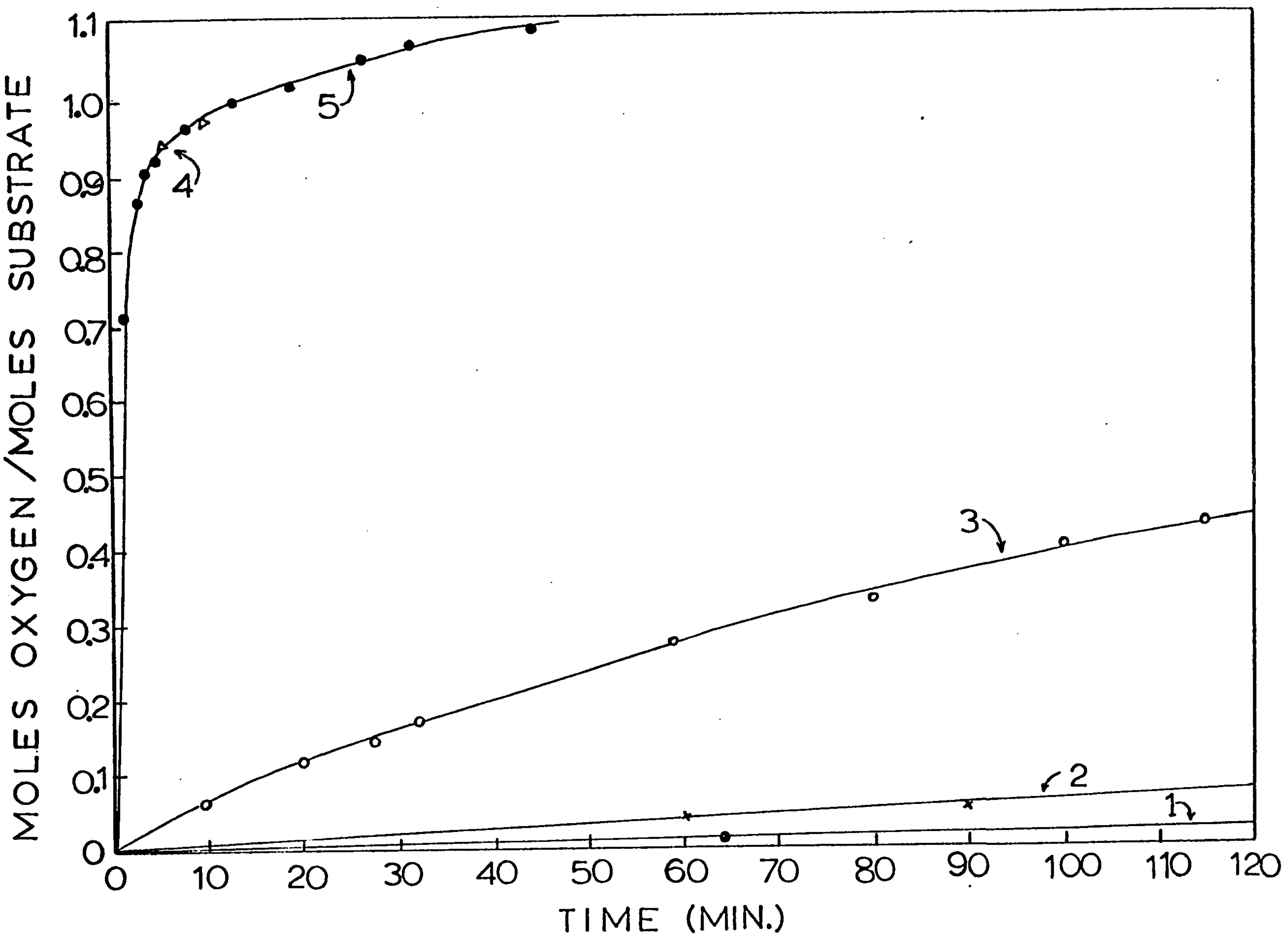

MOLES OXYGEN /MOLES SUBSTRATE
0
0·4
0·8
1·2
1·6
2·0
TIME (MIN.)
0
4
8
12
16
20
24
28
1
2
3

Figure 2. A comparison of the rates of oxidation of *p*-nitrocumene in *t*-butyl alcohol, pyridine and dimethyl sulfoxide (25 ml. solvent)

Curve 1	4.8 mmoles *p*-nitrocumene, 10.7 mmoles lithium *t*-butoxide in pyridine
Curve 2	4.17 mmoles *p*-nitrocumene, 11.6 mmoles potassium *t*-butoxide in *t*-butyl alcohol
Curve 3	4.8 mmoles *p*-nitrocumene, 7.1 ml. Triton B (40% in methanol) in pyridine
Curve 4	3.44 mmoles *p*-nitrocumene, saturated with potassium hydroxide in dimethyl sulfoxide
Curve 5	2.75 mmoles *p*-nitrocumene, 6.4 mmoles lithium *t*-butoxide in dimethyl sulfoxide


MOLES OXYGEN /MOLES SUBSTRATE
TIME (MIN.)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
0
10
20
30
40
50
60
70
80
90
100
110
120
1
2
3
4
5

20% t-butyl alcohol[1] containing potassium t-butoxide the initial rate of oxidation of p-nitrotoluene was faster than in t-butyl alcohol although in pure pyridine containing lithium t-butoxide it was slower.

p-Nitrocumene oxidized 20 times faster in a pyridine-methanol solution containing Triton B[2] than in t-butyl alcohol containing potassium t-butoxide (Figure 2). Attempts to obtain a reasonable concentration of Triton B in pyridine free of methanol met with little success since most of the dissolved Triton B precipitated in the form of droplets of oil when all the methanol was removed. Similar to p-nitrotoluene the oxidation of p-nitrocumene in a solution of lithium t-butoxide in pure pyridine was slower than in t-butyl alcohol containing potassium t-butoxide. However in solutions of lithium t-butoxide or potassium hydroxide in dimethyl sulfoxide, p-nitrocumene oxidized very rapidly (Figure 2).

The use of an ionizing system consisting of pure potassium t-butoxide in dimethyl sulfoxide was precluded by our finding that this basic solvent was not stable to oxygen but in fact absorbed oxygen rapidly (Figure 3). The oxidation of dimethyl sulfoxide could best be explained by extensive ionization followed by carbanion oxidation.

$$(86) \quad CH_3SOCH_3 + (CH_3)_3COK \longrightarrow CH_3SO\overset{\ominus}{C}H_2K^+ + (CH_3)_3COH$$

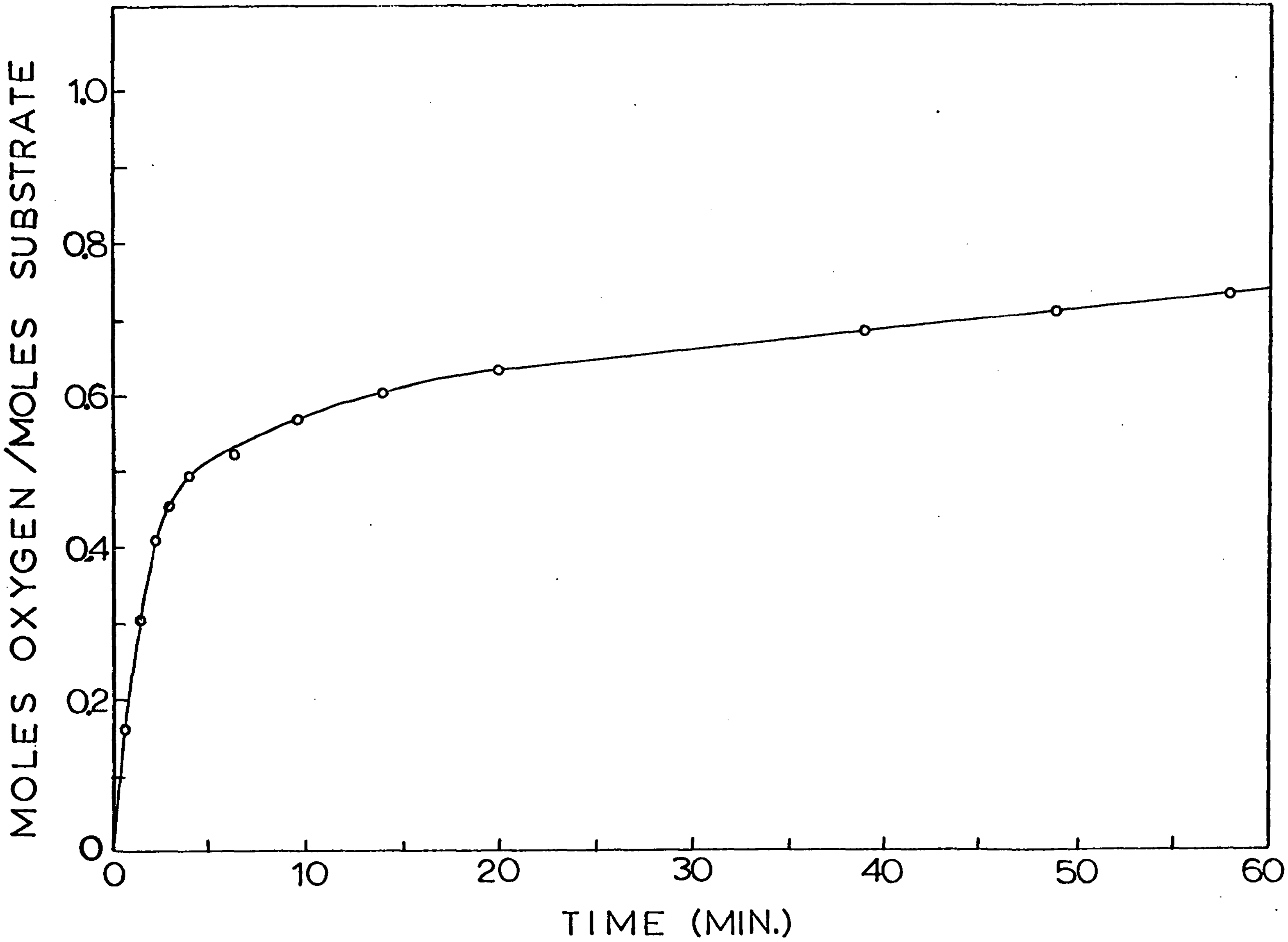
$$(87) \quad CH_3SO\overset{\ominus}{C}H_2K^+ + O_2 \longrightarrow CH_3SOCH_2O\overset{-}{O}K^+ \longrightarrow \text{oxygenated products}$$

---

[1] The presence of t-butyl alcohol in the solution facilitates solution of potassium t-butoxide; the latter is relatively insoluable in pure pyridine.

[2] Triton B = benzyltrimethylammonium methoxide, commercially available as a 40% solution in methanol.

Figure 3. Oxidation of dimethyl sulfoxide in pure dimethyl sulfoxide containing potassium t-butoxide (2.75 mmoles potassium t-butoxide in 25 ml.)


MOLES OXYGEN / MOLES SUBSTRATE
1.0
0.8
0.6
0.4
0.2
0
0
10
20
30
40
50
60
TIME (MIN.)

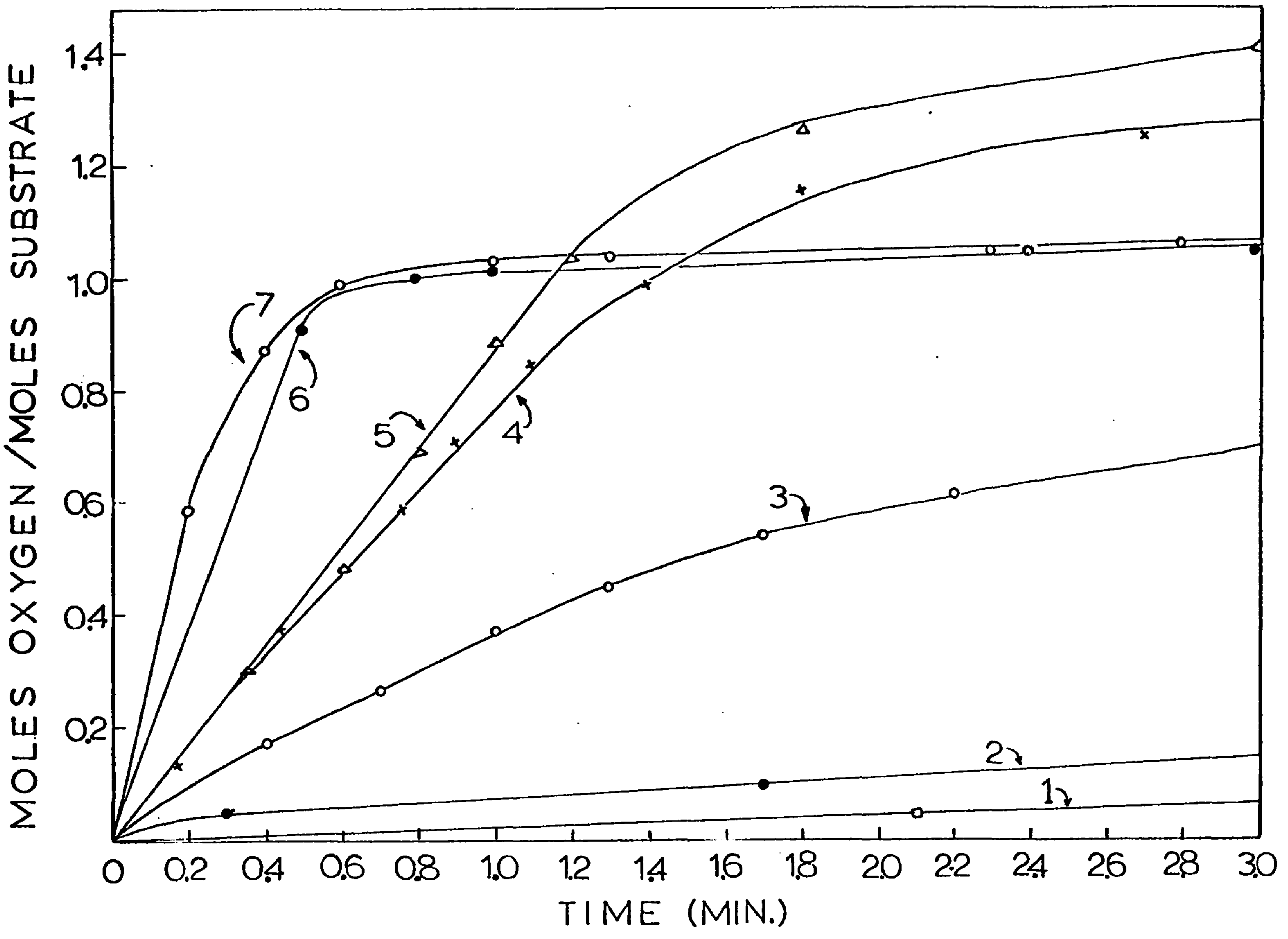
At the time of this work the ionization of dimethyl sulfoxide by potassium t-butoxide was not reported in the literature but examples of the reaction of the "methylsulfinyl" carbanion have been reported since (110). It was thought that possibly the addition of t-butyl alcohol to dimethyl sulfoxide might suppress the ionization equilibrium to the extent that the solvent system might be stable to oxygen. It would be advantageous to use as little t-butyl alcohol as possible so as to preserve the solvating ability of dimethyl sulfoxide. A solvent mixture containing 80 parts dimethyl sulfoxide and 20 parts t-butyl alcohol was found to be adequately stable to oxygen for oxidation rate measurements and was a good ionizing medium. We were able to ionize and oxidize ortho- and para-substituted toluenes and diphenylmethanes having pK_a's in the order of 35.

During the course of scouting for solvent systems we investigated an additional number of solvent mixtures containing t-butyl alcohol for the oxidation of fluorene. Figure 4 shows the oxidation plots obtained when 20 parts t-butyl alcohol containing potassium t-butoxide in dimethyl sulfoxide, pyridine, piperidine, dioxane, morpholine or benzene were used. In an 80% - 20% mixture of a given solvent the oxidation was faster than in pure t-butyl alcohol by approximately 90 times for dimethyl sulfoxide, 70 times for pyridine, 30 times for piperidine or morpholine, 14 times for dioxane and 2 times for benzene. A larger total uptake of oxygen was observed for the secondary amines, piperidine and morpholine, than for any other solvent tried.

The addition of 10 parts dimethyl sulfoxide to t-butyl alcohol increased the rate of oxidation of fluorene by 15 times that in pure

Figure 4. Solvent effect on the autoxidation of fluorenyl anion (25 ml. solvent)

Curve 1	2.92 mmoles fluorene, 6.0 mmoles potassium *t*-butoxide in *t*-butyl alcohol
Curve 2	2.94 mmoles fluorene, 4.65 mmoles potassium *t*-butoxide in 80% benzene - 20% *t*-butyl alcohol
Curve 3	3.08 mmoles fluorene, 4.65 mmoles potassium *t*-butoxide in 80% dioxane - 20% *t*-butyl alcohol
Curve 4	3.05 mmoles fluorene, 4.65 mmoles potassium *t*-butoxide in 80% morpholine - 20% *t*-butyl alchol
Curve 5	3.20 mmoles fluorene, 4.65 mmoles potassium *t*-butoxide in 80% piperidine - 20% *t*-butyl alcohol
Curve 6	2.94 mmoles fluorene, 4.65 mmoles potassium *t*-butoxide in 80% pyridine - 20% *t*-butyl alcohol
Curve 7	2.96 mmoles fluorene, 6.05 mmoles potassium *t*-butoxide in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol


MOLES OXYGEN / MOLES SUBSTRATE
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
TIME (MIN.)
7
6
5
4
3
2
1

_t_-butyl alcohol (Figure 5) although the addition of 0.09 millimoles (3 equivalent per cent) had no effect on the rate. Dimethyl sulfoxide filled the role of a true solvent and not that of an oxidation catalyst. Since 80% dimethyl sulfoxide - 20% _t_-butyl alcohol increased the rate of oxidation (approximately 90-fold) to the extent that the rate was near the fastest rate measurable on our system it follows that this solvent would show a "levelling" effect for the rates of oxidation of many substrates having pK_a's in the range of that of fluorene.

The levelling effect of 80% dimethyl sulfoxide - 20% _t_-butyl alcohol in the oxidation of _p_-nitrotoluene, _p_-nitroethylbenzene and _p_-nitrocumene is shown in Figure 6. In solvents containing less dimethyl sulfoxide (Figures 7 and 8) the relative rates of oxidation could be separated. These rates reflect the extent of ionization in the formation of primary, secondary and tertiary carbanions in the order of $1^\circ > 2^\circ > 3^\circ$. The ease of oxidation of carbanion to radical species should increase in the order $3^\circ > 2^\circ > 1^\circ$ as found by Russell, Moye and Nagpal (18). The rate of oxidation of _p_-nitrotoluene was essentially the same in all mixtures of dimethyl sulfoxide and _t_-butyl alcohol (Figure 9), although the total amount of oxygen absorbed increased noticeably with an increase in the ratio of dimethyl sulfoxide in the solvent. The levelling effect of the 80% dimethyl sulfoxide - 20% _t_-butyl alcohol solvent system forced us to select various mixtures of solvents to allow a comparison of rates as a function of a chosen variable within a given series.

The dimethyl sulfoxide solvent system was much better than any previously used ionizing solvent in studies of autoxidation of carbanions.

Figure 5. The effect of addition of dimethyl sulfoxide on the rates of oxidation of fluorene in *t*-butyl alcohol (25 ml. solvent)

Curve 1	2.92 mmoles fluorene, 6.0 mmoles potassium *t*-butoxide in *t*-butyl alcohol; also containing 0.09 mmoles dimethyl sulfoxide
Curve 2	2.92 mmoles fluorene, 6.06 mmoles potassium *t*-butoxide in 90% *t*-butyl alcohol - 10% dimethyl sulfoxide
Curve 3	2.96 mmoles fluorene, 6.05 mmoles potassium *t*-butoxide in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol

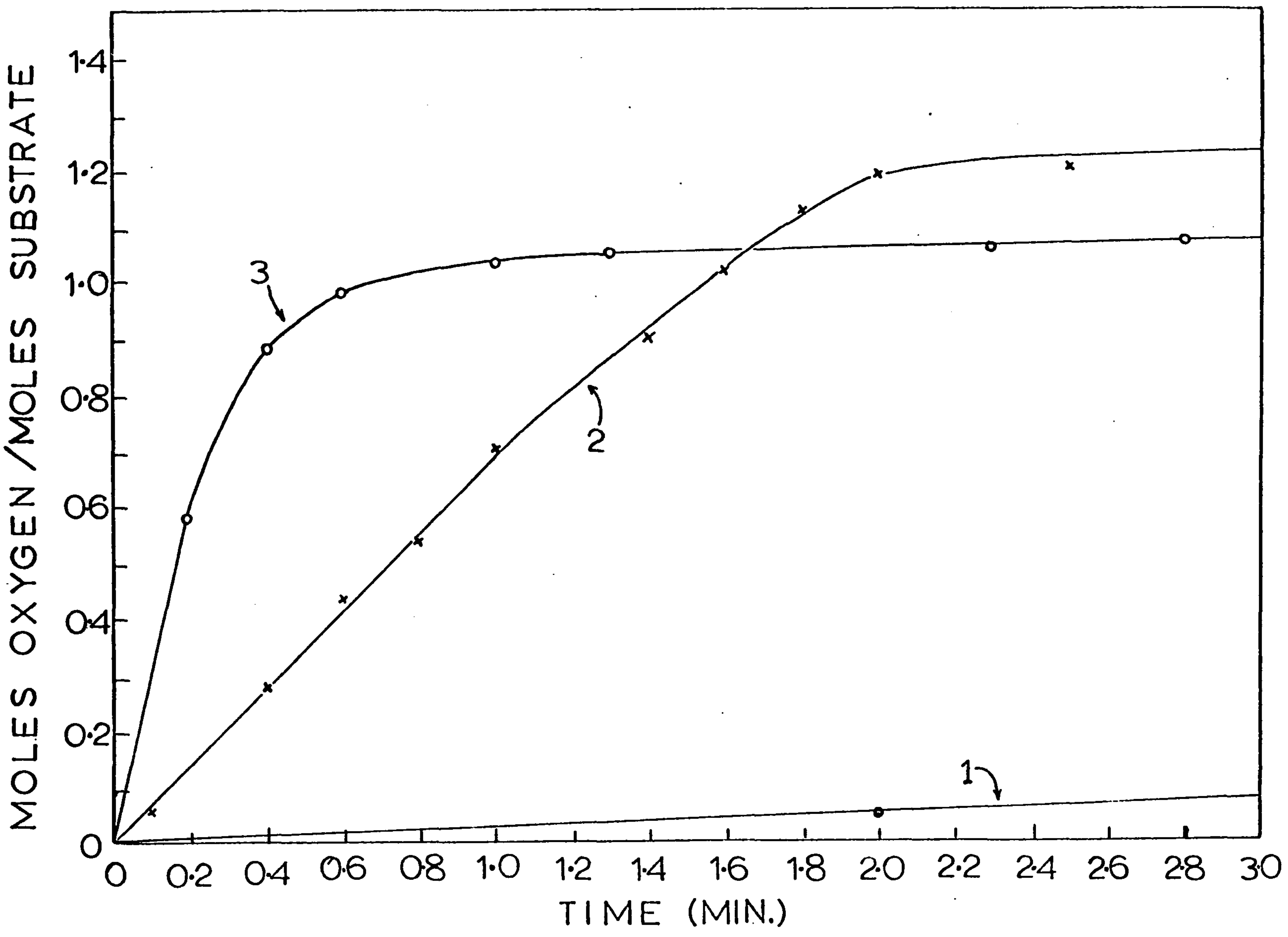

MOLES OXYGEN /MOLES SUBSTRATE
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0
0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0
2·2
2·4
2·6
2·8
3·0
TIME (MIN.)
3
2
1

Figure 6. Oxidation of para-alkyl nitrobenzenes in 80% dimethyl sulfoxide - 20% t-butyl alcohol (4 mmoles substrate (0.1 M); 8 mmoles potassium t-butoxide (.2 M); 40 ml. solvent)

Curve 1	p-nitrotoluene
Curve 2	p-nitroethylbenzene
Curve 3	p-nitrocumene

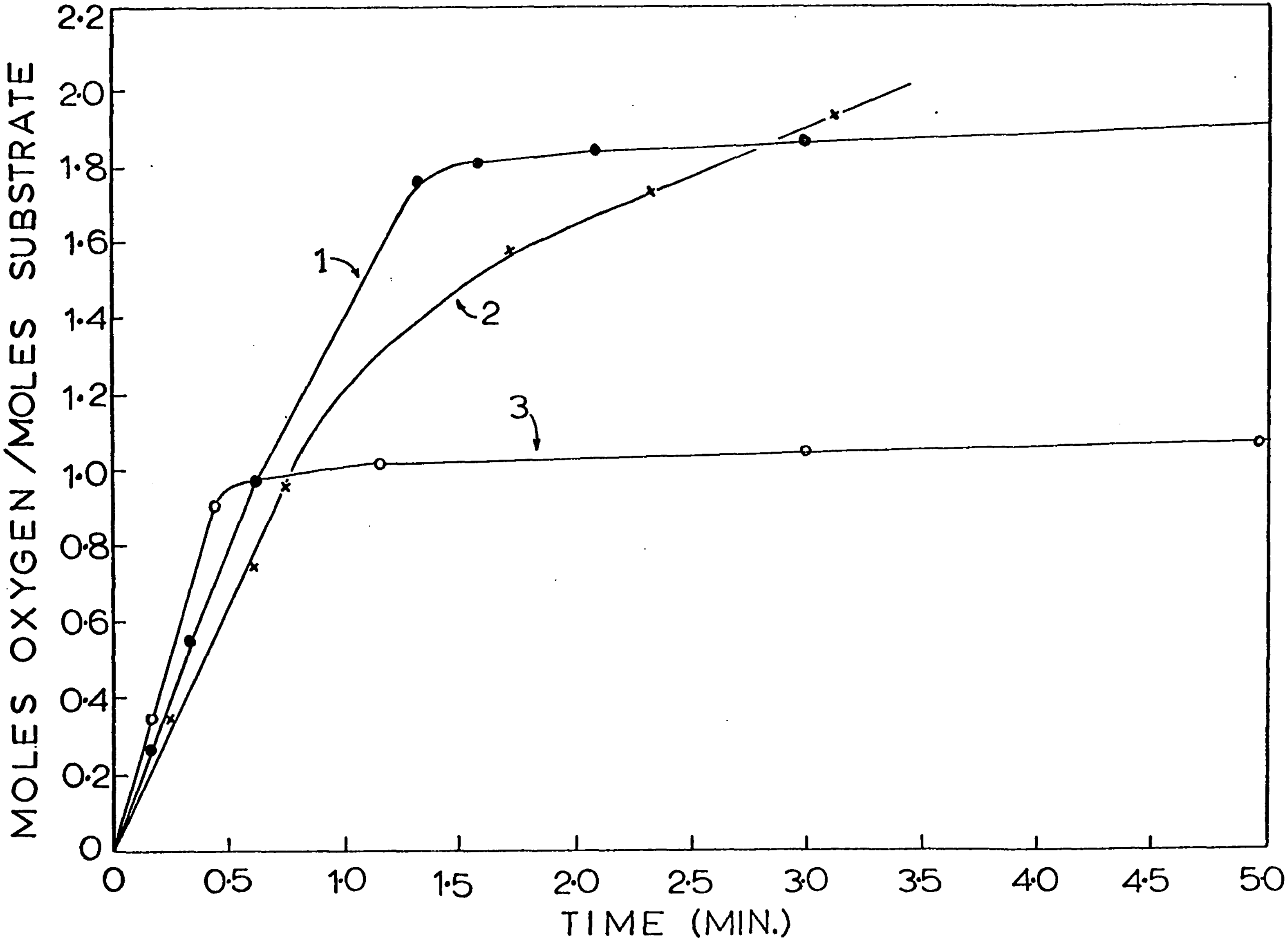

MOLES OXYGEN /MOLES SUBSTRATE
0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0
2·2
TIME (MIN.)
0
0·5
1·0
1·5
2·0
2·5
3·0
3·5
4·0
4·5
5·0
1
2
3

Figure 7. Oxidation of *para*-alkyl nitrobenzenes in 50% dimethyl sulfoxide - 50% *t*-butyl alcohol (4 mmoles substrate (0.1 M); 8 mmoles potassium *t*-butoxide (0.2 M); 40 ml. solvent)

Curve 1	*p*-nitrotoluene
Curve 2	*p*-nitroethylbenzene
Curve 3	*p*-nitrocumene

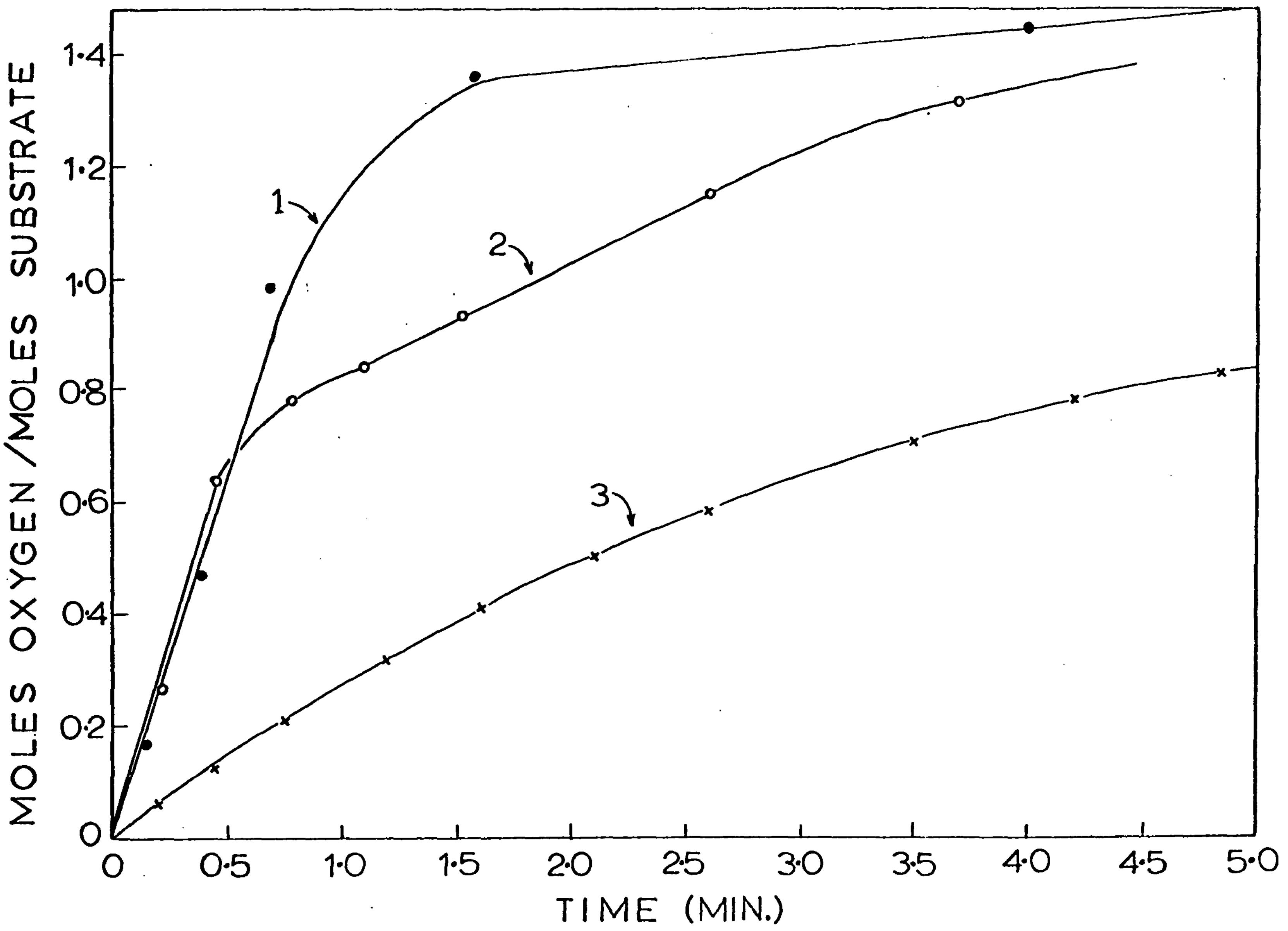

MOLES OXYGEN /MOLES SUBSTRATE
0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
0
0·5
1·0
1·5
2·0
2·5
3·0
3·5
4·0
4·5
5·0
TIME (MIN.)
1
2
3

Figure 8. Oxidation of *para*-alkyl nitrobenzenes in 20% dimethyl sulfoxide - 80% *t*-butyl alcohol (4 mmoles substrate (0.1 M); 8 mmoles potassium *t*-butoxide (0.2 M); 40 ml. solvent)

Curve 1	*p*-nitrotoluene
Curve 2	*p*-nitroethylbenzene
Curve 3	*p*-nitrocumene

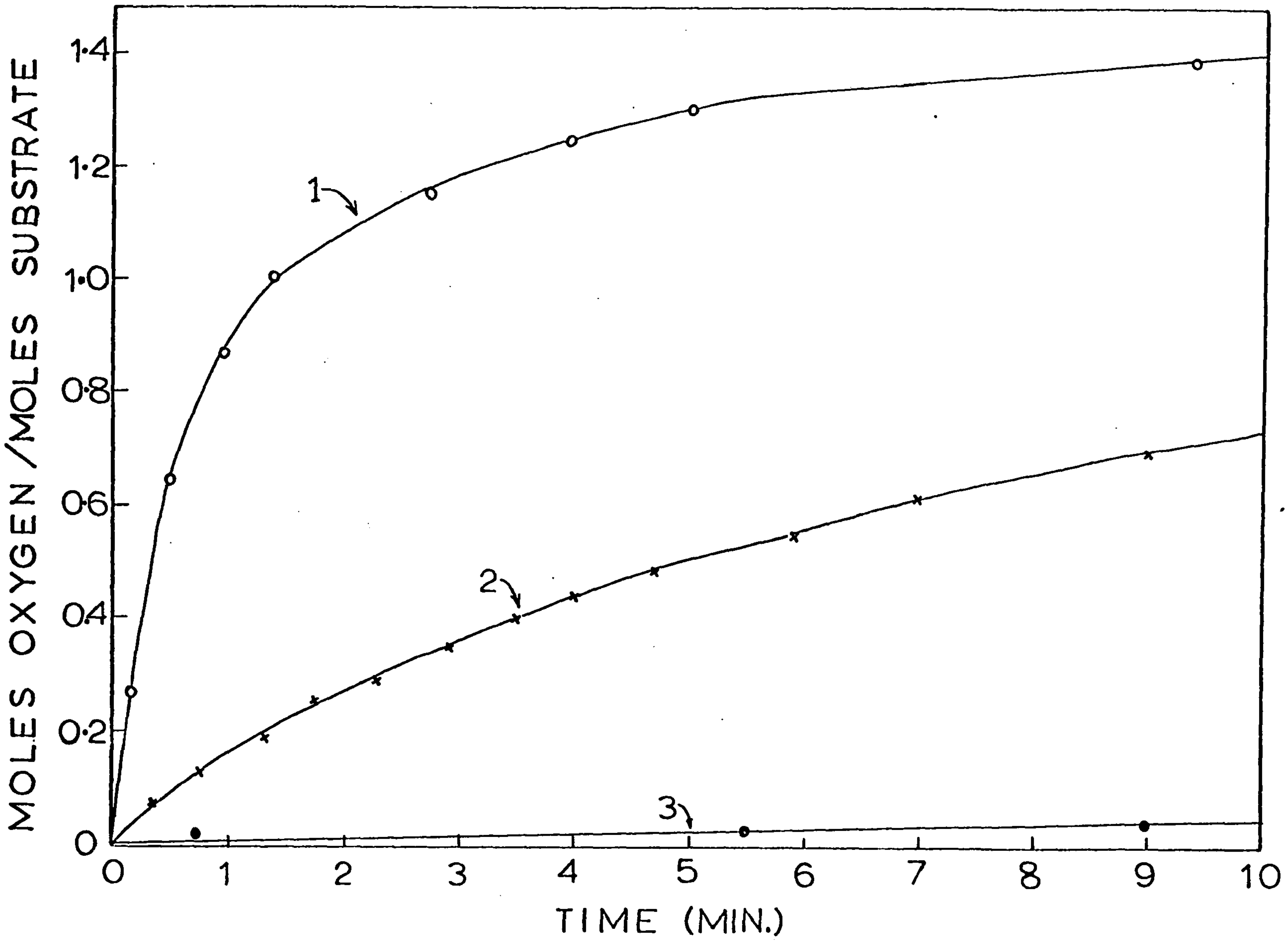
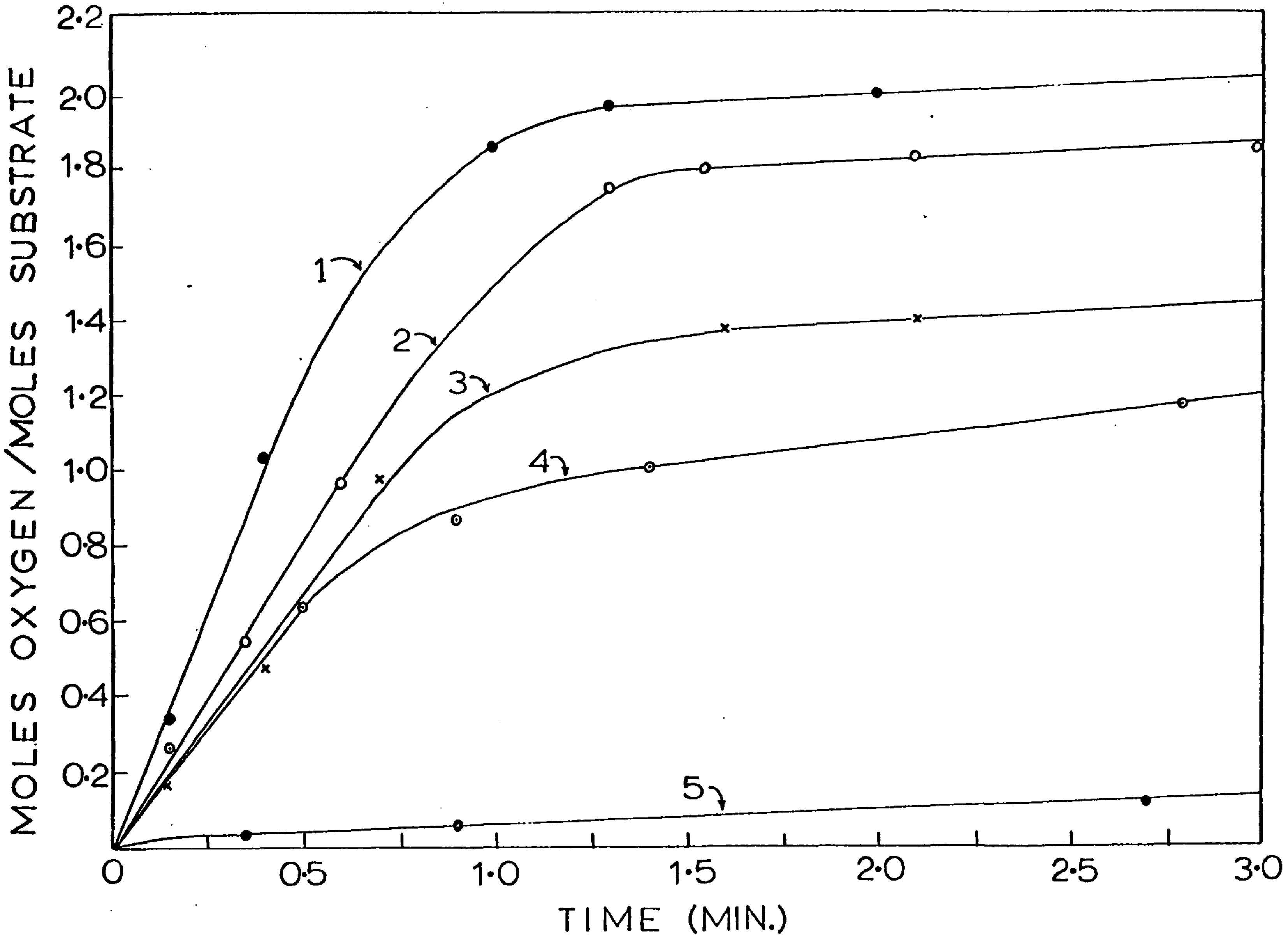

MOLES OXYGEN /MOLES SUBSTRATE
0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
0
1
2
3
4
5
6
7
8
9
10
TIME (MIN.)
1
2
3

Figure 9. Oxidation of *p*-nitrotoluene as a function of dimethyl sulfoxide content in *t*-butyl alcohol (4 mmoles *p*-nitrotoluene (0.1 M); 8 mmoles potassium *t*-butoxide (0.2 M); 40 ml. solvent)

Curve 1	in 100% dimethyl sulfoxide
Curve 2	in 80% dimethyl sulfoxide
Curve 3	in 50% dimethyl sulfoxide
Curve 4	in 20% dimethyl sulfoxide
Curve 5	in 100% *t*-butyl alcohol


MOLES OXYGEN /MOLES SUBSTRATE
2·2
2·0
1·8
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1·4
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TIME (MIN.)
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with pK_a's probably in the order of 36 would not ionize sufficiently in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol to initiate and maintain autoxidation, although diphenylmethane with pK_a of 35 did. In order to extend the range of autoxidation to even weaker acids than diphenylmethane, hexamethylphosphoramide, $\left[(CH_3)_2N\right]_3\overset{+}{P}-\overset{-}{O}$, was investigated as a solvent for the autoxidation of carbanions.

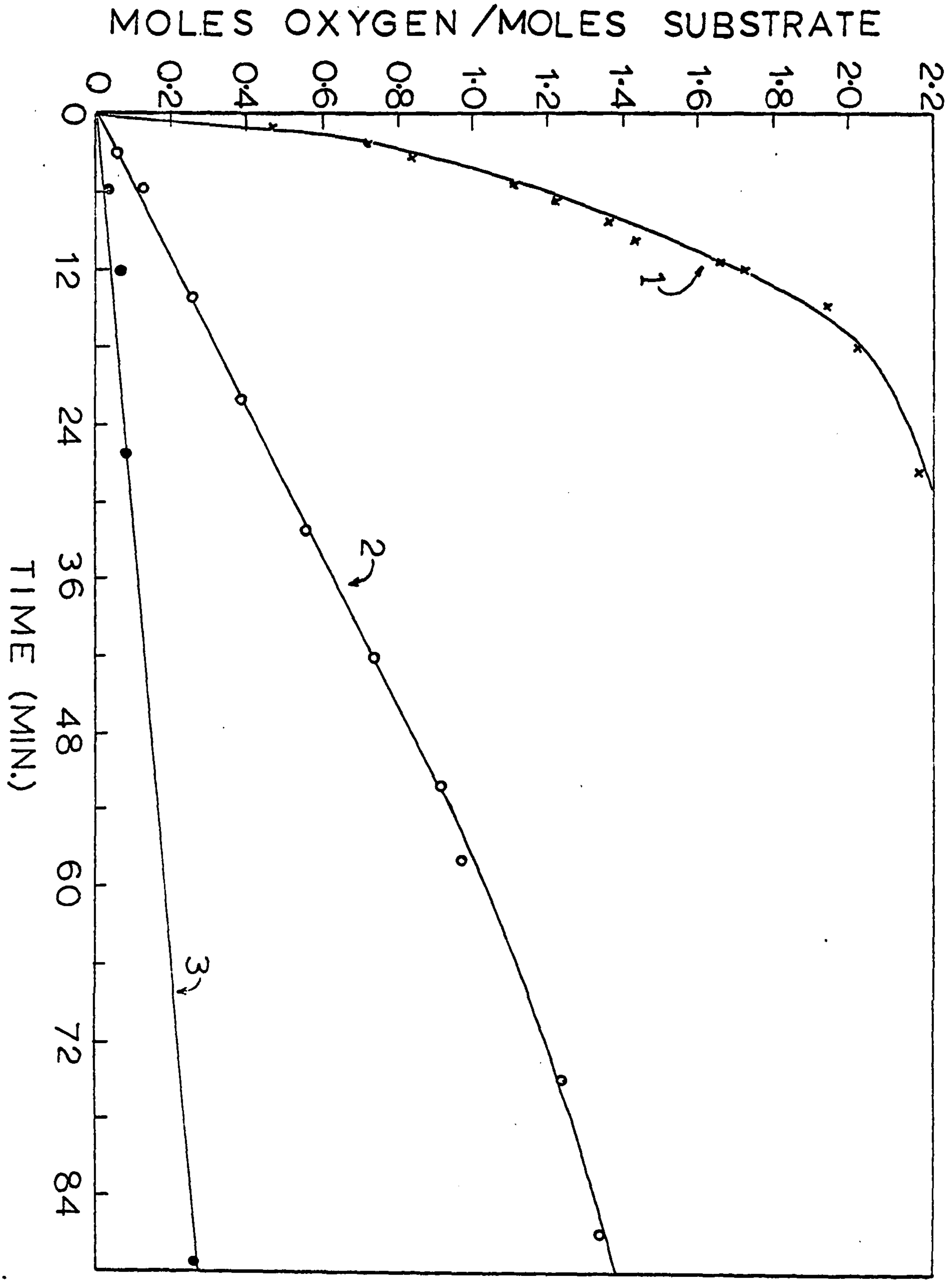
Hexamethylphosphoramide (HMPA) is a colorless liquid with a sweet amine-like odor. It dissolves dry potassium *t*-butoxide without any color change or evident reaction. A solution of hexamethylphosphoramide containing potassium *t*-butoxide absorbed oxygen slowly, approximately 15-20 ml. in 30 minutes (Figure 11).

A comparison of the two solvent systems, 80% dimethyl sulfoxide - 20% *t*-butyl alcohol and hexamethylphosphoramide containing potassium *t*-butoxide, could be made in the oxidation of the picolines. The rates of oxidation were slow for *α*- and *β*-picoline in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol and in the order of *γ*- > *α*- > *β*-picoline (Figure 10). Only in solutions containing 5 times excess base could the oxidation of *β*-picoline be observed. In hexamethylphosphoramide all picolines tried including *α*-, *β*-, *γ*-picoline, 2,6-lutidine and 2,4,6-collidine oxidized very rapidly and at approximately the same rate (Figure 11). For *β*-picoline the rate was approximately 100 times faster in hexamethylphosphoramide than in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol.

A similar comparison for the *α*- and *β*-methylnaphthalenes showed rates which were faster in hexamethylphosphoramide than in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol (Figure 12; the rates of oxidation of *α*- and *β*-methylnaphthalenes in 80% dimethyl sulfoxide - 20% *t*-butyl

Figure 10. Oxidation of picolines in 80% dimethyl sulfoxide - 20% _t_-butyl alcohol (4 mmoles substrate (0.1 M); 20 mmoles potassium _t_-butoxide (0.5 M); 40 ml. solvent)

Curve 1	_γ_-picoline
Curve 2	_α_-picoline
Curve 3	_β_-picoline


MOLES OXYGEN /MOLES SUBSTRATE
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2·2
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24
36
48
60
72
84
TIME (MIN.)
1
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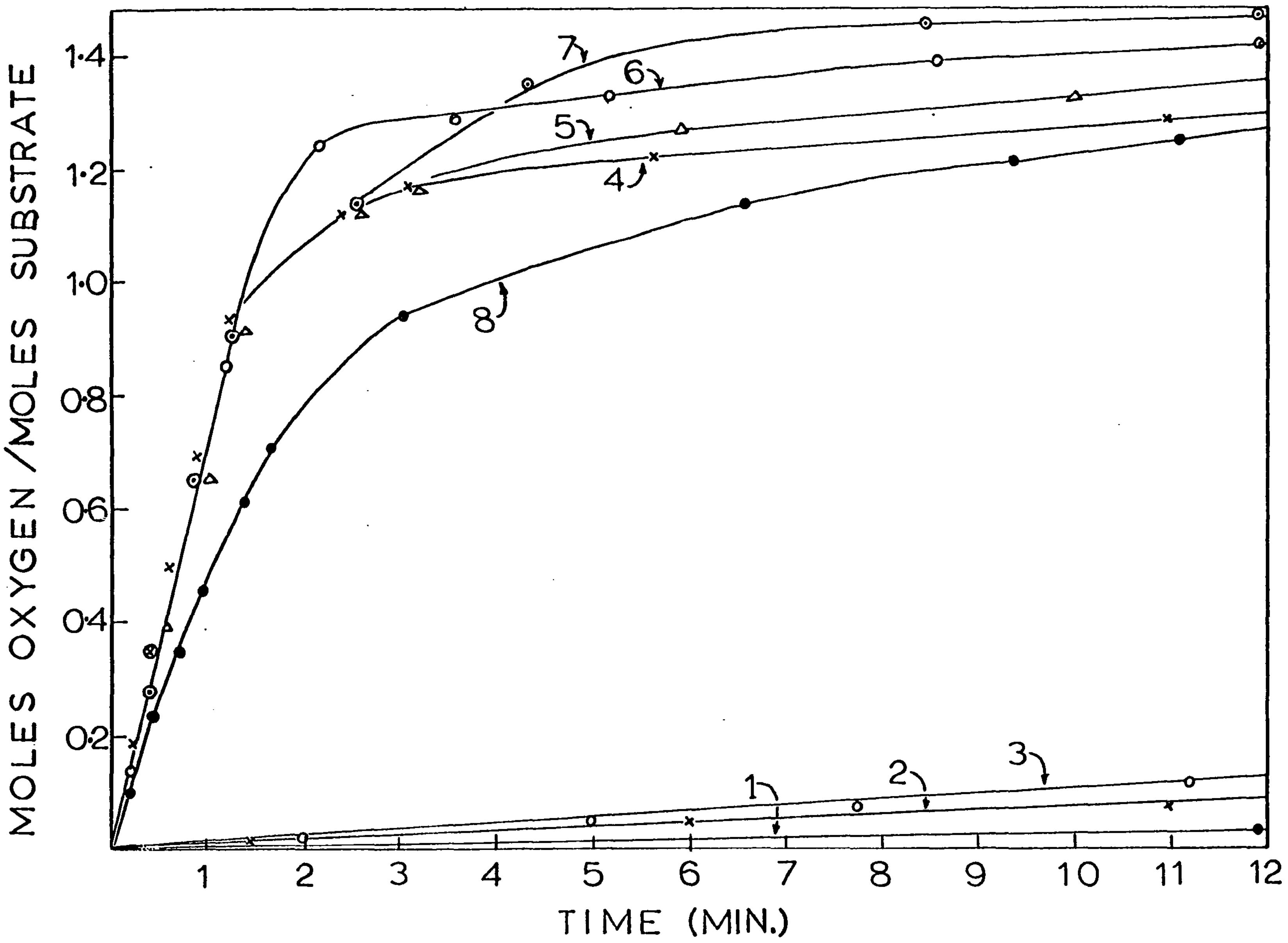
3

Figure 11. Oxidation of picolines in hexamethylphosphoramide (4 mmoles substrate (0.1 M); 10 mmoles potassium *t*-butoxide (0.2 M); 40 ml. solvent)

Curve 1	solvent oxidation
Curve 2	pyridine oxidation
Curve 3	*γ*-picoline in 80% hexamethylphosphoramide - 20% *t*-butyl alcohol
Curve 4	*γ*-picoline
Curve 5	2,4,6-collidine
Curve 6	*α*-picoline
Curve 7	2,4-lutidine
Curve 8	*β*-picoline


MOLES OXYGEN /MOLES SUBSTRATE
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TIME (MIN.)
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10
11
12
1
2
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4
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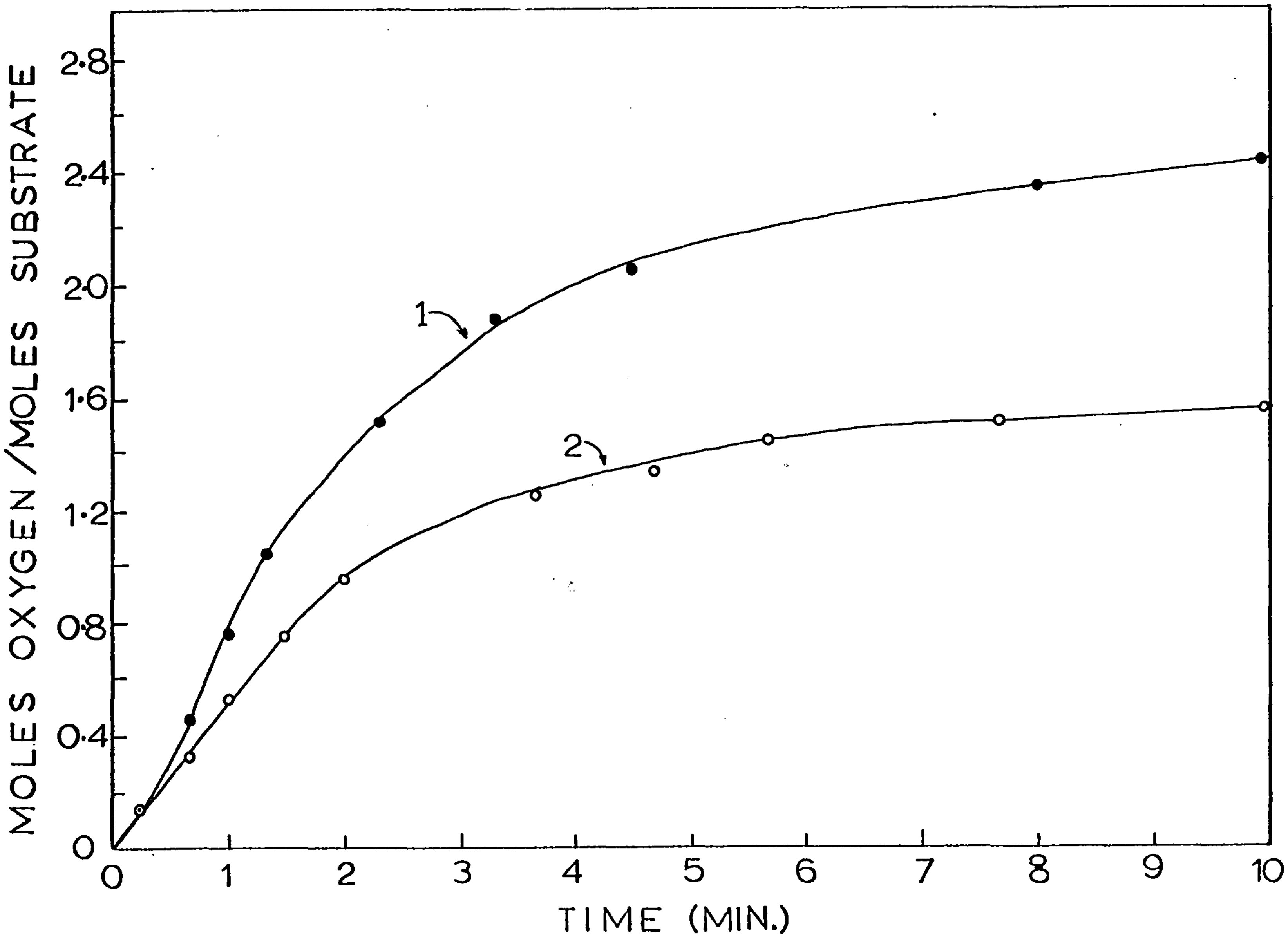
6
7
8

Figure 12. Oxidation of $\underline{\alpha}$- and $\underline{\beta}$-methylnaphthalenes in hexamethylphosphoramide (4 mmoles substrate (0.1 M); 20 mmoles potassium t-butoxide (0.2 M); 40 ml. solvent)

Curve 1 $\underline{\alpha}$-methylnaphthalene

Curve 2 $\underline{\beta}$-methylnaphthalene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alcohol were very slightly greater than the rate of oxidation of the solvent (solvent blank) and are not plotted).

C. Relative Rates and Products

1. Products as a function of solvent

The relative rates of oxidation of the nitro derivatives of aralkyl hydrocarbons as a function of solvent was discussed in the previous section. The character and yield of products isolated from the oxidations will be presented here.

Moye (3) found p,p'-dinitrobibenzyl and p-nitrobenzoic acid to be the only products in the base-catalyzed oxidation of p-nitrotoluene. Extended oxidation periods produced p,p'-dinitrostilbene as a result of oxidation of the bibenzyl derivative. There has not been a method devised which allows quantitative separation of the stilbene from the bibenzyl. The melting point of the isolated product gives an approximate idea of the main components of the dimeric products since the saturated dimer melts at 182-4° and the unsaturated dimer at 185-6° (cis), 304-6° (trans) (111). We have found that in solvents where oxidation is more rapid than in t-butyl alcohol, larger amounts of dimeric products are formed.

The product distribtuion in the oxidation of p-nitrotoluene in pyridine is given in Table 1. Runs 211-A and 212-A were experiments showing that results were reproducible. The fastest oxidations in the group of trials were Runs 211-A, 209-A and 207-A and these had approximately the same high yield of dimeric products (approximately 87%) although Run 207-A seems to be anomalous. Possibly some potassium carbonate was separated along with the dimeric products in the filteration

Table 1. Products of *p*-nitrotoluene oxidation in pyridine

Run	Solvent[a] (25 ml.)	PNT[b] (mmoles)	*t*-BuOK[c] (mmoles)	*t*-BuOK / PNT	Crude Yield			
					Dimer[d]		Acid[e]	
202-A	0	3.6	9.7	2.7	1.39	77%	1.25	35%
211-A	80	3.8	4.85	1.3	1.64	87%	.38	10%
212-A	80	4.0	4.85	1.2	1.74	87%	.40	10%
209-A[f]	80	3.8	4.85	1.3	1.69	88%	.35	9%
208-A	100	3.7	16.4[g]	4.5	1.04	56%	1.11	30%
207-A[f]	100	3.7	16.4[g]	4.5	1.65	89%	.92	25%

[a] Per cent by volume pyridine in *t*-butyl alcohol

[b] PNT = *p*-nitrotoluene

[c] *t*-BuOK = potassium *t*-butoxide

[d] Dimer = mmoles *p*,*p*'-dinitrobibenzyl + *p*,*p*'-dinitrostilbene

[e] Acid = mmoles *p*-nitrobenzoic acid

[f] Solution contains 1 g. pyridine-N-oxide

[g] Lithium *t*-butoxide

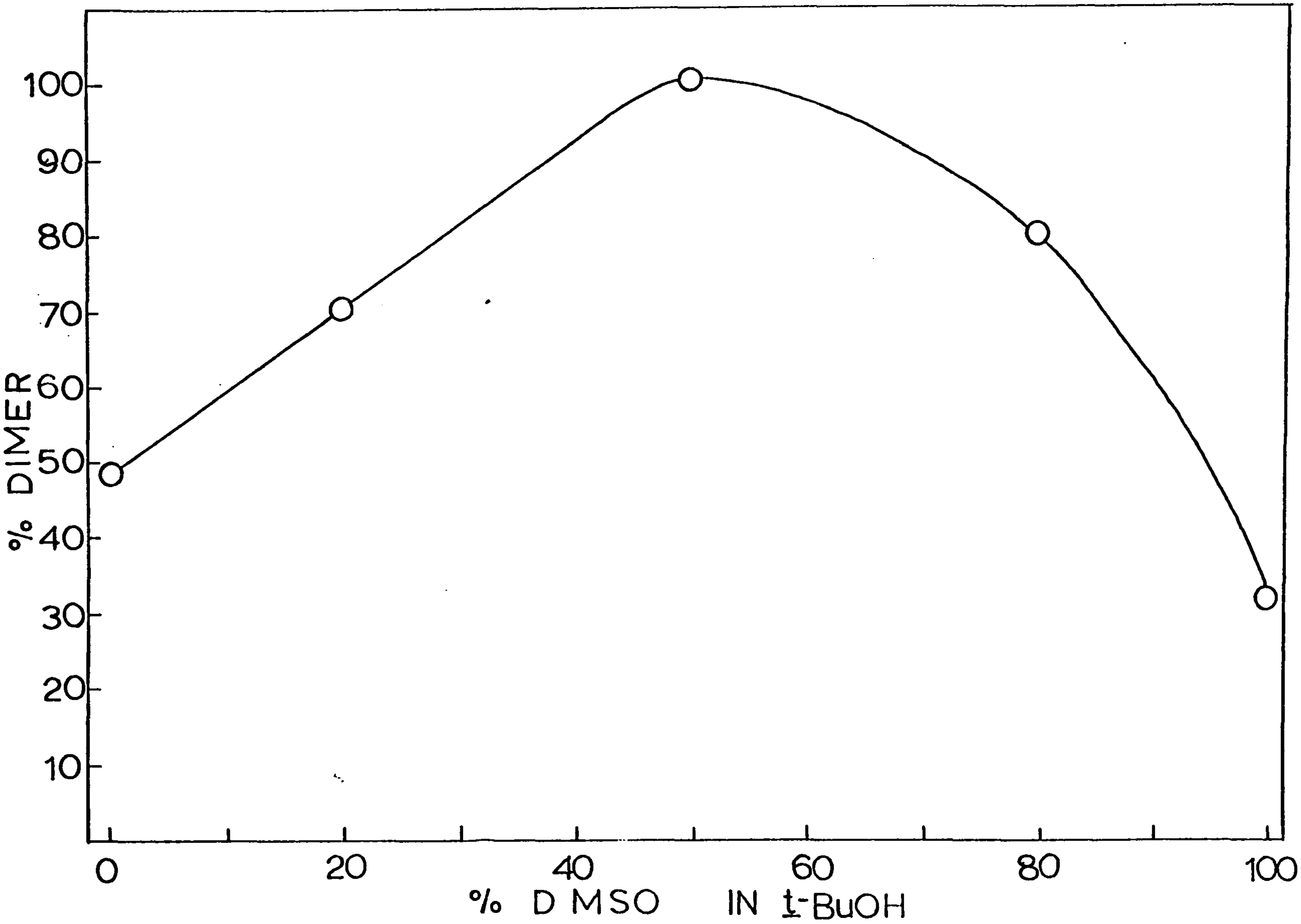
and increased the weight of the isolated product; the calculated recovery was over 100% for Runs 202-A and 207-A. The slower oxidations produced lower yields of dimeric products, the lowest being that for the pyridine-lithium *t*-butoxide system (56%) where the oxidation was slower than in *t*-butyl alcohol containing potassium *t*-butoxide.

Because of our interest in the products of oxidation of *p*-nitrotoluene in dimethyl sulfoxide we performed a series of oxidations in increasing amounts of dimethyl sulfoxide in *t*-butyl alcohol. The experiments produced high yields of dimeric products consisting of the stilbene derivative which increased to a maximum of 100% at a mixture of 50% dimethyl sulfoxide - 50% t-butyl alcohol but which fell off in the 80% dimethyl sulfoxide - 20% t-butyl alcohol mixture to 80% (Figure 13, Table 2). In pure dimethyl sulfoxide only a 32% yield of very impure dimeric products was obtained. The possibility of decomposition of dimer in the highly basic medium was substantiated by Run 108-B where p,p'-dinitrostilbene was completely decomposed, probably via a base-addition-oxidation mechanism to p-nitrobenzoic acid under more stringent conditions than existed in a normal oxidation. Although increasing the ratio of base to p-nitrotoluene had the effect of reducing the yield of isolated dimer in 80% dimethyl sulfoxide - 20% t-butyl alcohol (Run 107_1-B) which could be the result of dimer decomposition, decreasing the base to p-nitrotoluene ratio also decreased the yield of dimer (Run 107_2-B).

There seem to be important reaction steps in the rapid oxidation which respond in opposite directions when a given variable is changed. The catalytic effect by some components of this system must be very important, e.g., p,p'-dinitrostilbene. Figure 13 shows that a good straight line can be drawn through the first three points obtained for the oxidation in t-butyl alcohol, 20% and 80% dimethyl sulfoxide in t-butyl alcohol, but a smooth curve provides a better fit to the three points at 50% and 80% dimethyl sulfoxide in t-butyl alcohol and pure dimethyl sulfoxide.

The product of the oxidation of p-nitroethylbenzene in t-butyl alcohol was found by Moye (3) to be exclusively p-nitrobenzoic acid since p-nitroacetophenone, a supposed initial product, oxidized faster than p-nitroethylbenzene in this system. No dimeric product was formed in the

Figure 13. Per cent isolated dimer from the oxidation of _p_-nitrotoluene in progressive amounts of dimethyl sulfoxide in _t_-butyl alcohol (4 mmoles _p_-nitrotoluene (0.1 M); 8 mmoles potassium _t_-butoxide (0.2 M); 40 ml. solvent)



% DIMER
100
90
80
70
60
50
40
30
20
10
0
20
40
60
80
100
% DMSO IN t-BuOH

Table 2. Products of oxidation of *p*-nitrotoluene in dimethyl sulfoxide

Run	Solvent[a] (40 ml.)	PNT[b] (mmoles)	*t*-BuOK[c] (mmoles)	*t*-BuOK/PNT	Crude yield and melting point: Dimer[d]	Acid[e]
44_1-B	0	4	8	2	48% 175-8°	
44_2-B	100	4	8	2	32% 288-290°	
50-B	20	4	8	2	70% 280-290°	238-241°
53-B	50	4	8	2	104% 303-5°	trace
57-B	80	4	8	2	80%	
107_1-B	80	3.6	9.6	2.7	74% 295-8°	19% 225-230°
107_2-B	80	3.8	6	1.6	71% 287-290°	32% 225-230°
109-B	80	3[f]	6	2	83% 290-300°	15% 229-235°
108-B	80[g]	.87[h]	3.6	4.2		120% 228-233° [i]

[a] Per cent volume dimethyl sulfoxide in *t*-butyl alcohol

[b] PNT = *p*-nitrotoluene

[c] BuOK = potassium *t*-butoxide

[d] Dimer = *p*,*p*'-dinitrobibenzyl, M.P. 282-4° and *p*,*p*'-dinitrostilbene, M.P. *cis* 185-186° *trans* 304-6° (111); mixture of *cis* and *trans* 150-255° (111)

[e] Acid = *p*-nitrobenzoic acid, M.P. 242°

[f] *p*,*p*'-Dinitrobibenzyl

[g] 25 ml.

[h] *p*,*p*'-Dinitrostilbene

[i] After recrystallization from ether/Skelly A, M.P. 234-5°; mixed melting point, 236-240°

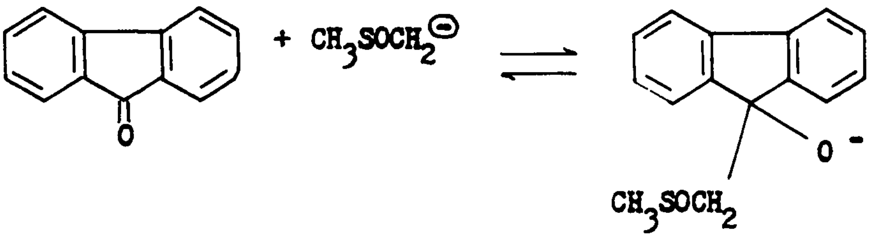
reaction. Since faster oxidations produced higher yields of dimer in the case of p-nitrotoluene the fast oxidation of p-nitroethylbenzene in mixtures of dimethyl sulfoxide might be expected to yield at least some dimeric species if the same mechanism of dimer formation held in both cases. In fact no dimer could be obtained from the oxidations of p-nitroethylbenzene in any combination of mixtures of dimethyl sulfoxide in t-butyl alcohol. The very fast oxidation in 80% dimethyl sulfoxide - 20% t-butyl alcohol only produced a small amount of red-brown sticky material which was not identified. A small amount of dimer was produced in the absence of air under similar conditions (see Spontaneous Dimerization).

The products of the oxidation of p-nitrocumene could be isolated and identified from a large scale experiment. Two oxidations were run each containing 0.2 M p-nitrocumene and 0.4 M potassium t-butoxide in 80 ml. 50% dimethyl sulfoxide - 50% t-butyl alchohol. The solutions were poured into water and the ether extracts combined. A very pale yellow viscous oil distilled at 110-120°at 1-2 mm. (112) which gave I.R. and N.M.R. spectra consistent with the structure of the p-nitrocumyl alcohol (α,α-dimethyl-p-nitrobenzyl alcohol). The alcohol appeared to be produced in good yield and was the only product isolated.

The I.R. absorptions included: 2.91 μ (broad peak for alcohol), 3.34 μ (methyl), and 6.24, 6.60, 7.42 μ (aromatic nitro group) in a capillary KBr cell; in CCl_4 the alcohol peak was sharp at 2.76 μ and the remaining peaks were essentially the same. The N.M.R. spectrum had peaks at 8.35 τ (single sharp peak, methyl), 7.42 τ (single sharp peak, alcohol) and aromatic peaks with an area ratio of 6:1:4 in accordance with the structure of *p*-nitrocumyl alcohol.

The oxidation of fluorene produced fluorenone in high yields in all but one of the solvent mixtures described previously. In *t*-butyl alcohol a 90% yield was obtained (Table 3); Moye (3) reported a 93% yield. In dimethyl sulfoxide the methylsulfinyl carbanion addition product was isolated.

(88)



An independent reaction performed with fluorenone and potassium *t*-butoxide in dimethyl sulfoxide produced the same addition product (see Appendix).

The yields of fluorenone and dimethyl sulfoxide adducts as a function of solvent and base concentration are listed in Table 3. A yield of adduct of approximately 75% could be obtained from the oxidation of fluorene in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol whether the ratio of base to fluorene was two or one as shown by Runs 21-A and 80-A. In a solvent containing less dimethyl sulfoxide the adduct formation was reduced accordingly. In 10% dimethyl sulfoxide - 90% *t*-butyl alcohol a yield of 8.6% adduct was isolated (Run 14-A). Fluorenol gave similar results to fluorene when oxidized in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol (Run 73-A).

Table 3. Products of fluorene oxidation

Run	Fluorene (g.)	*t*-BuOK[a] (mmoles)	Solvent[b] (25 ml.)	Product	Crude yield (g.)	Melting point
13-A	0.485	6	0	Fluorenone	0.481 (90%)	
21-A	.495	6	80	Adduct	.581 (78%)	149-152°
80-A	.511	3	80	Adduct	.574 (74%)	150-150.5° [c]
14-A	.486	6.1	10	Fluorenone	.466 (96%)	
				Adduct	.063 (8.6%)	145°
73-A[d]	.530	6.5	65	Adduct	.580 (72%)	146°

[a] *t*-BuOK = potassium *t*-butoxide

[b] Per cent by volume dimethyl sulfoxide in *t*-butyl alcohol

[c] Recrystallized from Skelly B

[d] Fluorenol

2. Rates and products as a function of structure

a. Nitro compounds The rates of oxidation of the series *p*-nitrotoluene, *p*-nitroethylbenzene and *p*-nitrocumene have been presented under the heading, Solvent Effects. Because of the levelling effect of 80% dimethyl sulfoxide - 20% *t*-butyl alcohol, the comparison of rates as the carbanion was varied from primary to secondary to tertiary could be made only in solvent systems where probably the extent of ionization was the controlling factor in the oxidation of the respective carbanions since the rates observed were in the order of $1^\circ > 2^\circ > 3^\circ$ (Figures 7 and 8). In 80% dimethyl sulfoxide - 20% *t*-butyl alcohol where ionization may be more rapid than diffusion of oxygen in the solvent the rates of oxidation of *p*-nitrotoluene, *p*-nitroethylbenzene and *p*-nitrocumene were essentially the same although if there was a difference it was in the order of $3^\circ > 1^\circ > 2^\circ$.

A number of interesting cases of steric inhibition of resonance between the nitro group and *ortho*-alkyl substituents have been uncovered in the oxidation of *ortho*-alkyl nitroaromatics. *o*-Nitrocumene was found to be completely unreactive in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol towards oxygen. Very little if any oxidation *via* the normal carbanion oxidation pathway took place. The oxidations of *o*-nitrotoluene and *o*-nitroethylbenzene in 20% dimethyl sulfoxide - 80% *t*-butyl alcohol were both slower than the *para*-isomers (Figure 14, which includes for comparison experiments for the *para*-isomers reported earlier). In 80% dimethyl sulfoxide - 20% *t*-butyl alcohol the oxidation of *o*-nitroethylbenzene was essentially as fast as the *para*-isomer; a slow oxidation was observed in *t*-butyl alcohol for *o*-nitroethylbenzene but nitromesitylene was completely stable in that solvent although it oxidized rapidly in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol. The ortho steric interaction contributing to non-planarity of the nitro group apparently followed the order *i*-propyl > dimethyl > ethyl > methyl.

In a series of oxidations of *ortho*-substituted *p*-nitrotoluenes in *t*-butyl alcohol

(89)

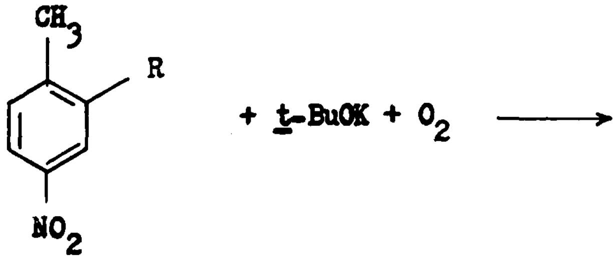
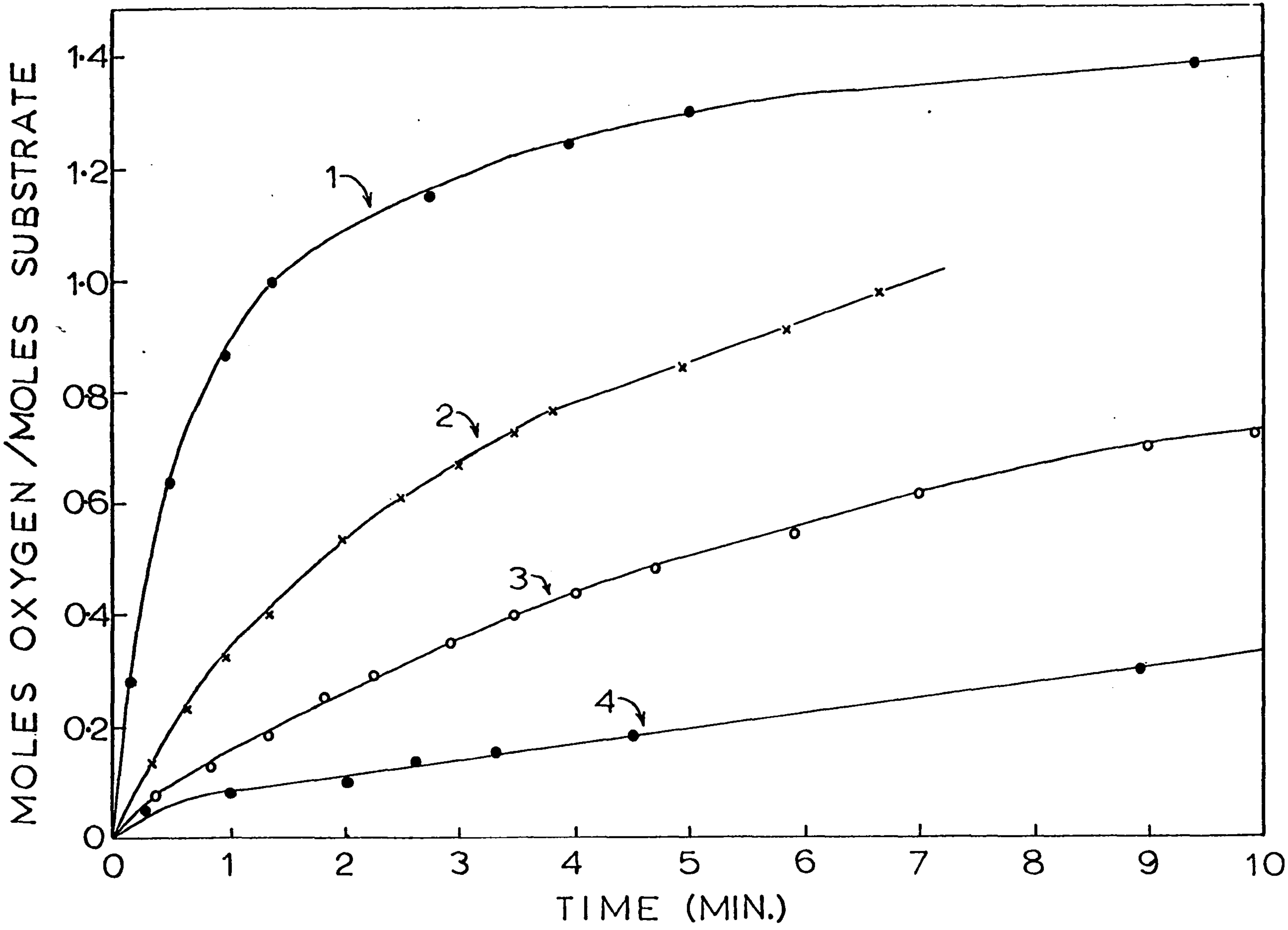


Figure 14. Comparison of the rates of oxidation of *ortho*-alkyl nitrobenzenes in 20% dimethyl sulfoxide - 80% *t*-butyl alcohol (4 mmoles substrate (0.1 M); 8 mmoles potassium *t*-butoxide (0.2 M); 40 ml. solvent)

Curve 1	*p*-nitrotoluene
Curve 2	*o*-nitrotolutene
Curve 3	*p*-nitroethylbenzene
Curve 4	*o*-nitroethylbenzene


MOLES OXYGEN /MOLES SUBSTRATE
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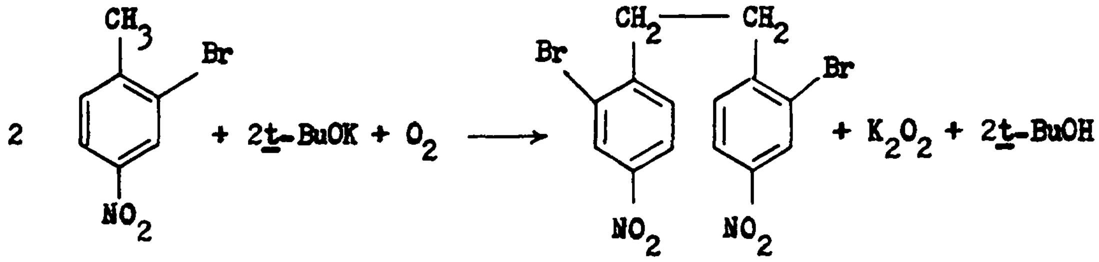
the following order of rates were observed: $Br \gg NO_2 > H \simeq NH_2 > CH_3$ (Figure 15). Because of the levelling effect of dimethyl sulfoxide it was thought that rates of oxidation of this series would show little or no difference in that solvent. In t-butyl alcohol the rate of oxidation within this series was probably controlled by the extent of ionization as for the series, p-nitrotoluene, p-nitroethylbenzene and p-nitrocumene.

In the case of the oxidation of 2-bromo-4-nitrotoluene an increase of rate of approximately 10 times over that for p-nitrotoluene was observed which indicated a large inductive effect aiding in the ionization of the substrate. For this compound a sharp break in the oxidation curve occurred at about 0.5 moles oxygen absorbed per mole starting substrate. Perhaps little or no acid was produced in this oxidation and the stoichiometry corresponded at this point to:

(90)



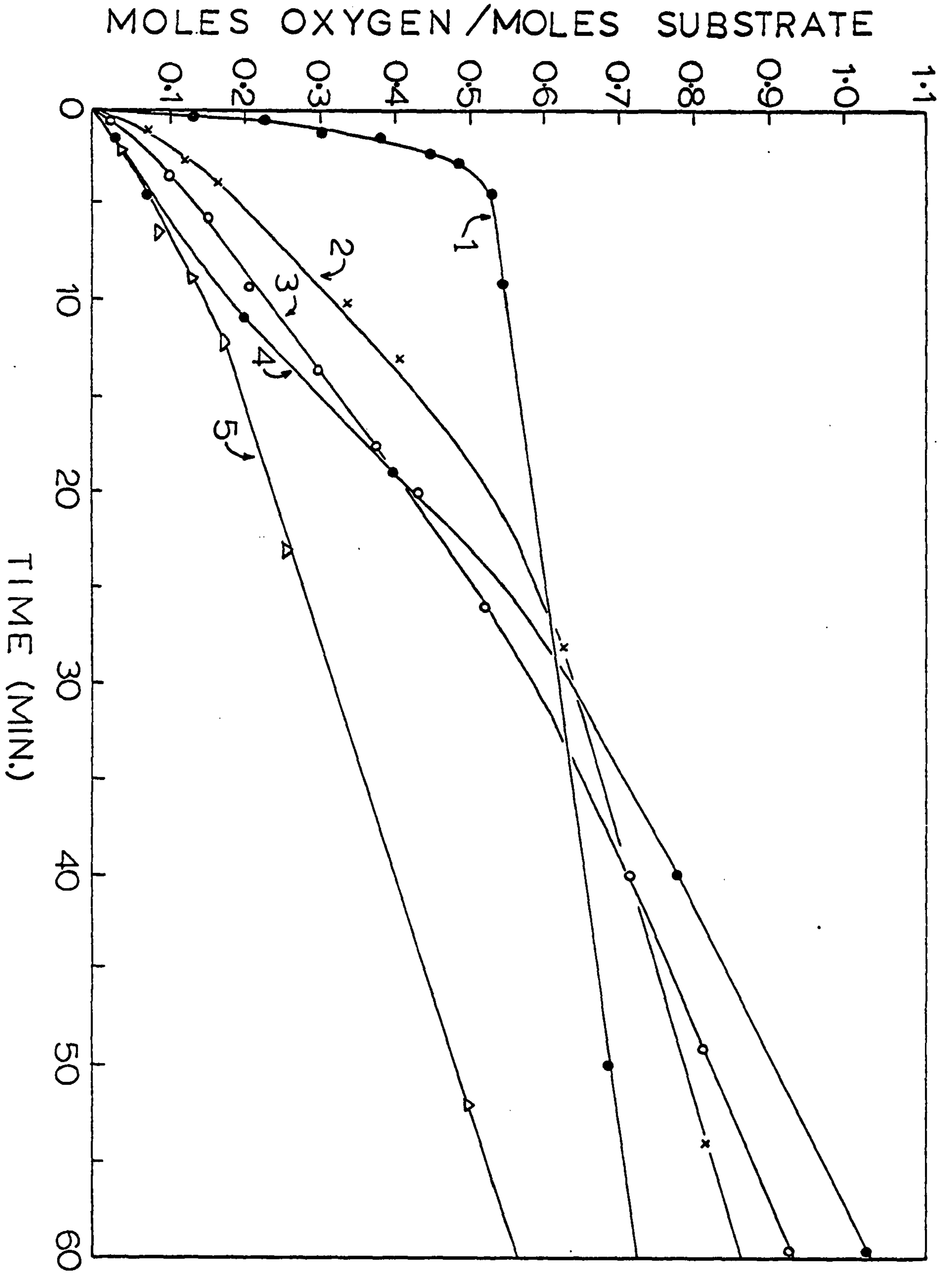
The occurrence of this reaction has not been established since products have not been characterized.

The slow oxidation of 2,4-dinitrotoluene was previously reported by Moye (3) and demonstrates the greater stability of the 2,4-dinitrobenzyl carbanion towards oxidation than the 2-bromo-4-nitrobenzyl carbanion.

The overall oxidation rate of 2-amino-4-nitrotoluene was very similar to that found for p-nitrotoluene. The well recognized electron-donating

Figure 15. Comparison of the rates of oxidation of *ortho*-substituted *p*-nitrotoluenes in *t*-butyl alcohol (3 mmoles substrate (0.1 M); 10 mmoles potassium *t*-butoxide (0.33 M); 30 ml. solvent)

Curve 1	*o*-bromo-*p*-nitrotoluene
Curve 2	*o*-nitro-*p*-nitrotoluene
Curve 3	*p*-nitrotoluene
Curve 4	*o*-amino-*p*-nitrotoluene
Curve 5	*o*-methyl-*p*-nitrotoluene


MOLES OXYGEN / MOLES SUBSTRATE
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TIME (MIN.)
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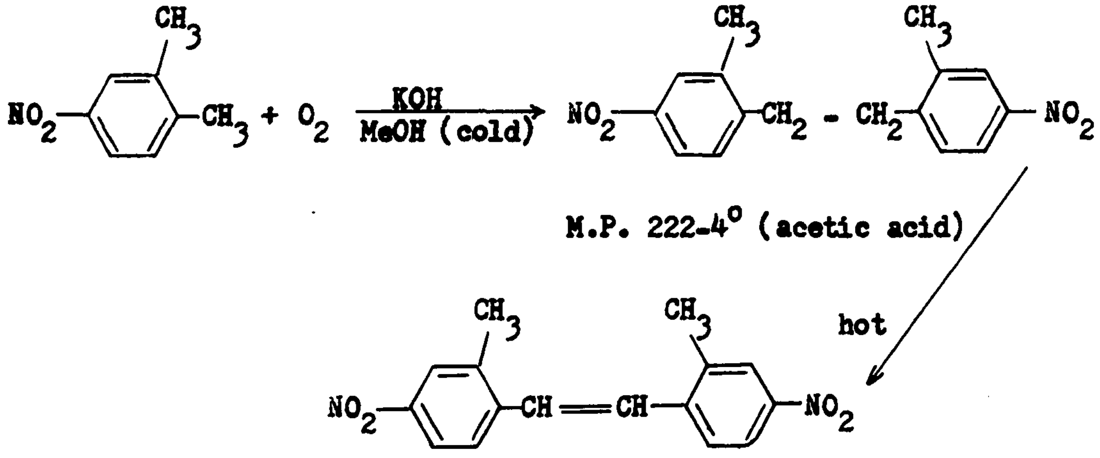
effect of an ortho- or para-amino substituent by resonance cannot come into play when the reaction site is already highly negative, and little effect is noticed by this substituent on the rate of ionization of substrate. It would be of interest to determine the fate of the amino group in this oxidation but no products were isolated for characterization.

The oxidation of 4-nitro-o-xylene was also slightly slower than that for p-nitrotoluene and this might be due to a destabilization of the carbanion by a slight positive inductive effect and/or an ortho steric effect of which examples were previously discussed. It has been previously reported that the oxidation of 4-nitro-o-xylene in methanolic potassium hydroxide gave dimeric saturated and unsaturated products (113):

(91)



M.P. 222-4° (acetic acid)

M.P. 288-290° (pyridine)

The product isolated gave upon recrystallization from acetic acid a pale yellow solid melting at 231-3°. Nothing precipitated from the aqueous acid solution indicating little, if any, acid was formed in the oxidation.

The 2-sulfonate derivative of p-nitrotoluene (5-nitro-o-toluenesulfonic acid) was also tried but the potassium salt was so insoluble in t-butyl alcohol that little oxidation was observed.

Moye (3) studied the oxidation of numerous α-substituted p-nitrotoluenes. Of these he found in t-butyl alcohol that oxidation was rapid for p-nitrodiphenylmethane and p-nitrobenzyl alcohol, slow for p,p'-dinitrodiphenylmethane and very slow for p-nitrophenylacetonitrile. A few additional members of this series were studied in 20% dimethyl sulfoxide - 80% t-butyl alcohol, p-nitrobenzyl phenyl ether, p-nitrophenyl acetic acid and p-nitrobenzyl bromide.

(92) $\text{p-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{-R} + \text{BuOK} + \text{O}_2 \longrightarrow$

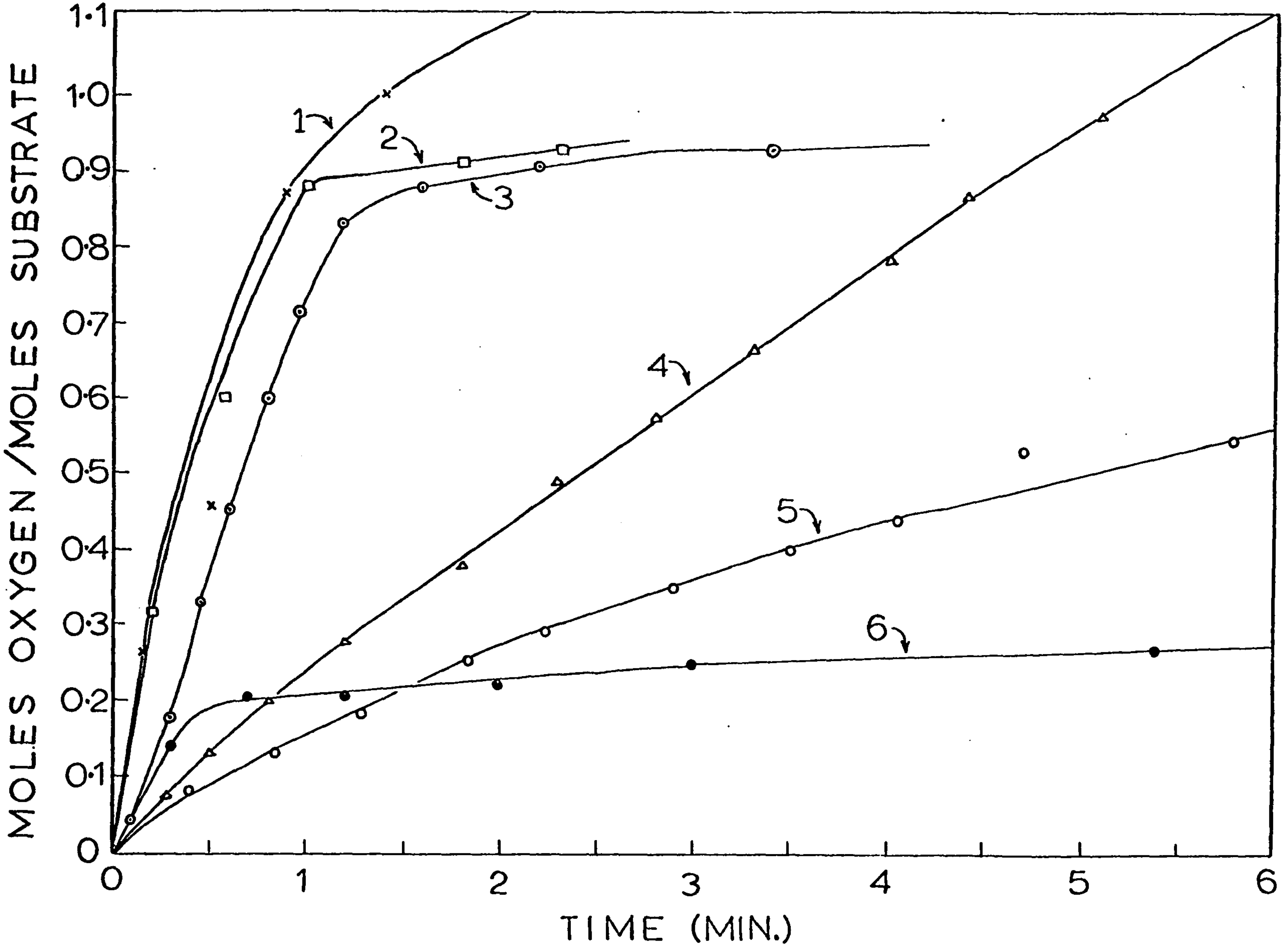
where R = CH_3, C_6H_5, $C_6H_4NO_2$, CN, O^- (Moye); C_6H_5O , COO^-, Br, O^-, CH_3 (this work).

The oxidation rates for p-nitrobenzyl phenyl ether and p-nitrophenyl acetic acid were fast and essentially the same as that for p-nitrotoluene (Figure 16). p-Nitrobenzyl alcohol oxidized slower than the latter, although faster than p-nitroethylbenzene. Oxidation of p-nitrobenzyl bromide began rapidly but stopped abruptly at approximately 0.2 moles oxygen per starting moles substrate. A considerable inductive effect is being exerted by the oxygen both in the ether and in the carboxy groups in stabilizing the p-nitrobenzyl carbanion.

The products of the oxidation of p-nitrobenzyl phenyl ether were p-nitrobenzoic acid (determined by melting point of isolated product) and phenol (observed by smell in acidic aqueous solution). The major course of the reaction probably was:

Figure 16. Comparison of rates of oxidation of *p*-nitrobenzyl derivatives in 20% dimethyl sulfoxide - 80% *t*-butyl alcohol (4 mmoles substrate (0.1 M); 8 mmoles potassium *t*-butoxide (0.2 M); 40 ml. solvent)

Curve 1	*p*-nitrotoluene
Curve 2	*p*-nitrobenzyl phenyl ether
Curve 3	potassium *p*-nitrophenylacetate
Curve 4	*p*-nitrobenzyl alcoholate
Curve 5	*p*-nitroethylbenzene
Curve 6	*p*-nitrobenzyl bromide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TIME (MIN.)
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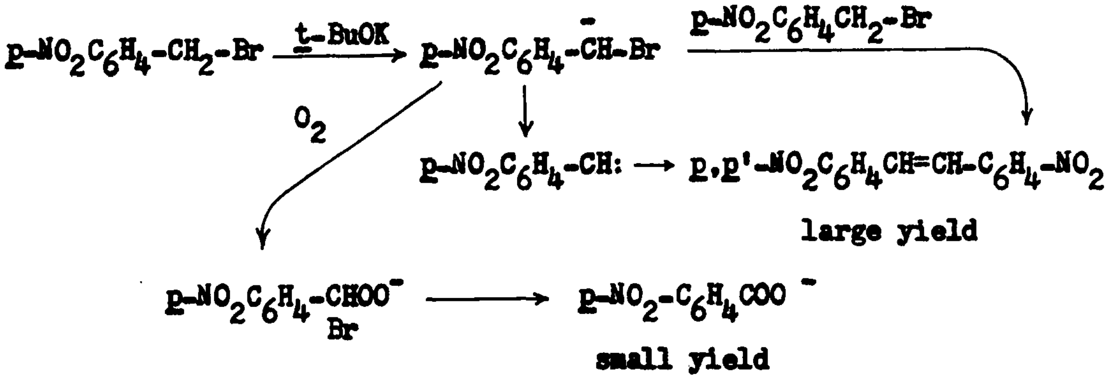
5
6

$$(93)\quad p\text{-}NO_2C_6H_4CH_2OC_6H_5 \xrightarrow{t\text{-}BuOK,\ O_2} p\text{-}NO_2C_6H_4COOC_6H_5 \xrightarrow{H_2O} p\text{-}NO_2C_6H_4COOH + C_6H_5OH$$

p-Nitrophenylacetic acid oxidation gave solids which precipitated from an acidic aqueous solution in the following order: ~0.4 g. yellow needles, M.P. 254°; 0.65 g. M.P. ~265° with decomposition, possibly decarboxylation; ~ 0.15 g. pale brown solid, M.P. 220-5° (from combined solutions of two oxidations). These products have not been characterized. From p-nitrobenzyl alcohol oxidation p-nitrobenzoic acid was obtained (determined by melting point). The attempted oxidation of p-nitrobenzylbromide produced an 85% yield of p,p'-dinitrostilbene either from a condensation reaction or from dimerization of a singlet carbene since very little oxygen was absorbed in the reaction:

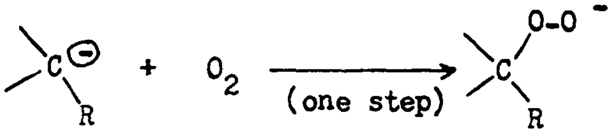
(94)



$$\begin{tikzcd}
p\text{-}NO_2C_6H_4\text{-}CH_2\text{-}Br \arrow[r, "t\text{-}BuOK"] & p\text{-}NO_2C_6H_4\text{-}\overset{-}{C}H\text{-}Br \arrow[d] \arrow[dr, bend left, "p\text{-}NO_2C_6H_4CH_2\text{-}Br"] \arrow[dl, "O_2"'] & \\
 & p\text{-}NO_2C_6H_4\text{-}CH: \arrow[r] & \underset{\text{large yield}}{p,p'\text{-}NO_2C_6H_4CH{=}CH\text{-}C_6H_4\text{-}NO_2} \\
\underset{Br}{p\text{-}NO_2C_6H_4\text{-}CHOO^-} \arrow[r] & \underset{\text{small yield}}{p\text{-}NO_2\text{-}C_6H_4COO^-} &
\end{tikzcd}$$

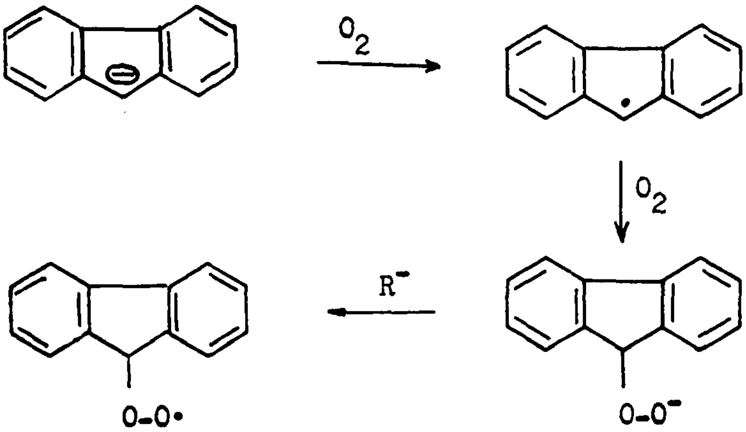
b. <u>Fluorene derivatives</u> The base-catalyzed oxidation of fluorene was studied by Sprinzak (7) in pyridine containing Triton B. Since at 0° he was able to isolate the hydroperoxides of 9-substituted fluorenes he suggested the following mechanism:

(20)



Moye (3) preferred a free radical mechanism for the oxidation of fluorene.

(95)



In an attempt to shed light on the mechanism of base-catalyzed oxidation of carbanions and specifically of fluorene, the effect of solvents, concentrations of reactants, substituents and catalysts on the initial rate of oxidation of fluorene was investigated. A description of the effects of catalysts will be presented under a future heading.

The solvent effect observed in the oxidation of fluorene has been described. The more polar solvents gave faster rates of oxidation as shown in Figure 4. This can be attributed to a faster rate of ionization, and possibly to an increased rate of electron transfer from carbanion to oxygen. In aprotic dipolar solvents (*e.g.*, dimethyl sulfoxide) anions are less solvated and have lower oxidation potentials (11). Increasing the concentration of both fluorene and potassium *t*-butoxide in an oxidation in t-butyl alcohol also increased the rate although the ratio of base to fluorene was held essentially the same (Figure 17).

The effect of ring substitution on the rate of oxidation was determined by comparing the rates of oxidation of 2-nitrofluorene, 2,7-dinitrofluorene, 2- and 3-hydroxyfluorene in 80% pyridine - 20% t-butyl alcohol[1] containing potassium t-butoxide. It was thought that if the rate-controlling step involved the rate of ionization, nitro groups in conjugation with the methylene hydrogens of fluorene should increase the rate of oxidation through more rapid ionization, while oxy anions should hinder the rate of ionization.

(96) $NO_2\text{-}R\text{-}H + B^- \longrightarrow NO_2\text{-}R^{\ominus} + B\text{-}H$ fast

(97) $^-O\text{-}R\text{-}H + B^- \longrightarrow {}^-O\text{-}R^{\ominus} + B\text{-}H$ slow

In t-butyl alcohol Moye (3) found 2-nitrofluorene oxidized faster than fluorene. In 80% pyridine - 20% t-butyl alcohol the oxidation of fluorene was about 150 times faster than in t-butyl alcohol. In this solvent fluorene oxidized faster than 2-nitrofluorene which in turn oxidized slightly faster than 2,7-dinitrofluorene (Figure 18). The predominant influence on the rate-controlling step in this series seems to be electron transfer from the carbanion and not ionization.

The rates of oxidation of the hydroxyfluorenes were considerably slower than that of fluorene in t-butyl alcohol, partly due to the insolubility of the potassium salts. In 80% pyridine - 20% t-butyl alcohol the rates were reasonably fast and in the order, fluorene >

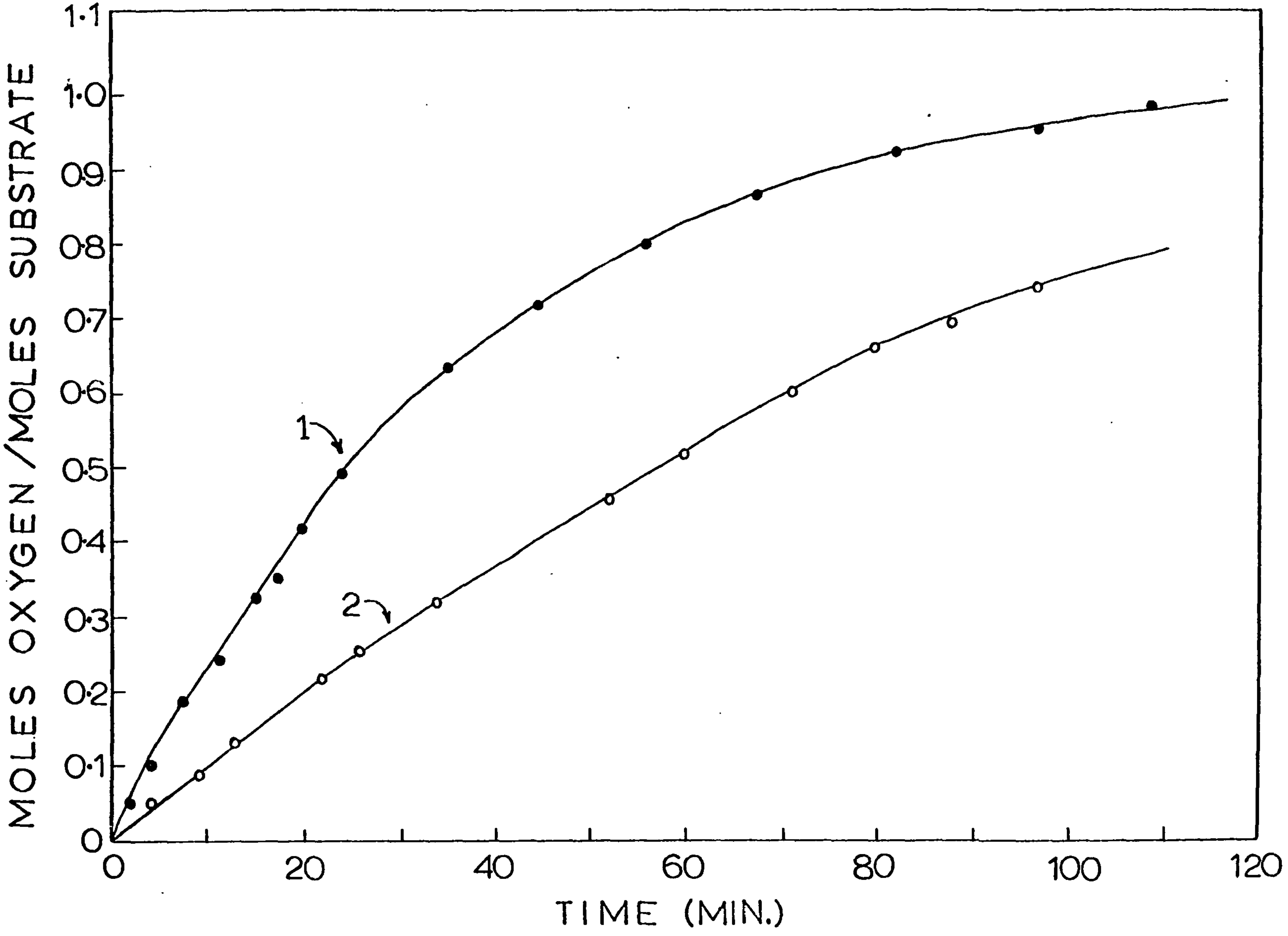
---

[1] 2,7-dinitrofluorene and the potassium salts of the hydroxyfluorenes were relatively insoluble in t-butyl alcohol.

Figure 17. Oxidation of fluorene in t-butyl alcohol at two concentrations (25 ml. solvent)

Curve 1 6 mmoles fluorene, 3.1 mmoles potassium t-butoxide

Curve 2 3.2 mmoles fluorene, 1.52 mmoles potassium t-butoxide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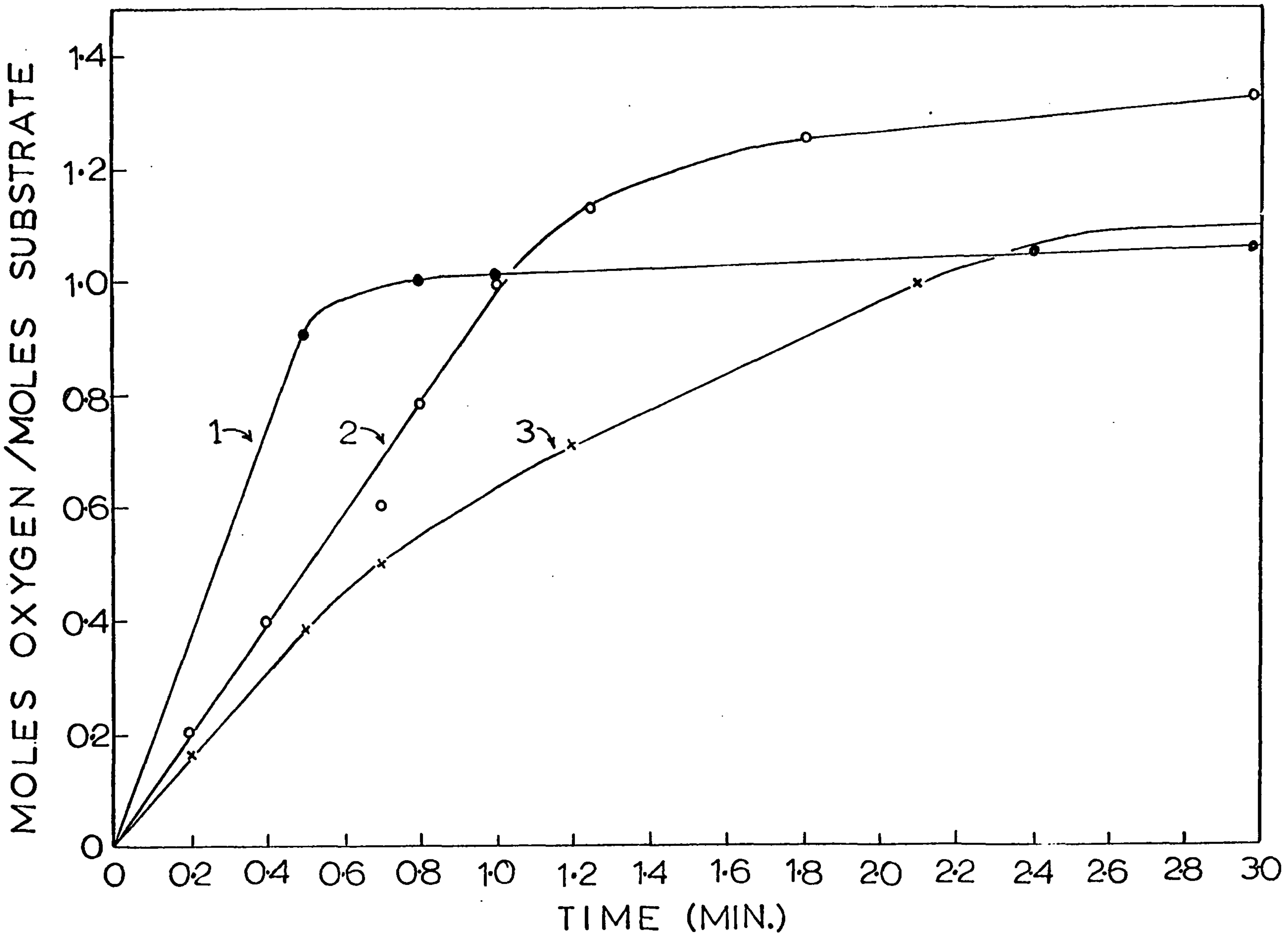
60
80
100
120
TIME (MIN.)
1
2

Figure 18. Oxidation of nitrofluorenes in 80% pyridine - 20% t-butyl alcohol (25 ml. solvent containing 4.65 mmoles potassium t-butoxide)

Curve 1	2.94 mmoles fluorene
Curve 2	2.91 mmoles 2-nitrofluorene
Curve 3	2.84 mmoles 2,7-dinitrofluorene


MOLES OXYGEN /MOLES SUBSTRATE
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3·0
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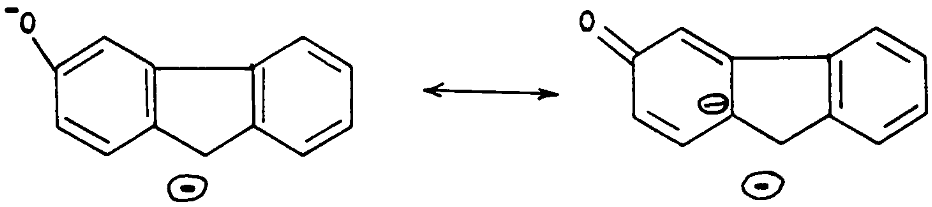
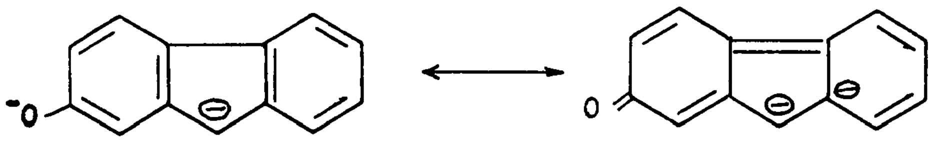
3

2-hydroxyfluorene > 3-hydroxyfluorene (Figure 19). Evidently this solvent system did not ionize the oxyfluorene carbanions fast enough for oxidation to become the rate-controlling step. The observed order of rates reflected the ease of ionization to carbanion controlling the rate of oxidation since the oxy substituent is more directly conjugated to the carbanion site when in the 3-position.



XII 3-oxyfluorene



XIII 2-oxyfluorene

The order of rates should be reversed if the ease of electron transfer were rate-limiting since the oxidation of carbanion to radical should be influenced by the stability of the resulting radical.

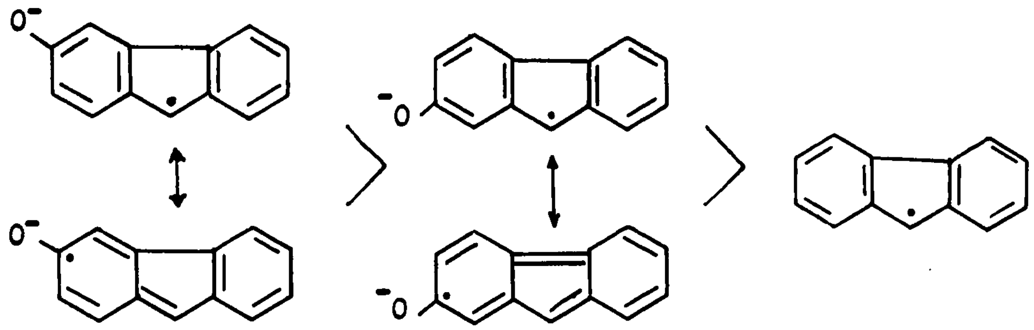
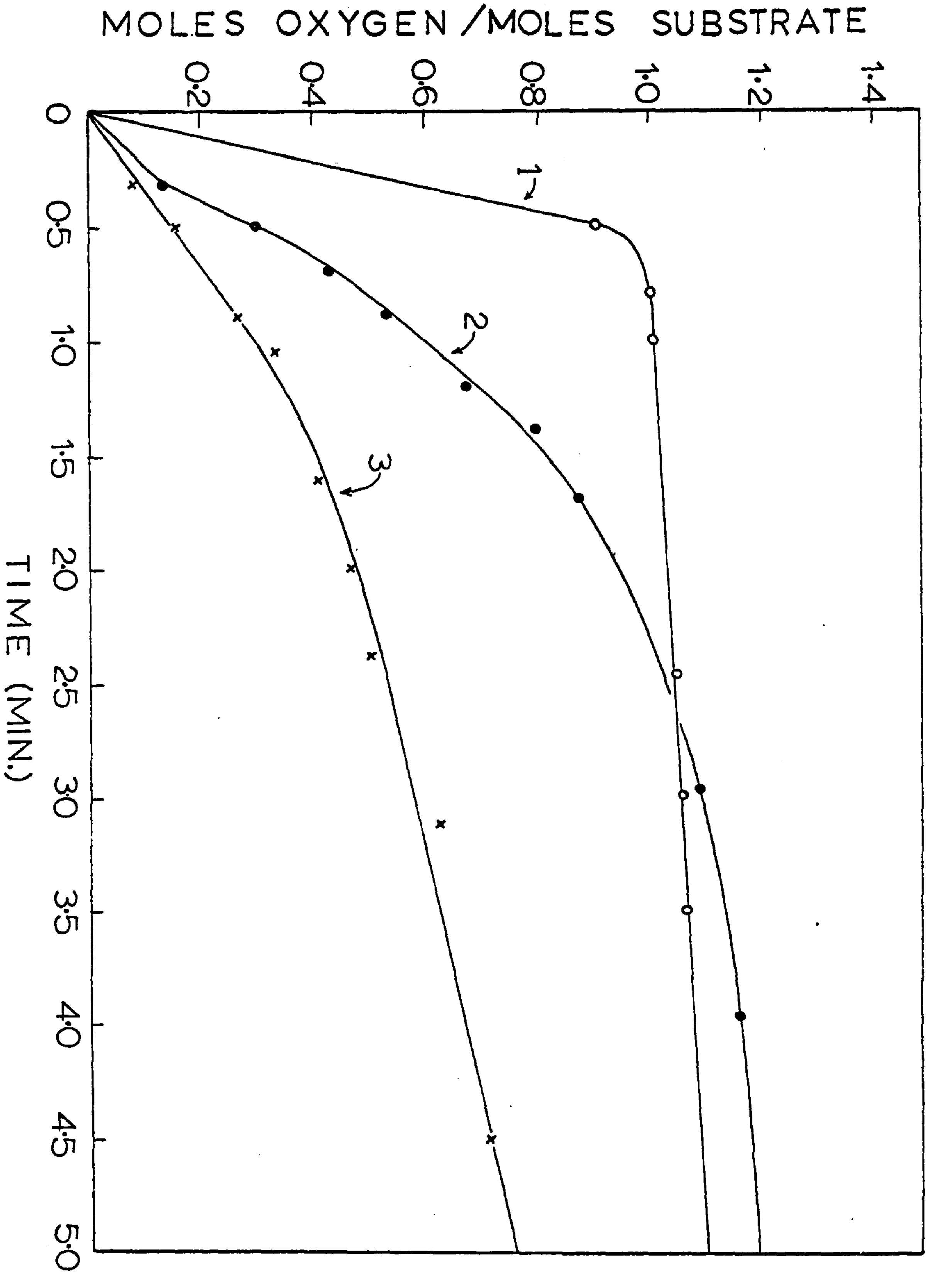


Figure 19. Oxidation of hydroxyfluorenes in 80% pyridine - 20% t-butyl alcohol (25 ml. solvent)

Curve 1	2.94 mmoles fluorene, 4.65 mmoles potassium t-butoxide
Curve 2	2.04 mmoles 2-hydroxyfluorene, 5.58 mmoles potassium t-butoxide
Curve 3	2.04 mmoles 3-hydroxyfluorene, 5.58 mmoles potassium t-butoxide


MOLES OXYGEN /MOLES SUBSTRATE
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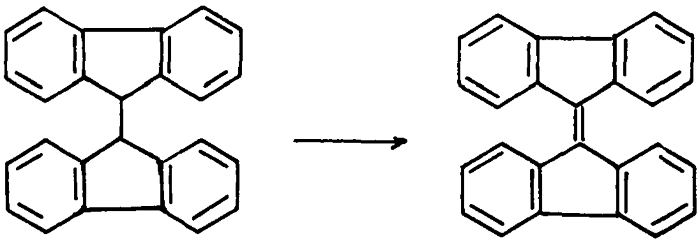
The products from the oxidation of the nitrofluorenes were not determined. Brown solids with melting points of approximately 170° and 235° for the 2-nitro- and 2,7-dinitrofluorene respectively were isolated. It is of interest to note that the oxidation of the hydroxyfluorenes gave yields of ketone products (Table 4). This is in contrast to the base-catalyzed oxidations of phenols which usually lead to base-degraded undefinied products. The ketones were isolated by filteration of the aqueous solution and determined by melting point and I.R.

An interesting reaction series was found in the oxidation of the three isomeric benzofluorenes. In 80% benzene - 20% t-butyl alcohol 3,4- and 1,2-benzofluorenes oxidized at approximately the same rate and 60 times faster than fluorene while 2,3-benzofluorene oxidized only slightly faster than fluorene (Figure 20). The same sequence was observed in t-butyl alcohol but the benzofluorenes were only partially soluble (Figure 21). It could be concluded that ionization was again exerting a large influence on the rate-controlling step since 2,3-benzofluorene oxidized rapidly in 80% pyridine - 20% t-butyl alcohol. The products were isolated in high yields and their melting points agreed with those of the reported ketones (see Table 4).

The oxidation of 9,9'-bifluorene was of interest because of the possibility of obtaining Δ-9,9'-bifluorene as an oxidation product.

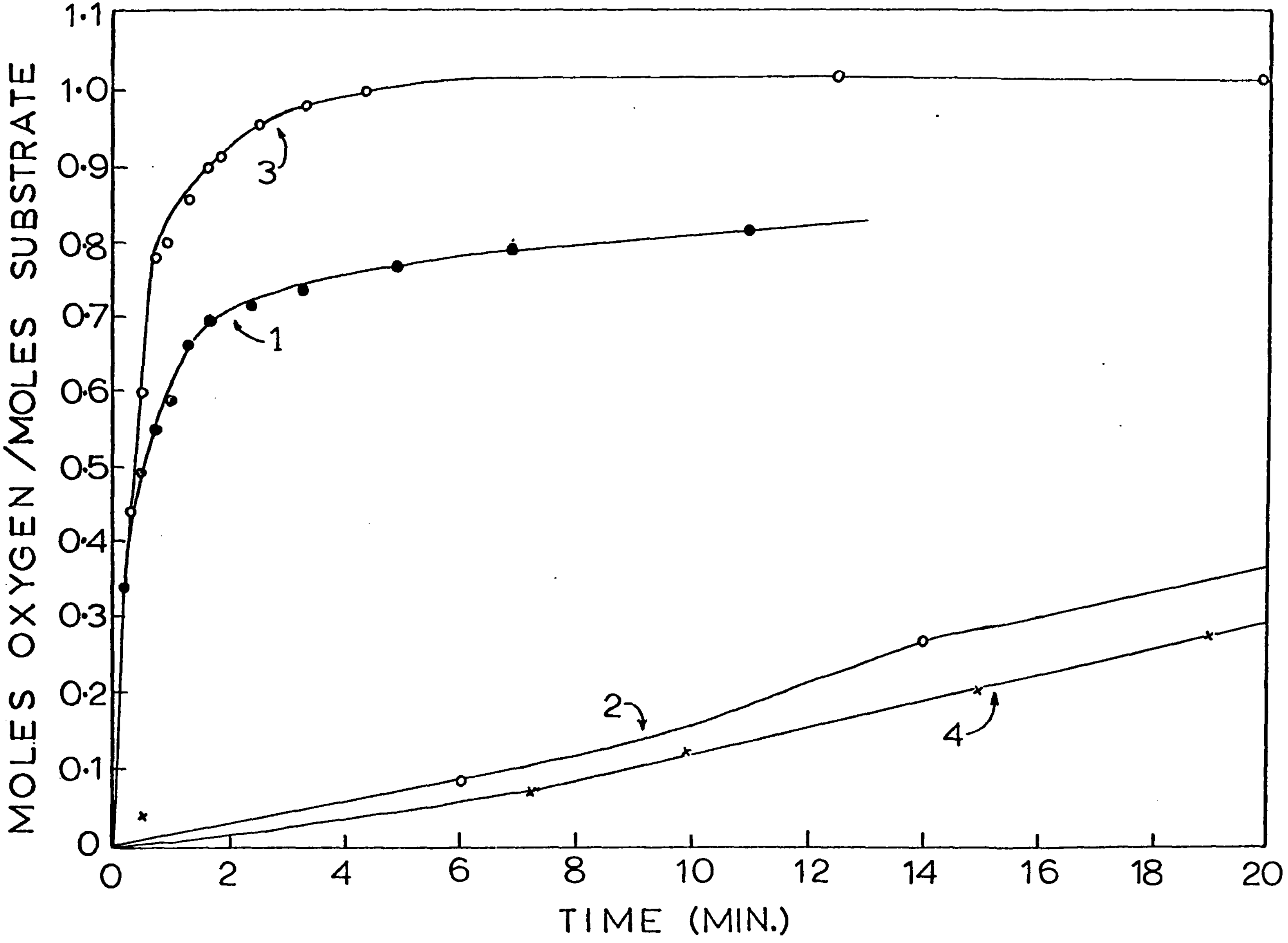
(98)



Δ-9,9'-bifluorene (bright red)

Figure 20. Oxidation of benzofluorenes in 80% benzene - 20% *t*-butyl alcohol (25 ml. solvent)

Curve 1	1.42 mmoles 1,2-benzofluorene, 3.05 mmoles potassium *t*-butoxide
Curve 2	1.40 mmoles 2,3-benzofluorene, 2.79 mmoles potassium *t*-butoxide
Curve 3	1.41 mmoles 3,4-benzofluorene, 2.84 mmoles potassium *t*-butoxide
Curve 4	1.43 mmoles fluorene, 2.88 mmoles potassium *t*-butoxide


MOLES OXYGEN /MOLES SUBSTRATE
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18
20
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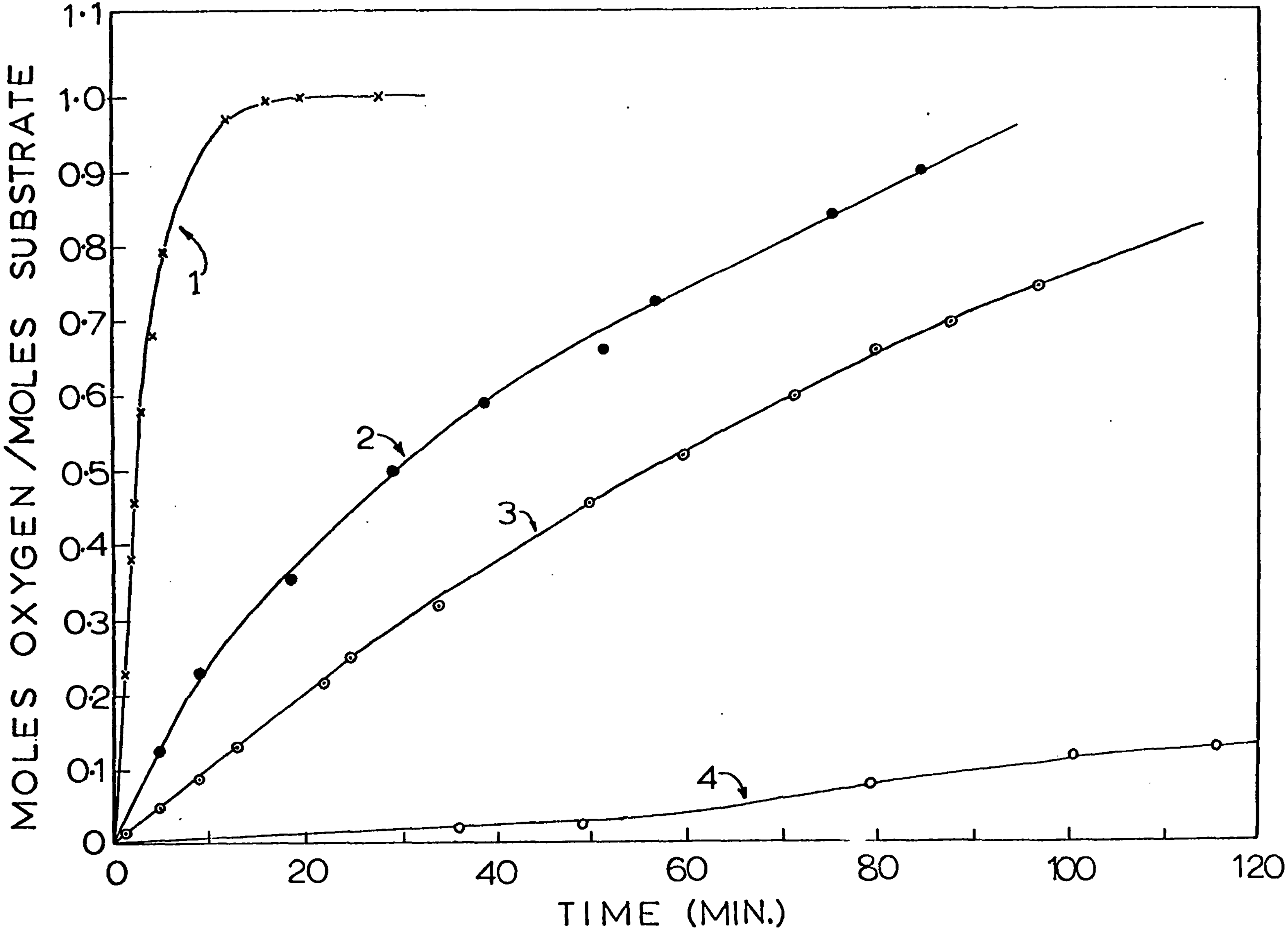
3
4

Figure 21. Oxidation of benzofluorenes in *t*-butyl alcohol (25 ml. solvent, 3.2 mmoles potassium *t*-butoxide)

Curve 1	1.55 mmoles 3,4-benzofluorene
Curve 2	1.56 mmoles 1,2-benzofluorene (only partially dissolved)
Curve 3	1.5 mmoles fluorene
Curve 4	1.52 mmoles 2,3-benzofluorene (only partially dissolved)


MOLES OXYGEN /MOLES SUBSTRATE
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60
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TIME (MIN.)
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3
4

Table 4. Oxidation products of substituted fluorenes

Run	Product	Solvent[a]	Yield	Melting point	Literature
238-A	2-hydroxyfluorenone	Py/t-BuOH	81%	217°	211° (114)
237-A	3-hydroxyfluorenone	Py/t-BuOH	65%	215-220°	225° (115)
228-A	1,2-benzofluorenone	Bz/t-BuOH	98%	108°	133° (116)
229-A	2,3-benzofluorenone	Bz/t-BuOH	95%	147-9°	152° (117)
230-A	3,4-benzofluorenone	Bz/t-BuOH	100%	157-9°	161° (118)
235-A	2,3-benzofluorenone	Bz/t-BuOH	94%	146-8°[b]	
	2-nitrofluorenone				219° (114)
	2,7-dinitrofluorenone				292° (119)

[a] 80 Per cent by volume pyridine or benzene in t-butyl alcohol; Py = pyridine, t-BuOH = t-butyl alcohol, Bz = benzene

[b] Melting point 151-2° after recrystallization from ethanol-water

The oxidation of 9,9'-bifluorene in t-butyl alcohol was very slow partly due to its insolubility in that solvent (Figure 22). A 78% yield of an orange colored solid which had an I.R. spectra identical with that of fluorenone was isolated melting at 79-81.5°[1]. A trace amount of Δ-9,9'-bifluorene may have been present which caused the color and melting point depression. In both 80% pyridine - 20% t-butyl alcohol and 80% dimethyl sulfoxide - 20% t-butyl alcohol the oxidation was extremely rapid (Figure 23). The product from the pyridine oxidation separated from the aqueous solution as a sticky orange material which gave an indefinite

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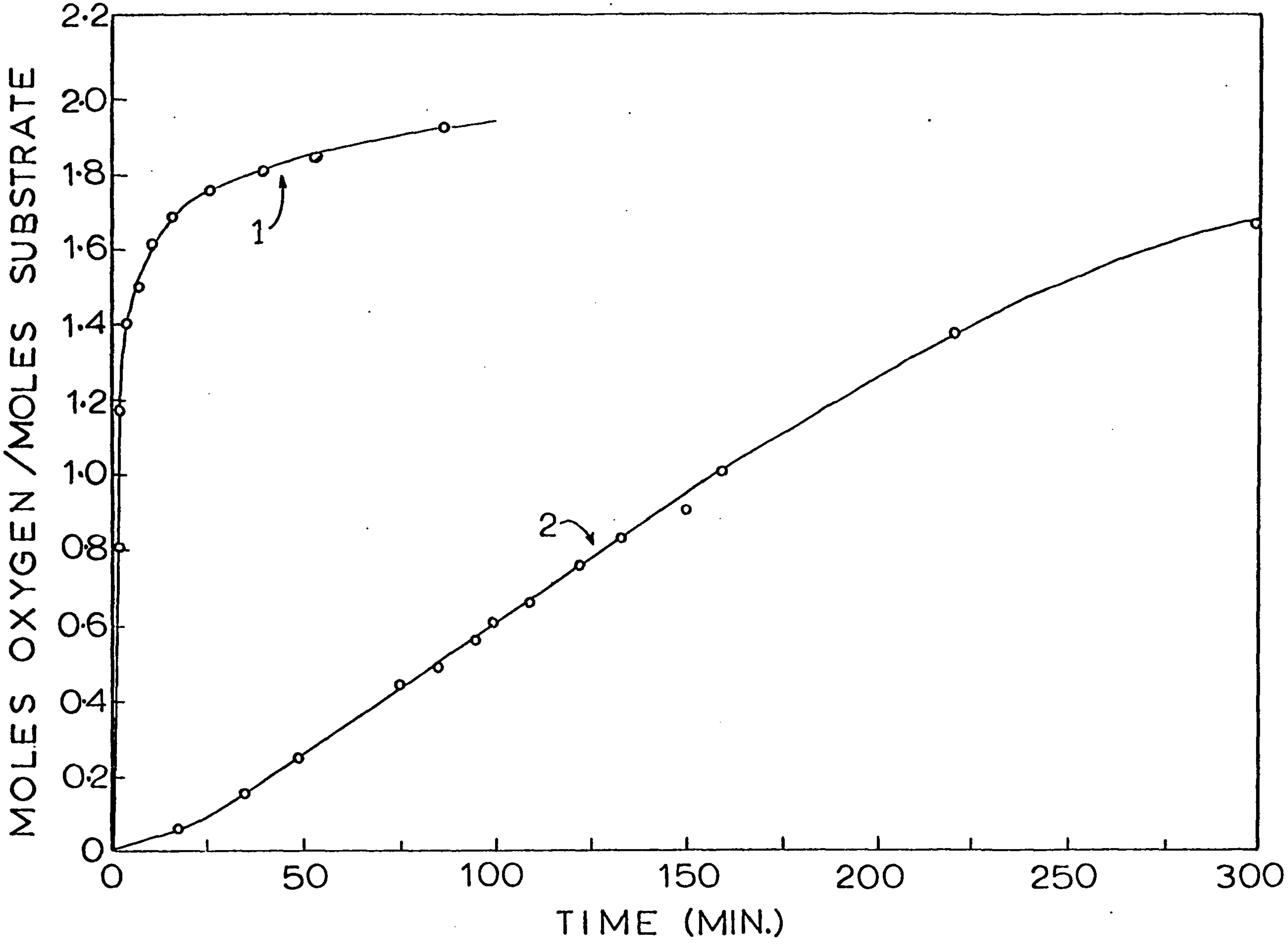
[1] Fluorenone is a greenish yellow solid; literature M.P. 83-4°.

Figure 22. Oxidation of 9,9'-bifluorene in t-butyl alcohol and pyridine (1.54 mmoles 9,9'-bifluorene, 5.70 mmoles potassium t-butoxide, 25 ml. solvent)

Curve 1	80% pyridine - 20% t-butyl alcohol
Curve 2	t-butyl alcohol


MOLES OXYGEN /MOLES SUBSTRATE
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0·4
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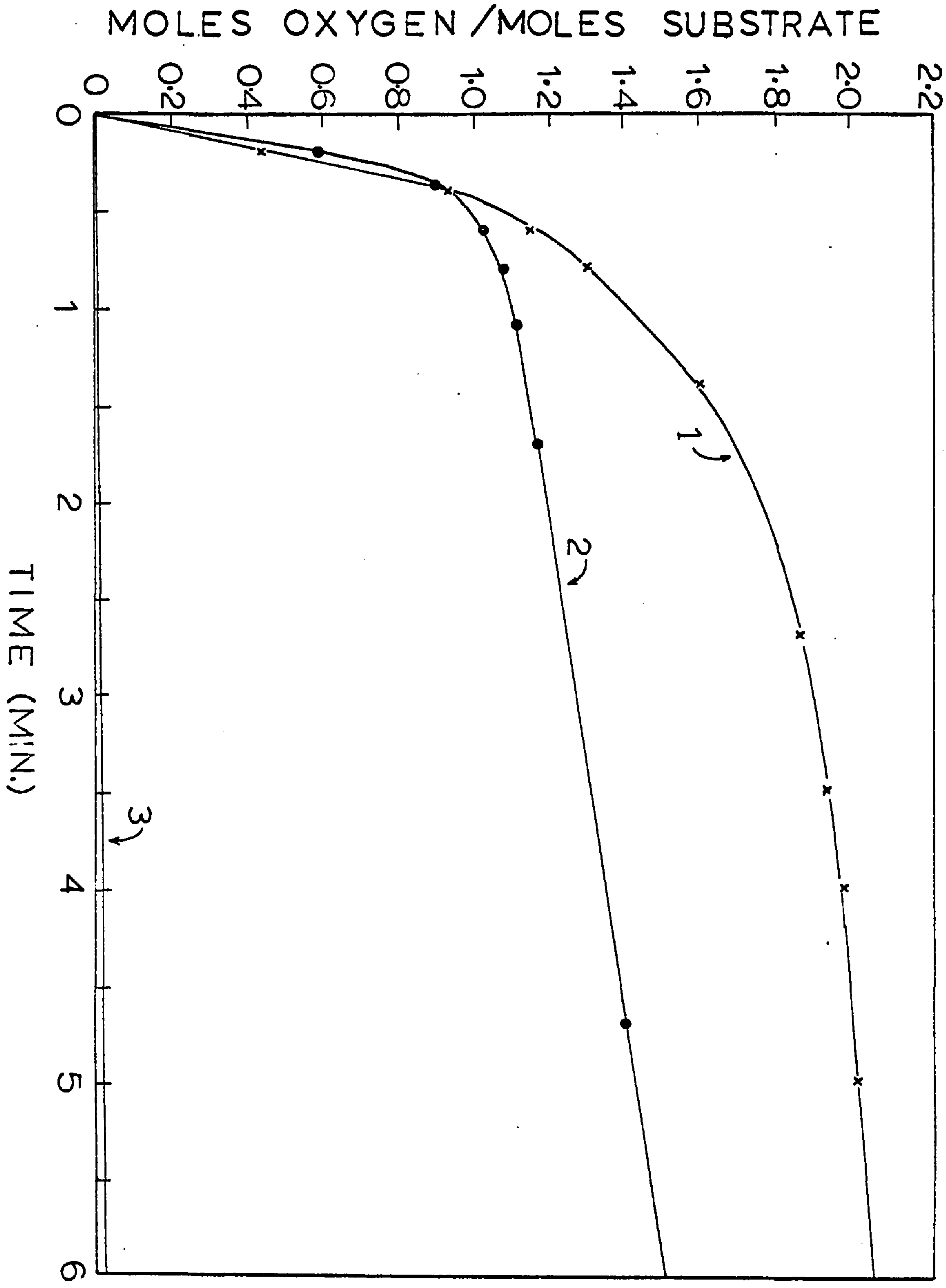
0
0
50
100
150
200
250
300
1
2

Figure 23. Oxidation of 9,9'-bifluorene in pyridine and dimethylsulfoxide (25 ml. solvent)

Curve 1	2.38 mmoles 9,9'-bifluorene, 4.85 mmoles potassium *t*-butoxide in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol
Curve 2	1.53 mmoles 9,9'-bifluorene, 5.70 mmoles potassium *t*-butoxide in 80% pyridine - 20% *t*-butyl alcohol
Curve 3	1.54 mmoles 9,9'-bifluorene, 5.70 mmoles potassium *t*-butoxide in *t*-butyl alcohol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melting point when dry. Its structure was not determined. A similar result was observed in the oxidation using dimethyl sulfoxide. Although a yellow material seemed to form in the aqueous solution after pouring into water, on acidification a red material formed similar to that noticed in the pyridine oxidation. A benzene extract of the solution separated the semi-solid some of which could be taken up in chloroform and could be precipitated by the addition of cyclohexane. It had the melting point of the dimethyl sulfoxide adduct of fluorenone, 154°. It is clear that fluorenone was a product under our conditions in the oxidation of 9,9'-bifluorene. This is understandable when the known high reactivity of Δ-9,9'-bifluorene is considered.

c. Toluene derivatives Base-catalyzed oxidation of tolyl derivatives exclusive of *p*-nitrotoluene had not been previously studied. In 80% dimethyl sulfoxide - 20% *t*-butyl alcohol substituted toluenes with para electron-withdrawing groups ionized in the presence of potassium *t*-butoxide to yield a high enough concentration of anions to initiate and maintain rapid autoxidation.

(99)

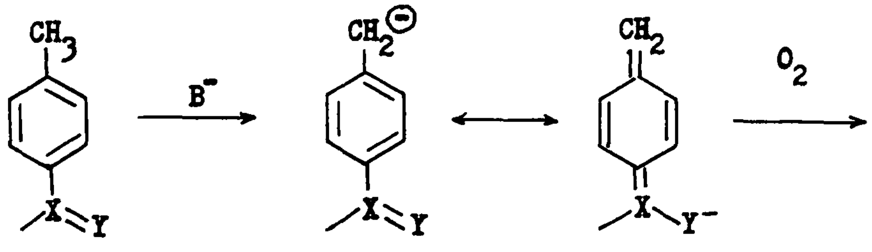

Table 5 lists the substituents and their σ or σ^- values in an order of decreasing electron-withdrawing ability suitable for this study, and summarizes the outcome of attempted ionization and oxidation.

Table 5. **Hammett's σ and σ^- constants[a] and rates of oxidation of substituted toluenes in 80% dimethyl sulfoxide - 20% t-butyl alcohol**

Para substituent	σ	σ^-	Oxidation rate	Log_{10} rate
IO_2	0.76		not available	
NO_2	0.778	1.27	1.0	0.0
$SO_2C_6H_5$			0.46	-0.335
p-$SO_2C_6H_4CH_3$			0.50[b]	-0.30
SO_3CH_3			no oxidation	
$N{=}N{-}C_6H_5$	0.640		0.67	-0.174
p-$C_6H_4N{=}N{-}C_6H_5$		1.088		
CN	0.660	1.000	0.53	-0.275
p-$SOC_6H_4CH_3$			0.17[b]	-0.769
CF_3	0.54	0.74	not available	
$COOCH_3$		0.636	0.35	-0.455
COC_6H_5	0.459		0.50	-0.30
p-$COC_6H_4CH_3$			0.50[b]	-0.30
$CH{=}CHC_6H_5$		0.619	not available	
$CONH_2$		0.627	no oxidation	
Br	0.232		very slow	
CHO	0.216	1.126	0.23	
NO	0.123		not available	
SO_3^-	0.09		no oxidation	
COO^-	0.00		no oxidation	
H	0.00		no oxidation	
C_6H_5	-0.01		no oxidation	

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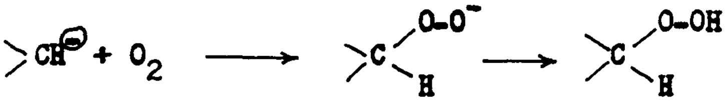
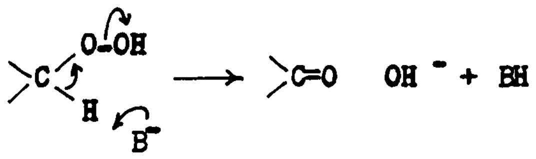
[a] Sigma constants from Leffler and Grunwald (120) and Hine (121)

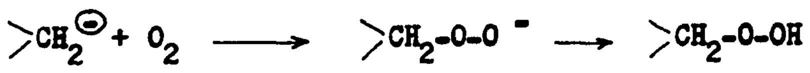
[b] A statistical correction has not been made (see text)

A detailed study of the mechanism of the oxidation of a primary carbanion was not attempted in the case of the substituted toluenes. However the scope of carbanion oxidation in dimethyl sulfoxide of tolyl derivatives was demonstrated and the nature of the isolable products suggested. Whereas secondary carbanions usually follow a relatively simple autoxidation pathway,

(100)


(101)


producing ketones (stable to oxidation when α-hydrogens are absent), the same mechanism for the reaction of primary carbanions produces aldehydes which are themselves oxidized rapidly to carboxylic acids.

(102)


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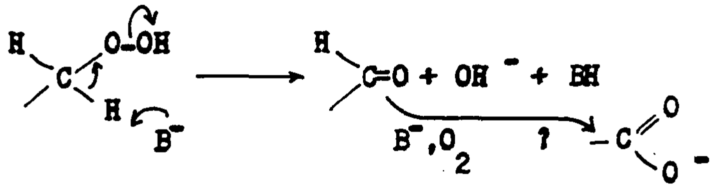

Evidence was found for an aldol type condensation occurring between the generated carbanion and the aldehyde intermediate which added to the complexity of the reaction. These considerations point out the difficulty in assessing the factor which most influenced the initial rate of oxidation of substituted toluenes.

Some attention was given to the oxidation products isolated by precipitation in water. In most cases the precipitates were mixtures of insoluble, high-melting and difficultly characterized materials. Very little literature data on di-functional stilbene derivatives is available. Although further investigation into the nature of the oxidation products was intended, the study of more interesting and fruitful avenues of research were begun and the complete characterization of the oxidation products from tolyl derivatives was not completed.

The oxidation plots of para-substituted toluenes are shown in Figure 24 (see Table 5). The observed initial rates decreased in the series $NO_2- > C_6H_5-N{=}N- > CN- > C_6H_5CO- > C_6H_5-SO_2- > CH_3OOC-$. Figure 25 contains oxidation plots of tolyl derivatives having two equivalent sites for carbanion formation. These oxidized in the rate sequence, p-$CH_3-C_6H_4-CO- >$ p-$CH_3-C_6H_4-SO_2- >$ p-$CH_3-C_6H_4-SO-$. 2,3,5,6-Tetrachloro-p-xylene oxidized faster than any of these although the base concentration was not comparable. p-Methylbenzophenone and p,p'-dimethylbenzophenone oxidized at exactly the same initial rate when compared at the same concentration although the latter eventually absorbed a larger amount of oxygen. If the rate of oxidation was completely controlled by the rate of ionization, p,p'-dimethylbenzophenone should oxidize twice as fast as p-methylbenzophenone due to a statistical factor. Since this was not observed more complex rate-controlling factors must be involved in the reaction.

Plots of the known values of both σ and σ^- for the para-substituents are given in Figures 26 and 27. Of the four points for the σ^- constants, the value for 4-methylazobenzene is actually that of p-phenylazophenyltoluene, p-$C_6H_5-N{=}N-C_6H_4-$. These might be similar

Figure 24. Oxidation of *para*-substituted toluenes in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol (25 ml. solvent)

Curve 1	2.92 mmoles *p*-nitrotoluene, 4.65 mmoles potassium *t*-butoxide
Curve 2	3.02 mmoles *p*-methylazobenzene, 4.65 mmoles potassium *t*-butoxide
Curve 3	2.5 mmoles *p*-methylbenzophenone, 4.65 mmoles potassium *t*-butoxide 3.26 mmoles *p*-tolunitrile, 6.1 mmoles potassium *t*-butoxide 2.94 mmoles *p*-tolyl phenyl sulfone, 4.65 mmoles potassium *t*-butoxide 3 mmoles *p*-methylacetophenone, 4.65 mmoles potassium *t*-butoxide (see Table 5)
Curve 4	2.98 mmoles methyl *p*-toluate, 6.05 mmoles potassium *t*-butoxide
Curve 5	3 mmoles *p*-methylbenzaldehyde, 4.65 mmoles potassium *t*-butoxide

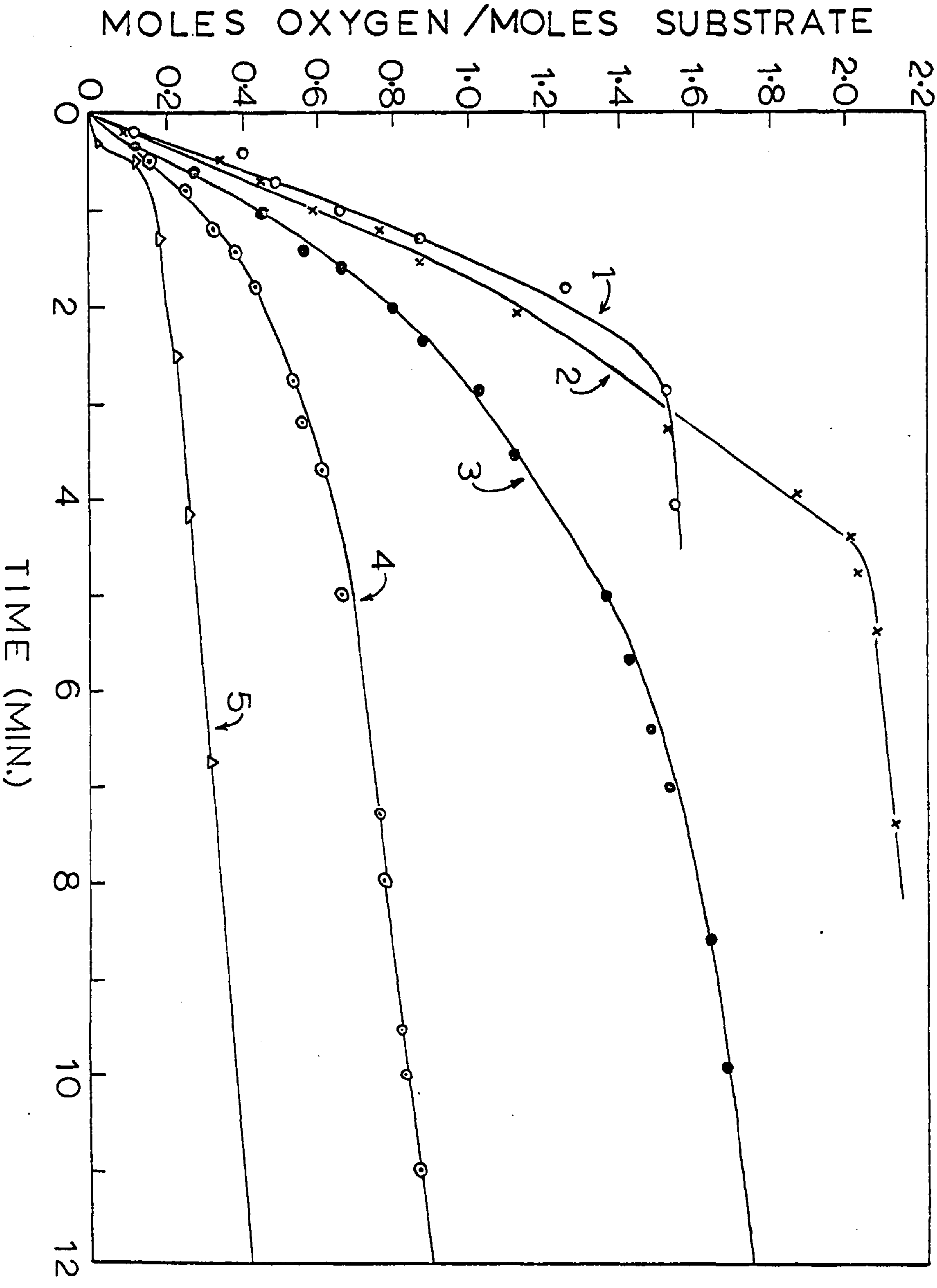
MOLES OXYGEN /MOLES SUBSTRATE
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Figure 25. Oxidation of ditolyl derivatives in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol

Curve 1 2.03 mmoles *p*,*p*'-dimethylbenzophenone, 8.37 mmoles potassium *t*-butoxide in 45 ml. solvent

Curve 2 2.03 mmoles tolyl sulfone, 8.37 potassium *t*-butoxide in 45 ml. solvent

Curve 3 2.03 mmoles tolyl sulfoxide, 8.37 potassium *t*-butoxide in 45 ml. solvent

Curve 4 4 mmoles 2,3,5,6-tetrachloro-*p*-xylene, 20 mmoles potassium *t*-butoxide in 40 ml. solvent

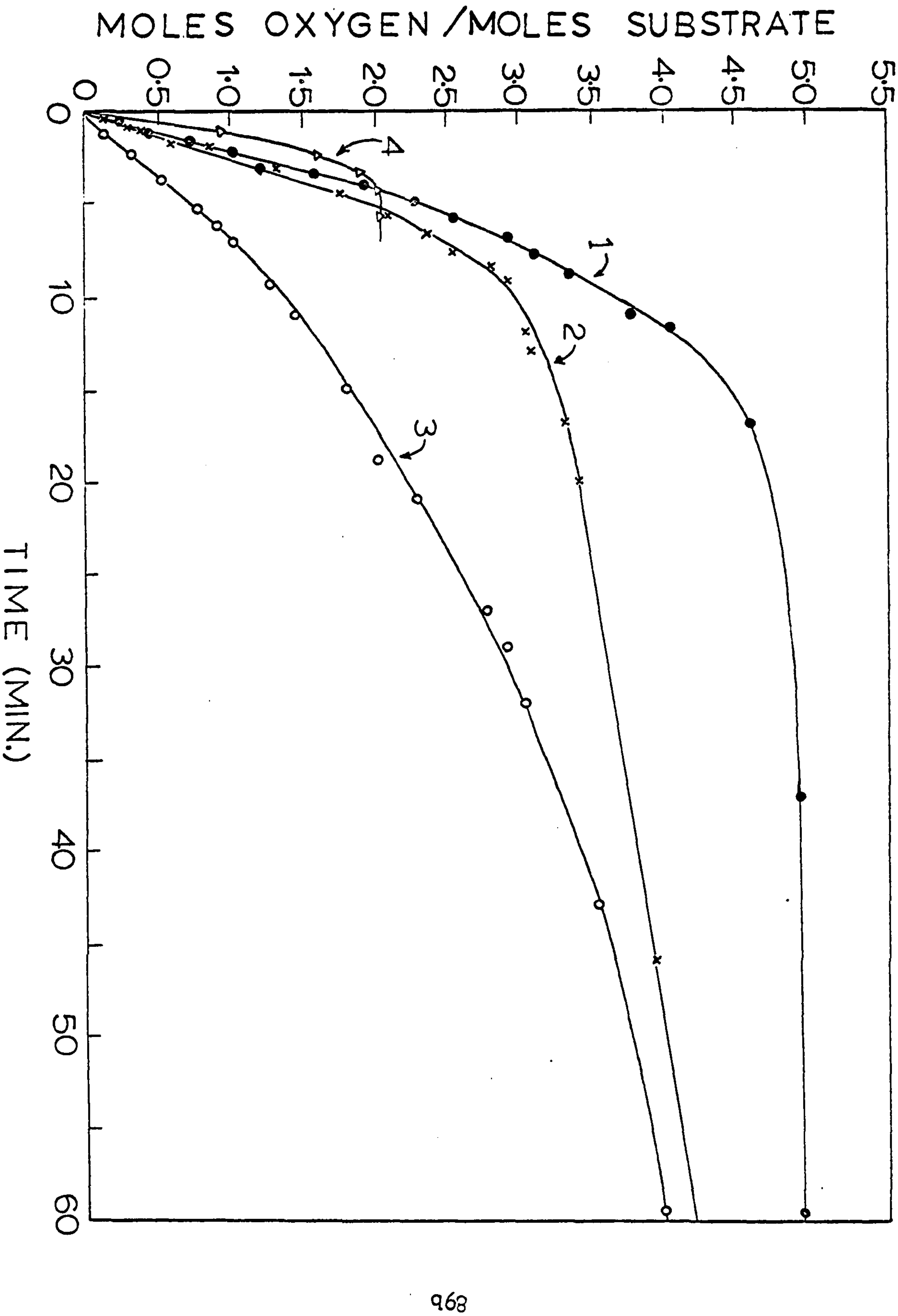

MOLES OXYGEN /MOLES SUBSTRATE
0
0·5
1·0
1·5
2·0
2·5
3·0
3·5
4·0
4·5
5·0
5·5
TIME (MIN.)
0
10
20
30
40
50
60
1
2
3
4

Figure 26. Initial rates of oxidation ($\log_{10}$) of _para_-substituted toluenes plotted _vs._ σ

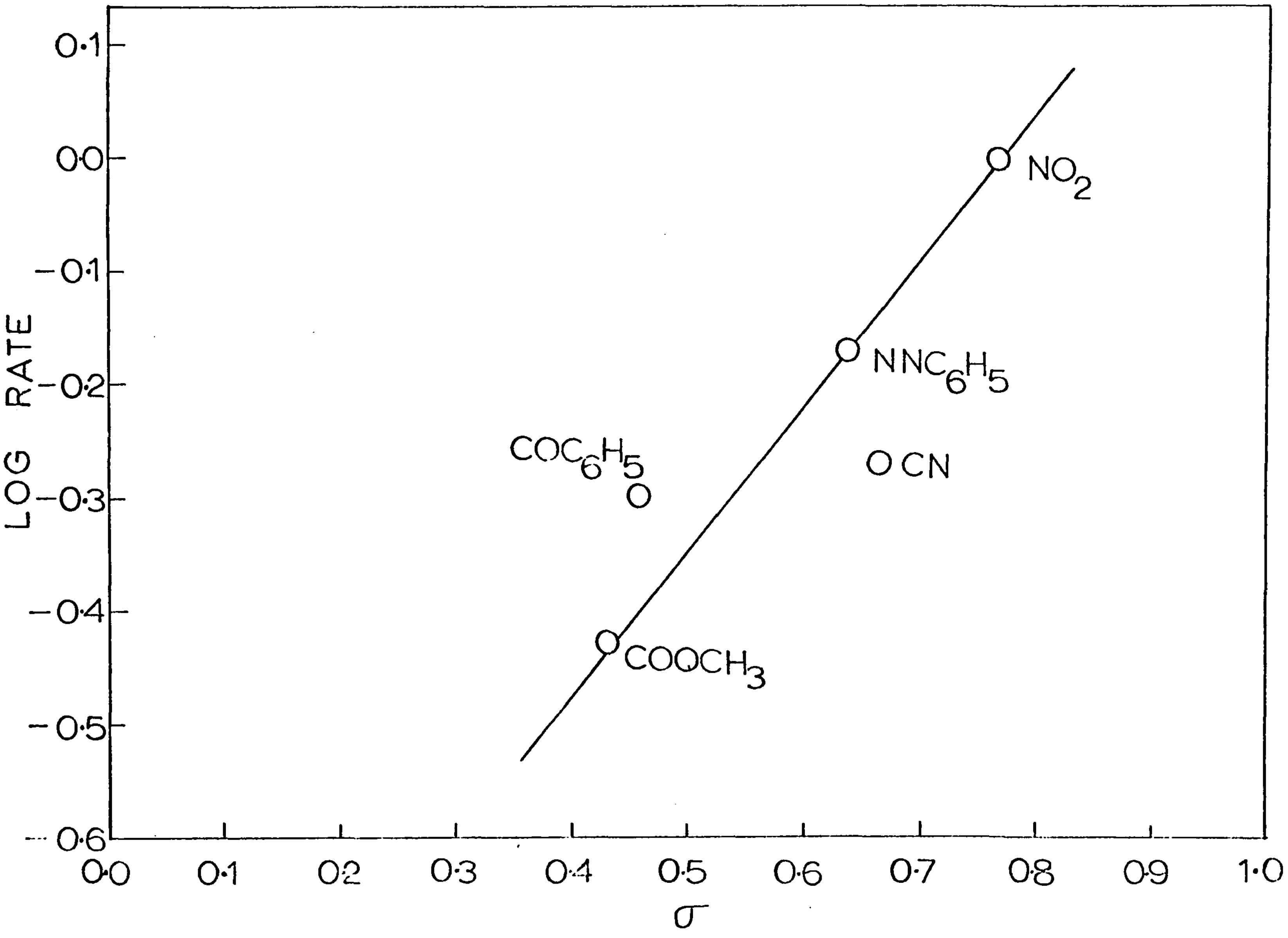
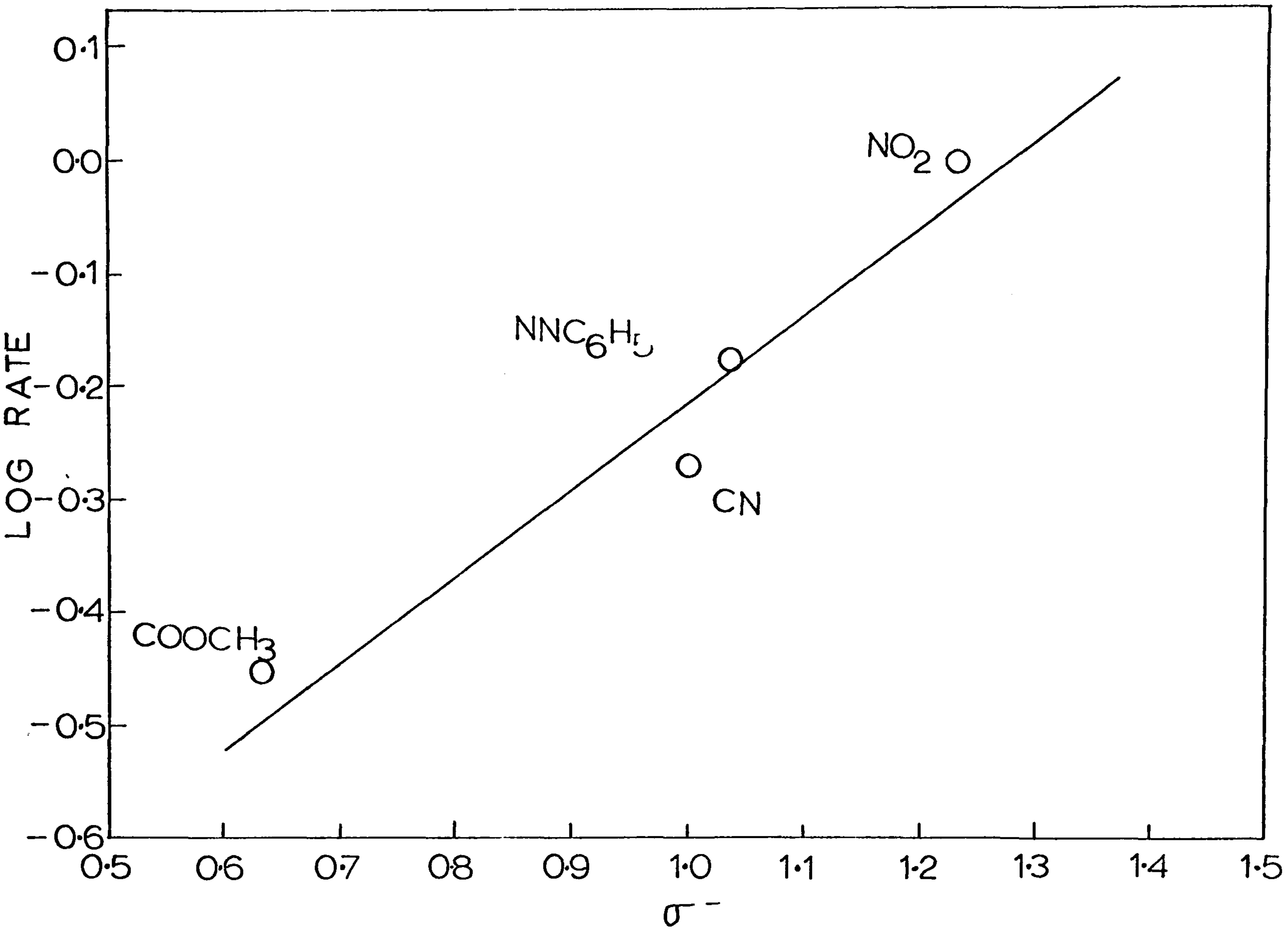

LOG RATE
0·1
0·0
−0·1
−0·2
−0·3
−0·4
−0·5
−0·6
0·0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
σ
NO_2
NNC_6H_5
COC_6H_5
CN
$COOCH_3$

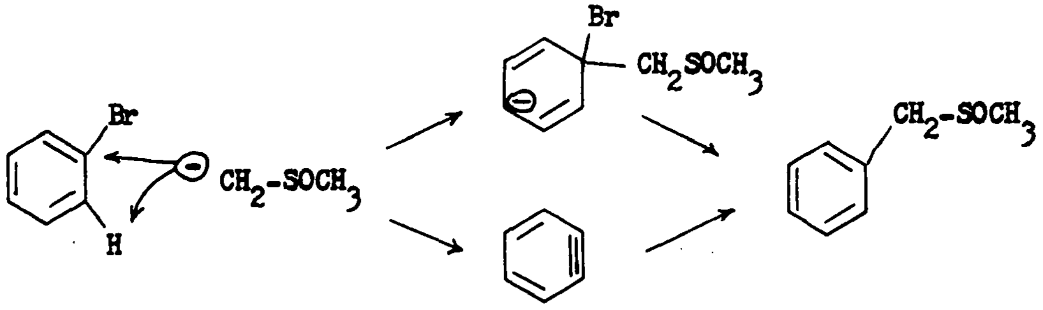
Figure 27. Initial rates of oxidation ($\log_{10}$) of *para*-substituted toluenes plotted vs. σ^-


LOG RATE
0·1
0·0
−0·1
−0·2
−0·3
−0·4
−0·5
−0·6
0·5
0·6
0·7
0·8
0·9
1·0
1·1
1·2
1·3
1·4
1·5
σ^-
NO_2
NNC_6H_5
CN
$COOCH_3$

enough to warrant the use of this value in our plot. Since more σ values were obtainable an appropriate plot using these values was also made. Within the range of the few constants known reasonably good straight line relationships were obtained for either σ or σ^- considering the complexity of the reaction studied, although from the few points available it is not possible to decide which constant provides a better fit. The slopes are 0.91 for σ^- and 1.34 for σ.

A number of substituted toluenes which were studied but have not been plotted are given in Table 5. p-Bromotoluene oxidized very slowly. Bromobenzene was run in comparison to check the possibility of the following reaction occurring which could lead to the slow oxidation observed,

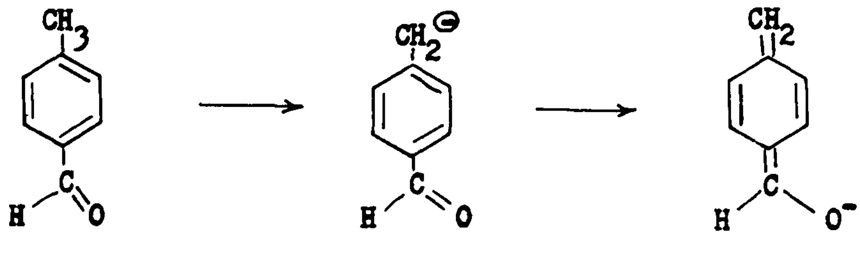
(104)



but it was stable under the given conditions; the only oxygen absorbed was caused by solvent oxidation.

The σ^- constant for the aldehyde substituent is very lareg (Table 5) and therefore one could expect extensive ionization of p-methylbenzaldehyde.

(105)

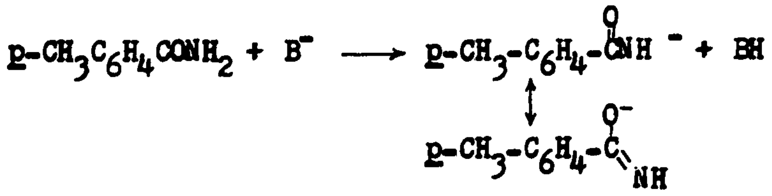


The oxidation of p-methylbenzaldehyde started out rapidly but slowed down to a rate of oxidation which was still greater than the oxidation of benzaldehyde. In an oxidizing medium the aldehyde substituent would be subject to oxidation and yield carboxylic acid. However the carboxylate anion is not electron-withdrawing enough to acidify the protons of p-toluic acid to bring about ionization and oxidation. Either p-methylbenzaldehyde oxidized in the normal fashion or a condensation product was subject to oxidation in the basic solvent.

p-Methylacetophenone oxidized rapidly and only slightly faster than the rate of oxidation of acetophenone; no conclusions could be made about which methyl was oxidizing predominantly since no products were isolated. The solution of methyl p-toluenesulfonate in base turned yellow instantaneously and absorbed 0.55 ml. oxygen at that moment, then turned colorless and showed no oxidation. Presumably a nucleophilic displacement was decomposing the sulfonate ester to the acid which did not oxidize under these conditions.

(106) $CH_3\text{-}C_6H_4\text{-}SO_3CH_3 + B^- \longrightarrow CH_3\text{-}C_6H_4\text{-}SO_3^- + CH_3\text{-}B$

Under the usual conditions p-methylbenzamide did not oxidize presumably due to preferential ionization on the nitrogen.

(107) 

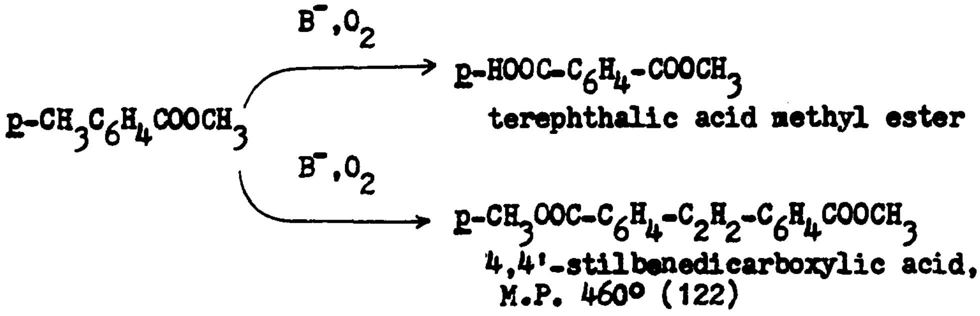
$$\text{p-}CH_3C_6H_4CONH_2 + B^- \longrightarrow \text{p-}CH_3\text{-}C_6H_4\text{-}\overset{O}{\overset{\|}{C}}NH^- + BH \;\updownarrow\; \text{p-}CH_3\text{-}C_6H_4\text{-}\overset{O^-}{\overset{|}{C}}{=}NH$$

These nitranions have been shown to be stable to oxygen by Smentowski[1].

No oxidation was observed for toluene, p-phenyltoluene, p-toluenesulfonic acid or p-toluic acid under similar conditions. In the latter case the solution was heterogeneous due to the insolubility of the potassium salt of p-toluic acid. A solution containing Triton B was homogeneous although no oxidation was observed. In hexamethylphosphoramide potassium p-toluenesulfonate barely began to oxidize, whereas potassium p-toluate did not show oxidation under similar conditions.

The products of methyl p-toluate were isolated by filteration and benzene extraction of an acidic aqueous solution containing the oxidized solution which had been boiled in 10% aqueous sodium hydroxide. After drying a titration equivalence was obtained for this product, presumably a mixture of dibasic acids.

(108)



$$p\text{-}CH_3C_6H_4COOCH_3 \xrightarrow{B^-,O_2} p\text{-}HOOC\text{-}C_6H_4\text{-}COOCH_3$$

terephthalic acid methyl ester

$$p\text{-}CH_3C_6H_4COOCH_3 \xrightarrow{B^-,O_2} p\text{-}CH_3OOC\text{-}C_6H_4\text{-}C_2H_2\text{-}C_6H_4COOCH_3$$

4,4'-stilbenedicarboxylic acid, M.P. 460° (122)

The basic solution from the hydrolysis of the oxidation mixture was homogeneous and the isolated acids could be dissolved in aqueous sodium hydroxide and back-titrated with standard acid. On the assumption that all the acids present were dibasic an average molecular weight could be

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[1] G. A. Russell and F. J. Smentowski, Dept. of Chemistry, Iowa State University of Science and Technology. Private communication concerning attempted autoxidation of amides, 1961.

calculated and from this an estimation could be made of the proportion of monomeric and dimeric acids present in the product.

Thus:

titration value/2 = titration equivalence = moles dibasic acid (A)

total weight of sample titrated (W)/A = average molecular weight (M)

$$\frac{W}{M} = \frac{\text{weight of monomeric acid } (W_m)}{\text{mol. wt. of monomeric acid } (M_m)} + \frac{\text{weight of dimeric acid } (W_d)}{\text{mol. wt. of dimeric acid } (M_d)}$$

$$W = W_m + W_d$$

$$W/M = (W - W_d)/M_m + W_d/M_d$$

$$W_d = WM_d(M - M_m)/M(M_d - M_m)$$

$$M_m = HOOC\text{-}C_6H_4\text{-}COOH = 166.13$$

$$M_d = HOOC\text{-}C_6H_4\text{-}C_2H_2\text{-}H_4COOH = 270.25$$

$$W_d = 2.595W\,(M - 166.13)/M$$

$$W_d \times 100/W = 259.5\,(M - 266.13)/M = \%\text{ dimeric dibasic acid}$$

Table 6 lists a number of oxidations of methyl p-toluate in dimethyl sulfoxide - t-butyl alcohol and the distribution of dimeric and monomeric dibasic acids isolated as calculated by the described procedure. In Run 20-A there was approximately a 1:1 ratio of oxygen absorbed by starting methyl p-toluate in a 25 ml. solution with vigorous shaking. By reducing the exposure to oxygen either by increasing the volume of solution being agitated in a given flask (Runs 93-A and 165-A) or by stirring with a magnetic stirring bar (Run 94-A), the ratio of the moles of oxygen absorbed

Table 6. Oxidation of methyl *p*-toluate in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol

Run	Substrate (mmoles)	*t*-BuOK[a] (mmoles)	Volume (ml.)	Time (hr.)	O_2[b]	Precipitated				From extraction	
						weight (g.)	M[c]	dimer (%)	monomer (%)	weight (g.)	M[c]
20-A	3 (0.45 g.)	6	25	1.9	1.12	0.43					
93-A	6 (0.92 g.)	7.9	50[d]	23	0.39	.662	270			0.173	332
94-A	6 (0.92 g.)	9.7	50[e]	6	.49	.574	242	81.3	18.7	.124	299
165-A	6 (0.92 g.)	18.2	50[d]	25	.67	.573	231	73	27	.107	283
160-A	4.6 (0.71 g.)	9.7	75	0.5	-[f]	.350	327			.070	164
163-A	6.8 (1.02 g.)[g]	14.5	75	1.5	-[h]	.510	220	64	36	.195	264

[a] *t*-BuOK = potassium *t*-butoxide

[b] O_2 = moles oxygen at S.T.P./moles substrate

[c] M = average molecular weight; molecular weight of dimeric and monomeric acids are 270.25 and 166.13 respectively

[d] 50% Dimethyl sulfoxide - 50% *t*-butyl alcohol

[e] Agitation by magnetic stirring bar

[f] Parr hydrogenation apparatus, 4 atmospheres oxygen pressure

[g] Substrate added slowly over a period of 0.5 hr.

[h] High speed stirrer, 1 atmosphere oxygen pressure

to the moles of starting material decreased. A lower base to substrate ratio as well as a lower intrinsic basicity of solvent, as in 50% dimethyl sulfoxide - 50% *t*-butyl alcohol, also seemed to favor a lower consumption of oxygen. Moreover the molecular weight determinations although subject to large variations gave every indication that the product was predominantly dimeric. These observations led to the conclusions that dimerization if occurring in the autoxidation of primary carbanions might in all cases result *via* an aldol type condensation mechanism,

$$\text{R-CH}_2^{\ominus} + \text{O}_2 \longrightarrow \longrightarrow \text{R-CHO}$$

$$(109) \quad \text{R-CH}_2^{\ominus} + \text{R-CHO} \longrightarrow \text{R-CH=CH-R}$$

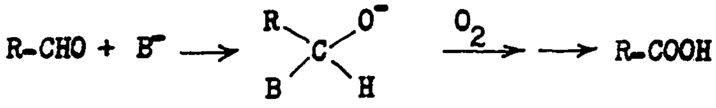
since this mechanism would require less oxygen to form dimeric products in high yield than coupling of benzyl radicals followed by dehydrogenation.

$$(110) \quad \text{R-CH}_2^{\ominus} + \text{O}_2 \longrightarrow \text{R-CH}_2\cdot + \text{O}_2^{\overset{\cdot}{-}}$$

$$(111) \quad 2\text{R-CH}_2\cdot \longrightarrow \text{R-CH}_2\text{-CH}_2\text{-R} \xrightarrow{\text{O}_2} \text{R-CH=CH-R}$$

The condensation reaction would be favored by low oxygen exposure thereby increasing the lifetime of the intermediate aldehyde for reaction with carbanion and not with oxygen. That lower base strength apparently favored condensation may be due to the trapping of the aldehyde by base in the highly basic medium leading eventually to the monomeric oxidation product.

(112)



$$\text{R-CHO} + \text{B}^{-} \longrightarrow \text{R(B)(H)C-O}^{-} \xrightarrow{\text{O}_2} \longrightarrow \text{R-COOH}$$

The addition reaction has been shown to occur by Russell et al. (93) and is consistent with the higher ratio of monomeric acid isolated in Run 165-A. However the stability of p,p'-dicarbomethoxystilbene towards the strongly basic solution is not known and the possibility exists that as the base strength is increased the dimer undergoes decomposition by a base-addition-oxidation mechanism.

It was surprising to find that in an oxidation under 4 atmospheres oxygen pressure no significant change in the ratio of dimeric to monomeric product was observed (Run 160-A), nor did the use of a high speed stirrer have much influence on the product distribution (Run 163-A). If these results are correct the oxidation of methyl p-toluate proceeds through intermediates which predominately undergo condensation reactions in preference to oxidation.

For the oxidation of di-p-tolyl sulfone the basic solution was red even when poured into water although the color changed to yellow on acidification. The precipitate was non-crystalline and difficult to filter but could be separated into two different acids by boiling water. A white solid separated from the water solution upon cooling which was soluble in aqueous sodium carbonate and dilute sodium hydroxide giving colorless solutions. A pale yellow residue remained behind upon treatment with boiling water which was only partially soluble in dilute sodium hydroxide but completely soluble in hot dilute sodium hydroxide producing in the cold solution a reddish-orange color and in the hot solutions a brick-red color. The melting point of the crude acid mixture was 280-400°, of the colorless water-soluble acid 270-370° and of the pale-yellow water-insoluble acid 310-330°, all melting points occurring with decomposition. The I.R. spectra in a KBr wafer were identical for the two acids except for one peak at 6.39 μ which was present only for the colored acid. The molecular weight of the yellow acid was approximately 680 as determined by the neutralization method.

The two products expected from the oxidation of p-tolyl sulfone were:

$HOOC\text{-}C_6H_4\text{-}SO_2\text{-}C_6H_4\text{-}COOH$ (M.W. 304) M.P. 370° (123, 124)

XIV

$HOOC\text{-}C_6H_4\text{-}SO_2\text{-}C_6H_4\text{-}CH{=}CH\text{-}C_6H_4\text{-}SO_2\text{-}C_6H_4\text{-}COOH$ (M.W. 542)

XV

The best assignment of structure of the two isolated acids with the given information was that the colorless water-soluble acid was XIV, the monomeric dibasic acid, and the yellow water-insoluble acid was XV, the dimeric unsaturated dibasic acid. Presumably the I.R. peak at 6.39 μ was due to the ethylenic double bond of the colored acid, the extensive conjugation possible in the dicarboxylate anion causing the colored anion in basic solution. There remained the possibility that some trimeric acid was present causing the high molecular weight, 680 as compared to 542 for XV and that this was the colored species. Under similar conditions Russell et al. reported the isolation of p-(phenylsulfonyl)-benzoic acid and p,p'-(phenylsulfonyl)-stilbene (93) in yields of 60% and 33% respectively from the oxidation of p-tolyl phenyl sulfone under similar conditions.

In the oxidation of p-tolunitrile three product portions were isolated. A solid melting with decomposition at 345-355° was filtered from the basic aqueous solution. This solid gave indications from an I.R. spectrum (in KBr) of the presence of an amide and a nitrile group although the latter in smaller amounts. No bands which could be attributed to the sulfoxide group could be detected, although a peak at 6.20 μ possibly indicated the presence of an ethylenic bond. This information suggested that the product could be either of the following:

p,p'-CN-C_6H_4-CH=CH-C_6H_4-$CONH_2$, M.P. ?

XVI

p,p'-NH_2CO-C_6H_4-CH=CH-$CONH_2$, M.P. ? with traces of

p,p'-CN-C_6H_4CH=CH-C_6H_4CN, M.P. 284° (*trans*), 154° (*cis*) (125) XVII

A literature search for the stilbene diamide and the amide nitrile derivatives did not uncover a description of their melting points. The high melting point of our product indicated that a large portion could be *p,p*'-NH_2CO-C_6H_4-CH=CH-C_6H_4-$CONH_2$. From the acidic portion a solid melting at 275-280° was isolated. The I.R. spectrum indicated carboxyl, amide and nitrile groups although the latter in small amount. No sulfoxide bands were indicated. Of the possible expected acids,

p-$NH_2COC_6H_4COOH$, M.P. 300° (126)

XVIII

p-CN-C_6H_4COOH, M.P. 219° (127)

XIX

$\underline{p},\underline{p}'$-$NH_2COC_6H_4$-CH=CH-$C_6H_4$-COOH, M.P. ?

XX

$\underline{p}$-CN-C_6H_4-CH=CH-C_6H_4-COOH, M.P. ?

XXI

a structure determination could not be made with the information on hand, although apparently p-cyanobenzoic acid was not the predominant product. A benzene extraction of the acidic aqueous solution provided a small amount of solid melting at 155-170°. The I.R. spectrum showed besides the absorption for amide and nitrile groups, peaks at 2.75-2.85 μ, 7.6-7.8 μ (broad doublet) and 8.8-9.2 μ (broad doublet) possibly due to amine and sulfone. This material may have been an addition product of dimethyl sulfoxide and a nitrile.

Apparently very few nitrile groups seemed to survive the oxidation; it is known that nitrile groups can be oxidized in basic solution by hydrogen peroxide (128) to amides. Since hydrolysis of p,p'-dicyanostilbene is extremely difficult in basic solution this pathway does not seem to be likely to the formation of amide derivatives. It has been shown that p-methylbenzamide does not oxidize, hence hydrolysis of the starting material followed by oxidation is not occurring. It seemed likely that the product was being oxidized to the amide.

$$(113)\quad \underline{p},\underline{p}'\text{-CN-}C_6H_4\text{-CH=CH-}C_6H_4\text{-CN} \xrightarrow{B^-,O_2} \text{CN-}C_6H_4\text{-CH=CH-}C_6H_4\text{-CONH}_2$$

The oxidation of p,p'-dimethylbenzophenone produced a yellow acid which had a molecular weight of approximately 560 and showed a peak at

6.24 μ in the I.R. spectrum run in a KBr wafer. The absence of sulfoxide bands in the spectra was surprising since dimethyl sulfoxide adducts form readily with benzophenone. The isolated product gave indications of being the dimeric rather than the monomeric dibasic acid,

$COOH-C_6H_4-CO-C_6H_4-COOH$ (M.W.280)

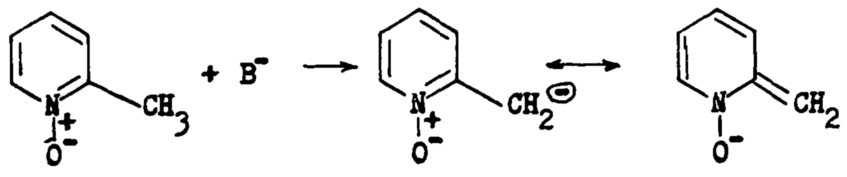
XXII

$COOH-C_6H_4-CO-C_6H_4-CH=CH-C_6H_4-CO-C_6H_4-COOH$ (M.W. 496)

XXIII

The oxidation of a number of other primary carbanions will be discussed here although they are not tolyl derivatives. It was previously mentioned that the picolines oxidized slowly in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol (see Solvent Effects); however the picoline-N-oxides oxidized at a reasonably fast rate (Figure 28).

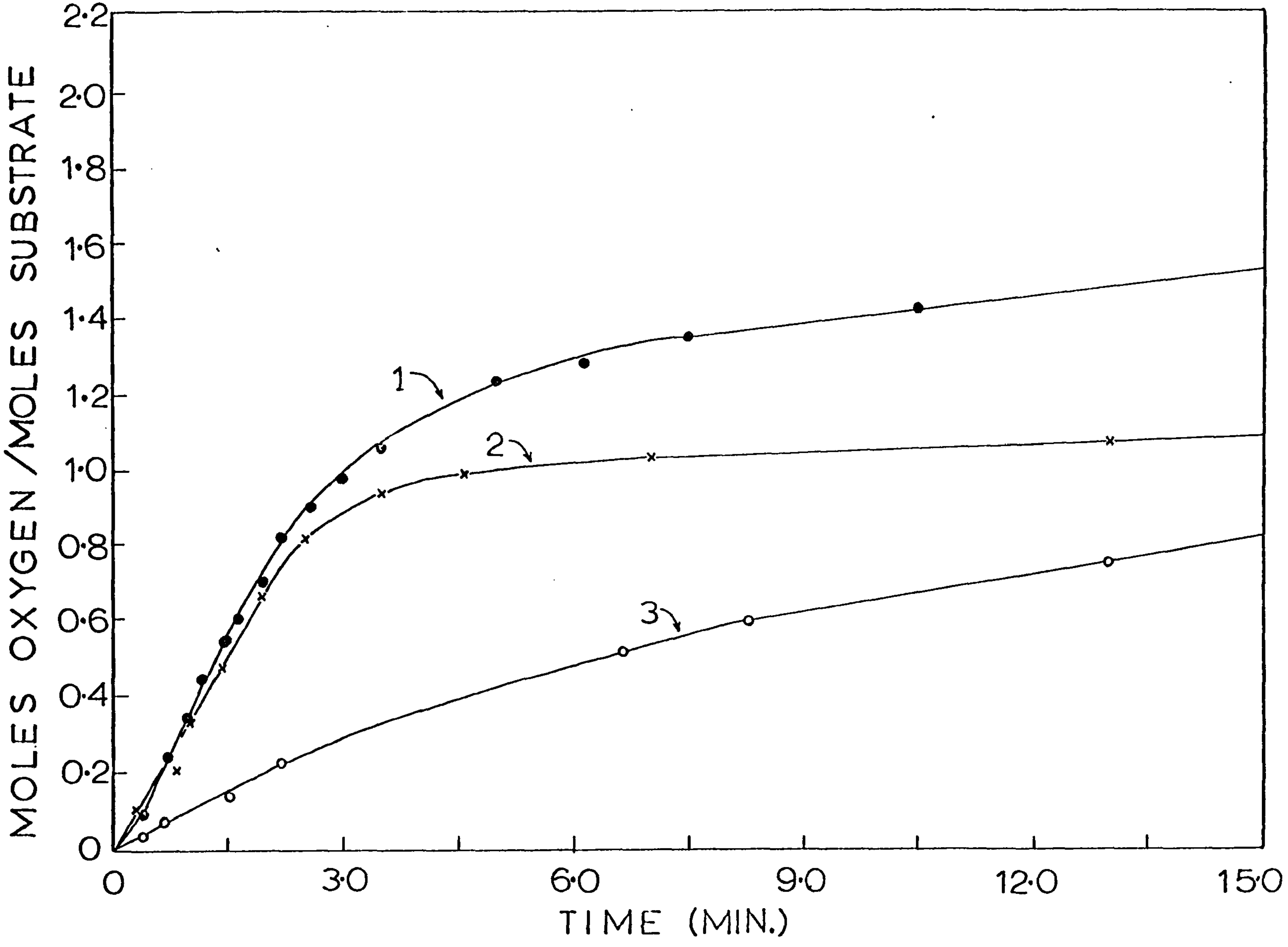
(114)



The relative rates for picoline-N-oxides followed the sequence $\gamma \simeq \alpha > \beta$ similar to the order observed in the oxidation of picolines in hexamethylphosphoramide (Figure 11). It seems surprising that the β-isomers oxidized in both cases at a rate not too much slower than the α- or γ-isomers. This seems to indicate that structures of the following type are of low energy and contribute significantly to the resonance hybrid of the carbanion of β-picolines.

Figure 28. Oxidation of picoline-N-oxides in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol (3 mmoles substrate, 4.75 mmoles potassium *t*-butoxide, 25 ml. solvent)

Curve 1	*γ*-picoline-N-oxide
Curve 2	*α*-picoline-N-oxide
Curve 3	*β*-picoline-N-oxide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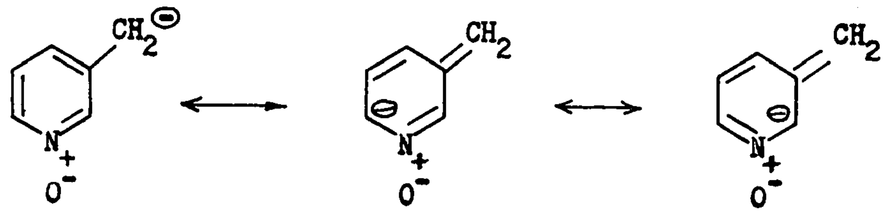
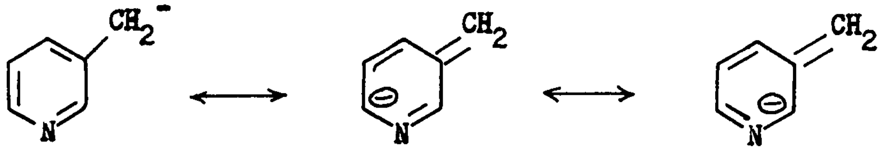
1·2
1·4
1·6
1·8
2·0
2·2
0
3·0
6·0
9·0
12·0
15·0
TIME (MIN.)
1
2
3



XXIV

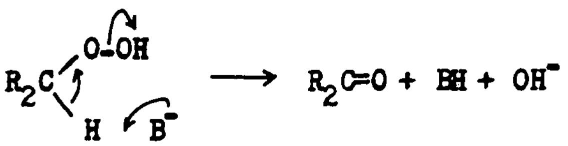


XXV

A description of the rates of oxidation of the methylnapthalenes has been presented under the heading, Solvent Effects. The products isolated from the oxidation of β-methylnaphthalene proved to be β-naphthoic acid, M.P. 181-5° (literature M.P. 185.5° (129)) in a 67% yield. A 48% yield of acid from the oxidation of α-methylnaphthalene was isolated with a melting point for the crude product of 130° (literature M.P. 162° (129)). It was very difficult to obtain a pure sample of α-methylnaphthalene and the product probably contained some impurity present in the starting material. There has not been evidence found for a dimeric product in the oxidation of methylnaphthalenes in hexamethylphosphoramide.

d. Diphenylmethane derivatives Under this heading the oxidation of diphenylmethane, xanthene, phenyl-4-pyridylmethane, and 9,10-dihydroanthracene as well as of triphenylmethane, 9,10-dihydrophenanthrene and acenaphthene will be described. Some of these oxidations were previously reported by Russell *et al.* (93). The rate of oxidation of diphenylmethane derivatives was found to be in the order 9,10-dihydroanthracene > xanthene > diphenylmethane > triphenylmethane (Figure 29). Phenyl-4-pyridylmethane oxidized very rapidly; however the experiment was not comparable in concentration of base. The oxidation of acenaphthene was surprisingly fast in 80% dimethyl sulfoxide - 20% t-butyl alcohol and was too fast to follow in hexamethylphosphoramide under the conditions used. There seemed to be a slow oxidation occurring also for 9,10-dihydrophenathrene in 80% dimethyl sulfoxide - 20% t-butyl alcohol although a rapid oxidation was observed in hexamethylphosphoramide.

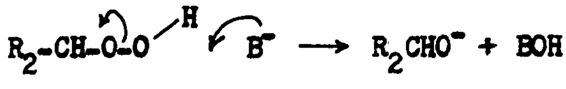
Table 7 summarizes the character of the products and the isolated yields. The most remarkable product obtained from these oxidations was benzhydrol from the oxidation of diphenylmethane (Run 301_1-A). Although an important step in the mechanism of the autoxidation of tertiary carbanions has been the decomposition of hydroperoxide by nucleophilic attack on oxygen to yield an alcoholate anion (7) this was the first actual proof of the occurrence of this reaction for a secondary carbanion by isolation of an intermediate alcohol more stable under the reaction conditions than the starting material. Instead of the usual base-catalyzed decomposition of the secondary hydroperoxide to yield a ketone,



$$R_2C(O{-}OH)(H) + B^- \longrightarrow R_2C{=}O + BH + OH^-$$

nucleophilic attack on oxygen had occurred at least to the extent of 60% by 10 min. for Run 301_1-A.

(115)



$$R_2{-}CH{-}O{-}O{-}H + B^- \longrightarrow R_2CHO^- + BOH$$

Figure 29. Oxidation of diphenylmethane derivatives in 80% dimethyl sufoxide - 20% *t*-butyl alcohol

Curve 1	3.13 mmoles triphenylmethane, 6.05 mmoles potassium *t*-butoxide, 25 ml. solvent
Curve 2	2.97 mmoles diphenylmethane, 6.3 mmoles potassium *t*-butoxide, 35 ml. solvent
Curve 3	3.05 mmoles xanthene, 6.1 mmoles potassium *t*-butoxide, 25 ml. solvent
Curve 4	3.08 mmoles 9,10-dihydroanthracene, 9.0 mmoles potassium *t*-butoxide, 50 ml. solvent
Curve 5	4.33 mmoles phenyl-4-pyridylmethane, 20 mmoles potassium *t*-butoxide, 40 ml. solvent
Curve 6	3.47 mmoles acenaphthene, 20 mmoles potassium *t*-butoxide, 40 ml. solvent

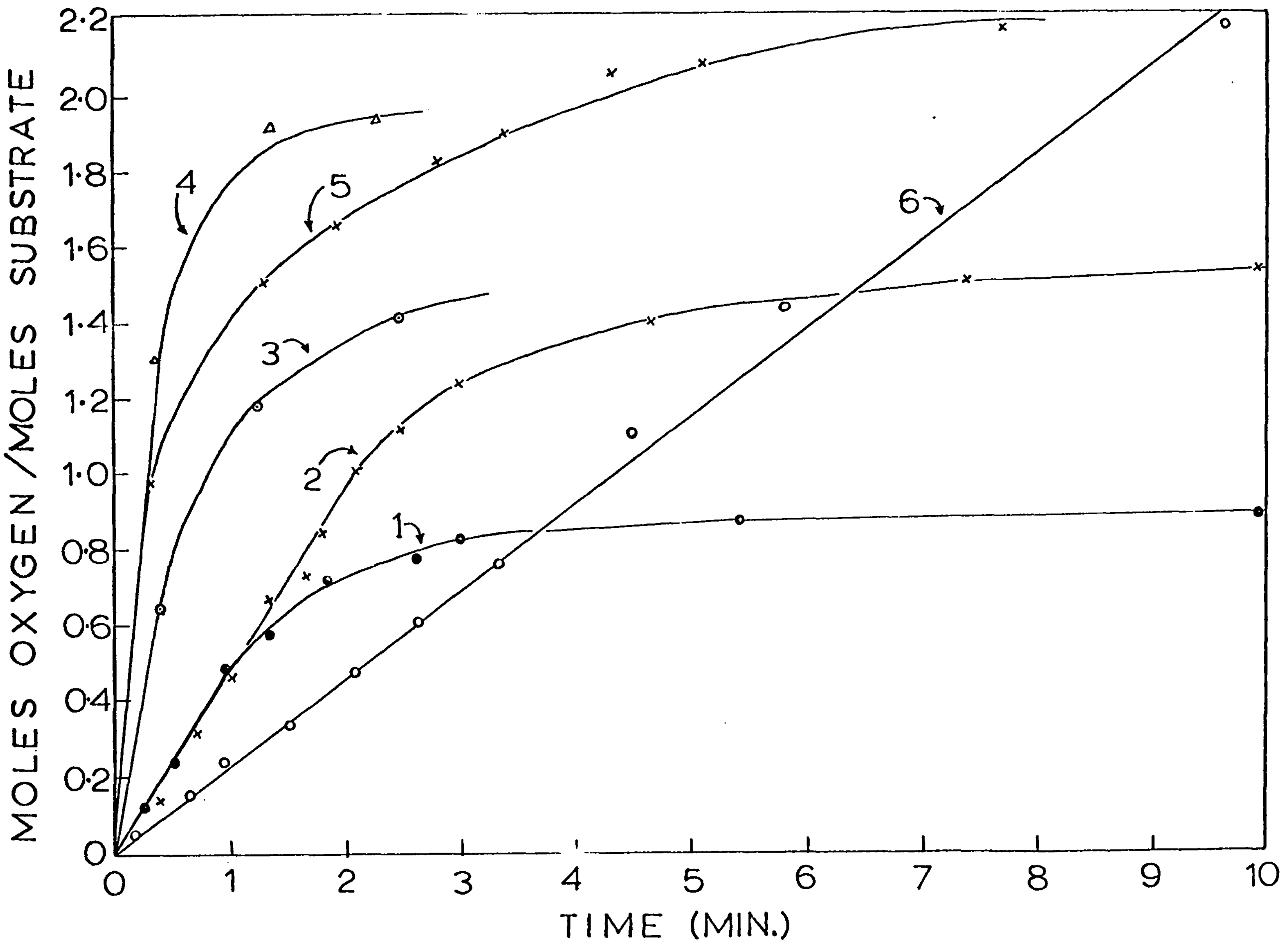

MOLES OXYGEN /MOLES SUBSTRATE
0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0
2·2
TIME (MIN.)
0
1
2
3
4
5
6
7
8
9
10
1
2
3
4
5
6

Table 7. Products of oxidations of hydrocarbons in 80% dimethyl sulfoxide - 20% t-butyl alcohol

Run	Substrate	O_2[a]	Product[b]	Yield	M.P.[c] (crude)
301_1-A	diphenylmethane	1.53 (2 min.)	benzhydrol	60%	60-2° (69°)
301_2-A	diphenylmethane	3.36 (4 hr.)	adduct[c]	96%	125° [d] (148°)[e]
26-A	xanthene	1.4 (2.5 min.)	xanthone	100%	172-3° (174°)
300-A	9,10-dihydroanthracene	2.03 (5 min.)	anthracene	77%	210-3° (217°)
15_2-A	triphenylmethane	0.83 (2 min.) 1.02 (20 min.)	triphenylcarbinol	96%	161° (163°)
148_2-C	9,10-dihydrophenanthrene	1.8 (5 min.) 3.4 (30 min.)	phenanthrene	88%	95-9° (100°)

[a] Ratio of moles oxygen at S.T.P./moles substrate

[b] The identity of each product was determined by a comparison of its I.R. spectra with that of the known compound.

[c] Literature values in parenthesis

[d] $(C_6H_5)_2C(OH)CH_2SOCH_3$ M.P. 147-8° after recrystallization from $CHCl_3/C_6H_{12}$ (63%)

[e] Reference 110

The fact that benzhydrol was isolated was the result of the slow oxidation observed for benzhydrol. In a study of the autoxidation of alcohols in polar solvents Russell and Geels[1] found benzhydrol oxidation to be very slow and slower than those of xanthydrol and fluorenol. Although the

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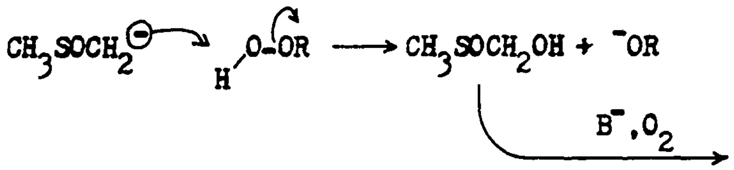
[1] Russell and Geels, op. cit. p. 14 herein.

possibility exists that reasonable amounts of alcohol were initially formed in the oxidation of xanthene and fluorene the isolation of these intermediates has not been attempted. The high oxygen consumption after longer periods of time in the oxidation of diphenylmethane in the presence of a higher base concentration (Run 301_2-A) was also consistent with the finding[1] that alcohols absorbed unusually large amounts of oxygen during autoxidation. Moreover if the basic attacking species was the methylsulfinyl anion, α-hydroxy dimethyl sulfoxide should be formed which would be expected to oxidize readily.

(116)



$$CH_3SOCH_2^{\ominus} \quad {}_{H}{/}O{-}OR \longrightarrow CH_3SOCH_2OH + {}^{-}OR \xrightarrow{B^{-},O_2}$$

The oxidation of both diphenylmethane and benzhydrol[1] produced benzophenone which in dimethyl sulfoxide was isolated as the dimethyl sulfoxide addition product of benzophenone (see Appendix, Dimethyl Sulfoxide Adducts).

Xanthone was produced from the oxidation of xanthene in dimethyl sulfoxide solution (Run 26-A). Apparently the reason that xanthone did not form an addition product with dimethyl sulfoxide was that the carbonyl in conjugation with the ether oxygen is not electrophilic enough to cause an addition to occur. A significant polar contribution to the resonance hybrid of xanthone is postulated to account for the determined dipole moment of xanthone (130).

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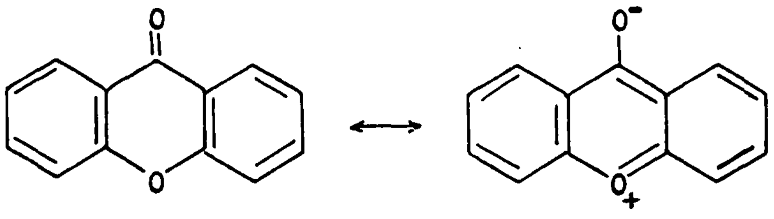
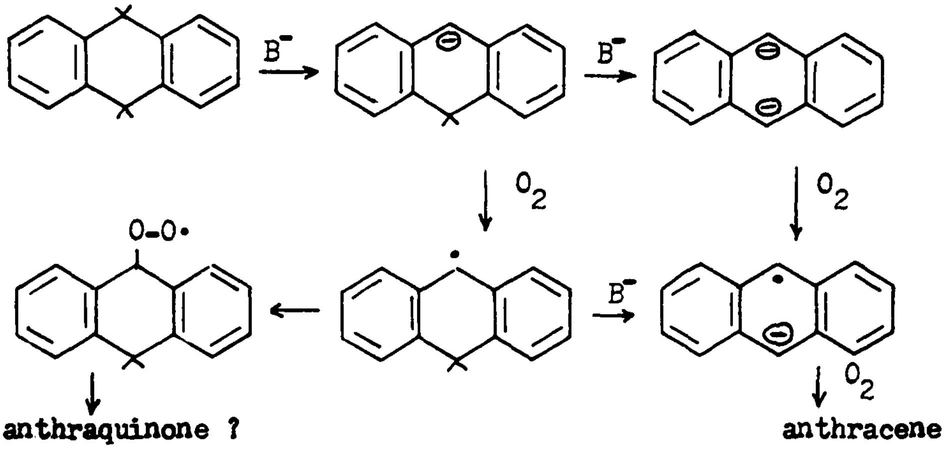
[1] Russell and Geels, *op. cit.* p. 14 herein.



XXVI

The examples of dehydrogenation of 9,10-dihydro derivatives by base and oxygen to produce the dehydro compounds can be considered to go through a radical anion intermediate.

(117)



Since less than 100% yield was obtained in both reactions, 77% for 9,10-dihydroanthracene and 88% for 9,10-dihydrophenanthrene, a small amount of dimethyl sulfoxide adduct of a quinone product could have been formed and since these adducts probably would be at least partially water soluble they remained in solution (see Appendix for information on the anthraquinone dimethyl sulfoxide mono-addition product). If these products were found they would provide evidence indicating that the rate of reaction of the radical with oxygen was faster than ionization to the radical ion.

The oxidation of triphenylmethane produced triphenylcarbinol probably a product of nucleophilic attack on oxygen of the triphenylmethyl hydroperoxide.

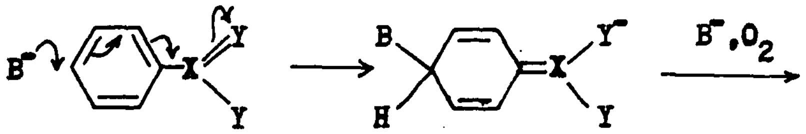
(118) $(C_6H_5)_3C{-}O{-}O{-}H \;\; B^- \longrightarrow (C_6H_5)_3C{-}O^- + BOH$

Since one mole oxygen was absorbed per mole starting material by the end of the oxidation (Figure 24) it seemed likely that the attacking base was in fact the methylsulfinyl anion since if the attack were solely by triphenylmethide anion the oxygen stoichiometry should have been one-half mole oxygen to one mole starting material. If the attacking base were the methylsulfinyl anion the oxygen consumption in the presence of higher concentrations of base would increase due to oxidation of the α-hydroxy dimethyl sulfoxide formed. The stability of triphenylmethylperoxide in the basic solvent used has not been investigated.

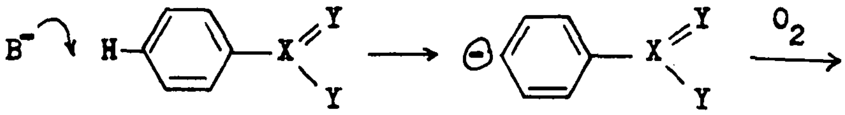
e. *Base-addition-oxidation* In a comprehensive study of carbanion oxidation in highly basic media the possibility of the base adding to the nucleus followed by oxidation is always present. Some reactions which we felt were base-addition-oxidations will be described here. Since products were not isolated in any case, there cannot be an undisputed mechanism for the oxidation suggested for these compounds. An alternate mechanism involves ionization of a ring proton followed by oxidation. It is our feeling that a base-addition mechanism is the correct one.

Base-addition followed by oxidation

(119)



Ring proton followed by oxidation

(120) 

Base addition to trinitrobenzene leads to the formation of an addition product now known as a Meisenheimer adduct (131). In t-butyl alcohol containing potassium t-butoxide the t-butoxy adduct was found to be extremely insoluble and Moye (3) observed only very slight oxidation after approximately 1 hr. of exposure to oxygen although the oxidation could be slightly accelerated by metal ions such as ferric chloride. In 80% dimethyl sulfoxide - 20% t-butyl alcohol both sym-trinitrobenzene and m-dinitrobenzene oxidized more rapidly than in t-butyl alcohol (Figure 30). Figure 31 indicates the effect of adding more base to the oxidizing solution containing trinitrobenzene. The rate of oxidation for dinitrobenzene was faster than trinitrobenzene in both solvents and also produced free radicals spontaneously in t-butyl alcohol containing potassium t-butoxide (100) whereas trinitrobenzene did not (see Spontaneous radical formation). The oxidation of m-dinitrobenzene in t-butyl alcohol containing only a slight excess of potassium t-butoxide was very slow although a bright purple solution was observed immediately upon mixing and during the oxidation. In dimethyl sulfoxide in deficient base a similar slow oxidation occurred and the purple color was formed initially although after 1 hr. the solution had turned black. In this case 26% yield of starting material was recovered by pouring the solution into water and filtering. The solutions containing sym-trinitrobenzene or 9-nitroanthracene were bright red immediately after mixing but changed

Figure 30. Base-addition-oxidation of polynitroaromatics

Curve 1	3 mmoles *sym*-trinitrobenzene, 6 mmoles potassium *t*-butoxide in 25 ml. 80% dimethyl sulfoxide - 20% *t*-butyl alcohol
Curve 2	3 mmoles *m*-dinitrobenzene, 6 mmoles potassium *t*-butoxide in 25 ml. 80% dimethyl sulfoxide - 20% *t*-butyl alcohol
Curve 3	3 mmoles *m*-dinitrobenzene, 6 mmoles potassium *t*-butoxide in 25 ml. *t*-butyl alcohol
Curve 4	1.5 mmoles 9-nitroanthracene, 1.6 mmoles potassium *t*-butoxide in 25 ml. 80% dimethyl sulfoxide - 20% *t*-butyl alcohol
Curve 5	4 mmoles 4-nitropyridine-N-oxide, 8 mmoles potassium *t*-butoxide in 40 ml. *t*-butyl alcohol

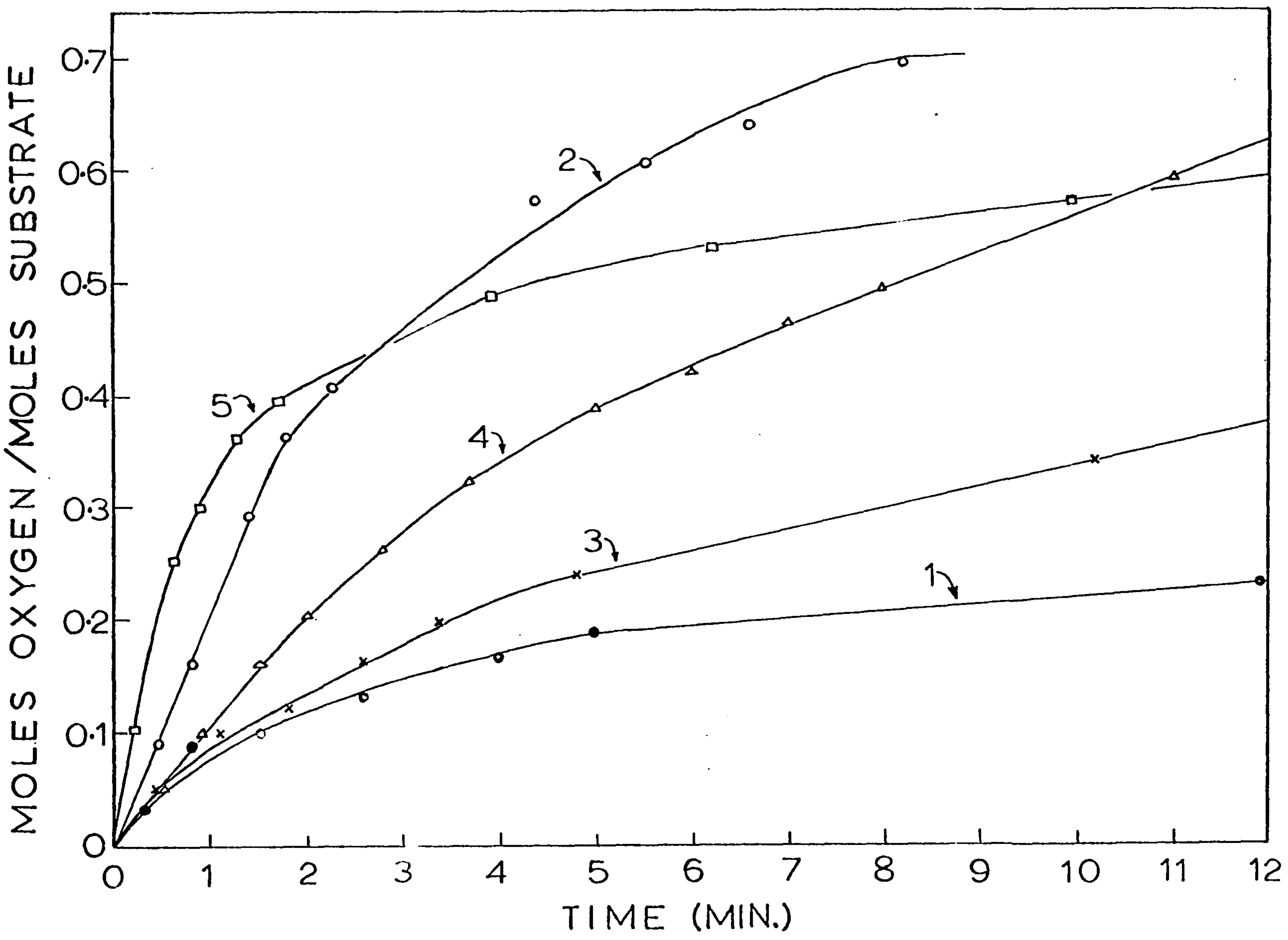

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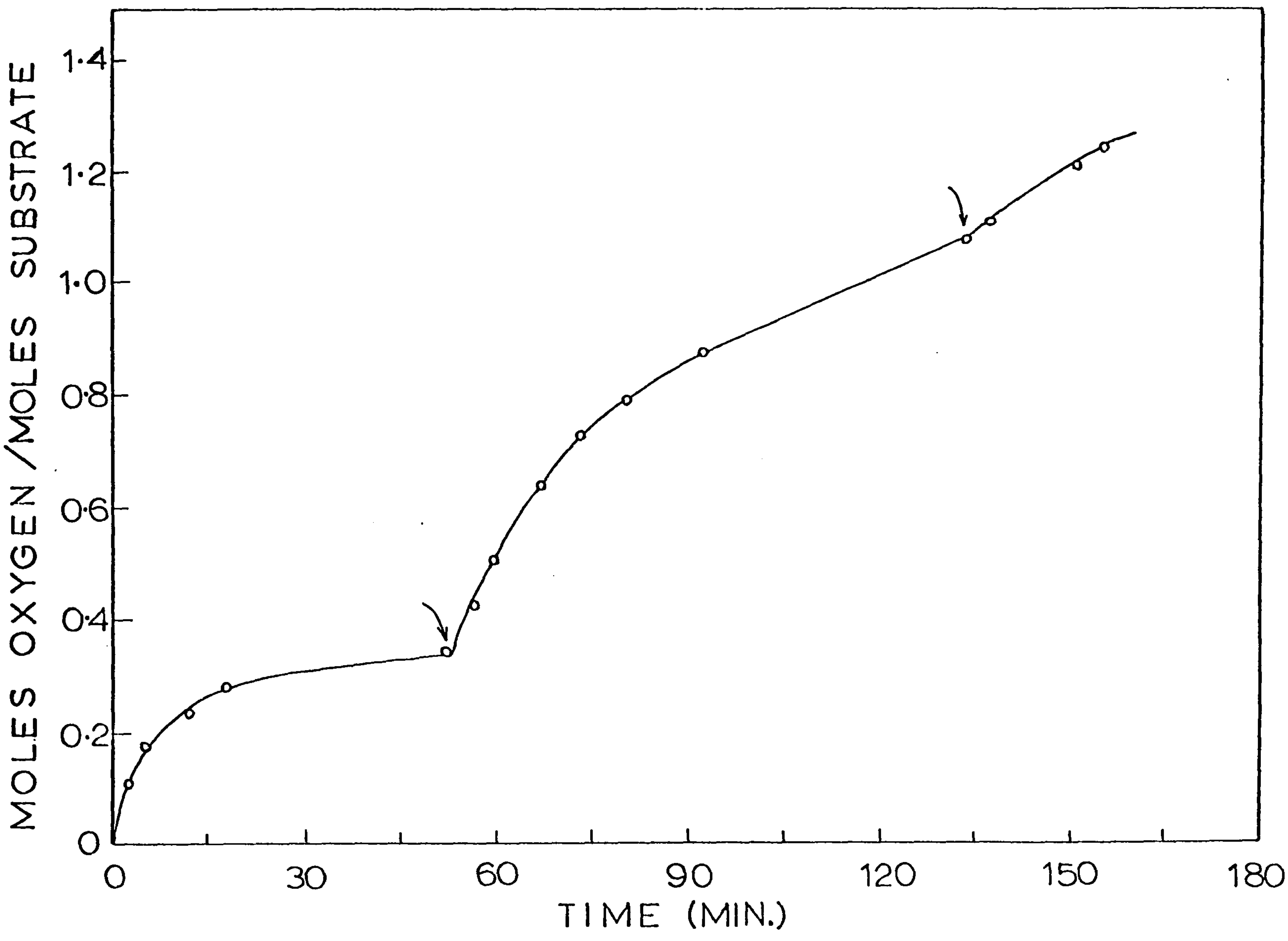
Figure 31. Oxidation of _sym_-trinitrobenzene in 80% dimethyl sulfoxide - 20% _t_-butyl alcohol (3 mmoles trinitrobenzene, 6 mmoles potassium _t_-butoxide in 25 ml. solvent; each discontinuity is the point of addition of 6 mmoles potassium _t_-butoxide)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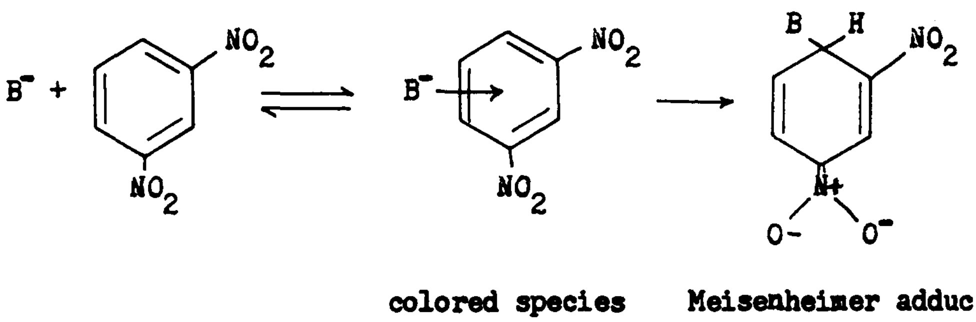
180
TIME (MIN.)

to brown during oxidation. The oxidizing solution of *p,p'*-dinitrostilbene in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol discussed previously was bright blue.

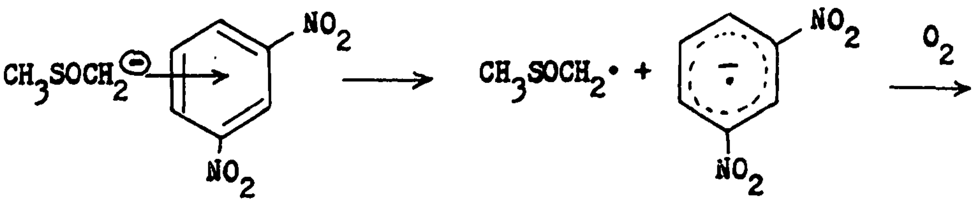
These findings are consistent with a number of color reactions of polynitroaromatic compounds with donators particularly bases (87). It is believed that a charge transfer complex is the initially formed colored species which subsequently rearranges to yield a *sigma*-bonded addition product.

(121)



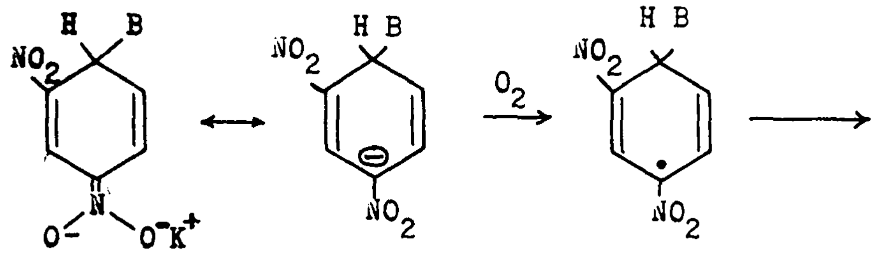
In deficient base dinitrobenzene produced the colored solution of the charge transfer complex which apparently was stable to oxygen. In dimethyl sulfoxide, if the donar were the methylsulfinyl carbanion there exists the interesting possibility of the charge transfer complex decomposing directly into two radical species,

(122)



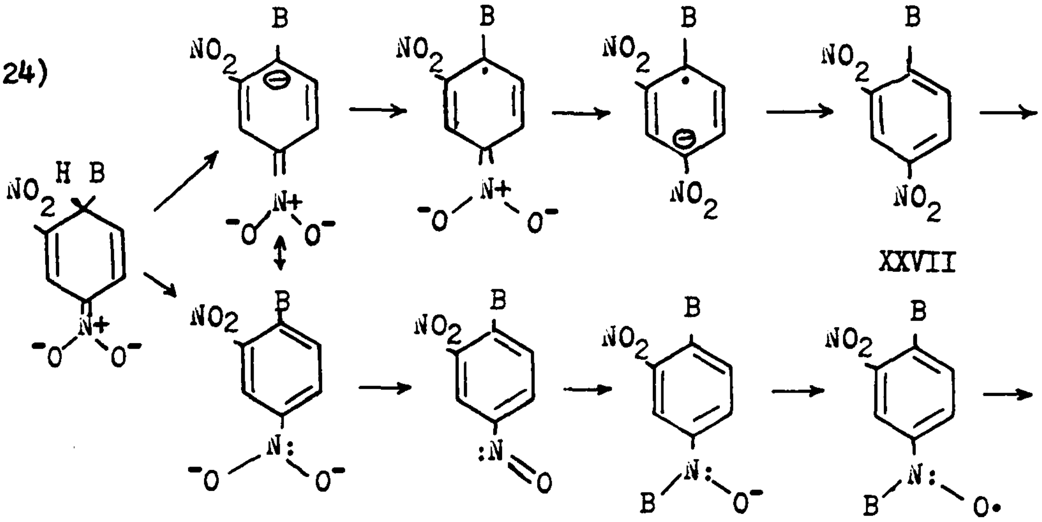
leading to a catalyzed oxidation of the methylsulfinyl anion. In polar solvents where the adduct is soluble one might expect it to react with oxygen.

(123)



However in excess base a competitive reaction should be proton removal and a number of subsequent reactions might take place:

(124)

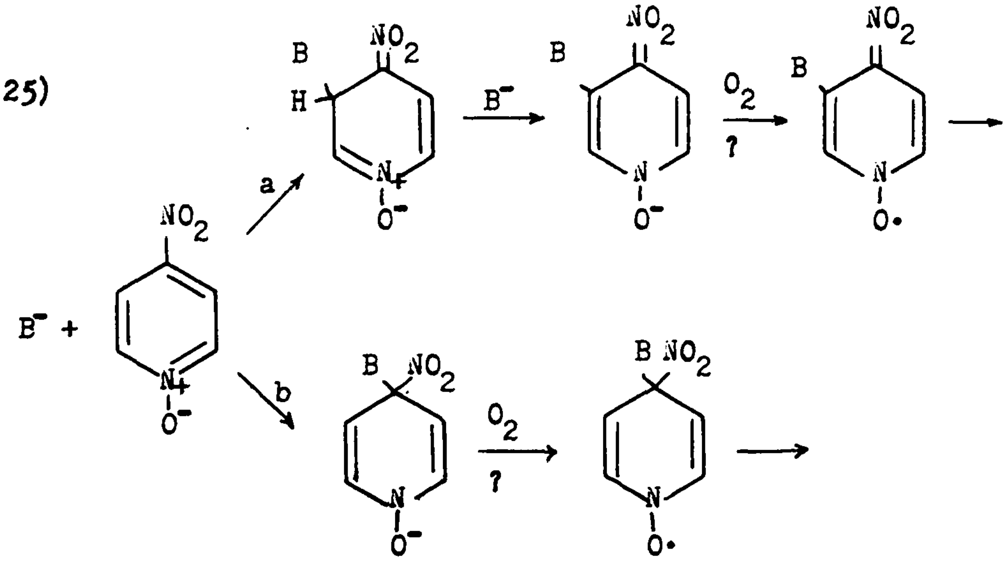


If the adding base was the methylsulfinyl carbanion and only reactions leading to product XXVII were taking place one might expect the end product to be benzoic acid derivatives. There were no precipitates in the basic or acidic aqueous solution after pouring the oxidation mixture into water which is evidence against this reaction pathway.

In 80% dimethyl sulfoxide - 20% t-butyl alcohol a very slow oxidation was observed for nitrobenzene. This could be interpreted either as a catalyzed oxidation of the methylsulfinyl carbanion or a base-addition-oxidation reaction; this solution was pink initially but turned deep red during oxidation. In hexamethylphosphoramide a much more rapid oxidation occurred; a dark green color appeared initially which turned to brown during the oxidation. Since very little is known about the behavior of base in this solvent a mechanism for the oxidation of nitrobenzene cannot be suggested although a base-addition-oxidation mechanism is a likely possibility.

In connection with a study of the effect of catalyst on the oxidation of fluorene, 4-nitropyridine-N-oxide was found to decompose very rapidly with oxygen absorption in *t*-butyl alcohol containing potassium *t*-butoxide (Figure 30). This was the fastest oxidation found in *t*-butyl alcohol for compounds of this type, and can be attributed to a base-addition-oxidation mechanism (Equation 125a or 125b)

(125)

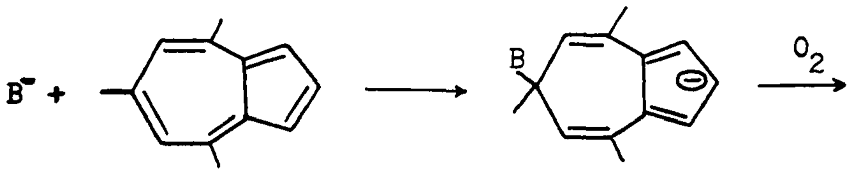


An interesting comparison should be available with p-dinitrobenzene but this oxidation was not tried.

A fast oxidation of 4,6,8-trimethylazulene in 80% dimethyl sulfoxide - 20% t-butyl alcohol was observed probably also *via* a base-addition-oxidation although ionization of a methyl group is also possible.

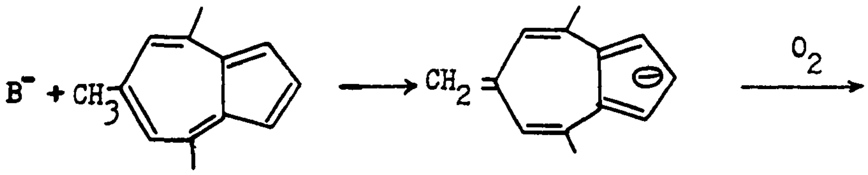
Base-addition-oxidation

(126)



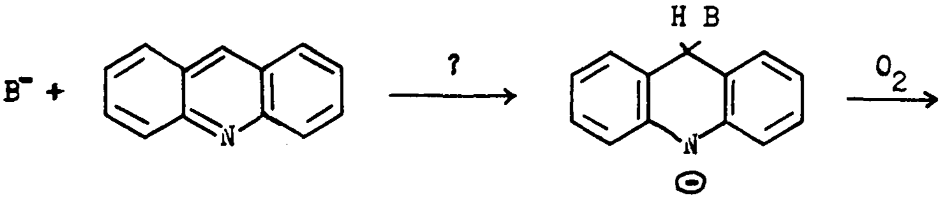
Carbanion oxidation

(127)



Polynuclear aromatic compounds possibly could undergo base-addition-oxidation reactions. In hexamethylphosphoramide containing potassium t-butoxide only acridine oxidized rapidly of the compounds tried.

(128)



Phenanthrene, phenanthridine, anthracene and naphthalene were stable or oxidized more slowly than the solvent.

3. Rates as a function of added catalyst

The effect of catalysts on the autoxidation of carbanions was studied extensively by Moye (3). The most remarkable effect caused by added metal ions was found in the autoxidation of alcohols and diphenylacetonitrile where ferric chloride and cupric chloride increased the rate of oxidation of the latter but inhibited the oxidation of alcohols. The study of the mechanism of autoxidation of fluorene discussed earlier included the investigation of the effect of additive to the oxidizing medium. The addition of lead sub-acetate tried by Moye (3) had the effect of slightly slowing down the rate of oxidation. In the presence of relatively large amounts ($\sim$ 6 mole %) of ferric chloride or arsenic trioxide the rate of oxidation of fluorene increased slightly in t-butyl alcohol containing excess potassium t-butoxide; a slightly faster rate was also noted when 10 mole % fluorenone was added to the solution before oxidation. The presence of potassium superoxide (produced by a prior autoxidation of benzhydrol in t-butyl alcohol containing potassium t-butoxide) made very little change in the oxidation of fluorene in t-butyl alcohol. The oxidation in 80% dimethyl sulfoxide - 20% t-butyl alcohol could not be inhibited by ferric chloride or arsenic trioxide even in deficient base (1:5). A faster oxidation was observed in the presence of benzaldehyde although this result was ambiguous since benzaldehyde probably absorbed oxygen during the reaction. These results indicate that the base catalyzed oxidation of fluorene is not very sensitive to the usual radical chain initiators or inhibitors.

The rate of oxidation of fluorene should increase with an increase in the concentrations of hydrocarbon, base or oxygen, or by a net increase in the rate of electron transfer of carbanion to oxygen. One might have expected ferric chloride to increase the rate of electron transfer to oxygen,

(129) $R^{\ominus} + Fe^{+3} \longrightarrow R\cdot + Fe^{+2}$

(130) $Fe^{+2} + O_2 \longrightarrow Fe^{+3} + \cdot O_2^{-}$ etc.

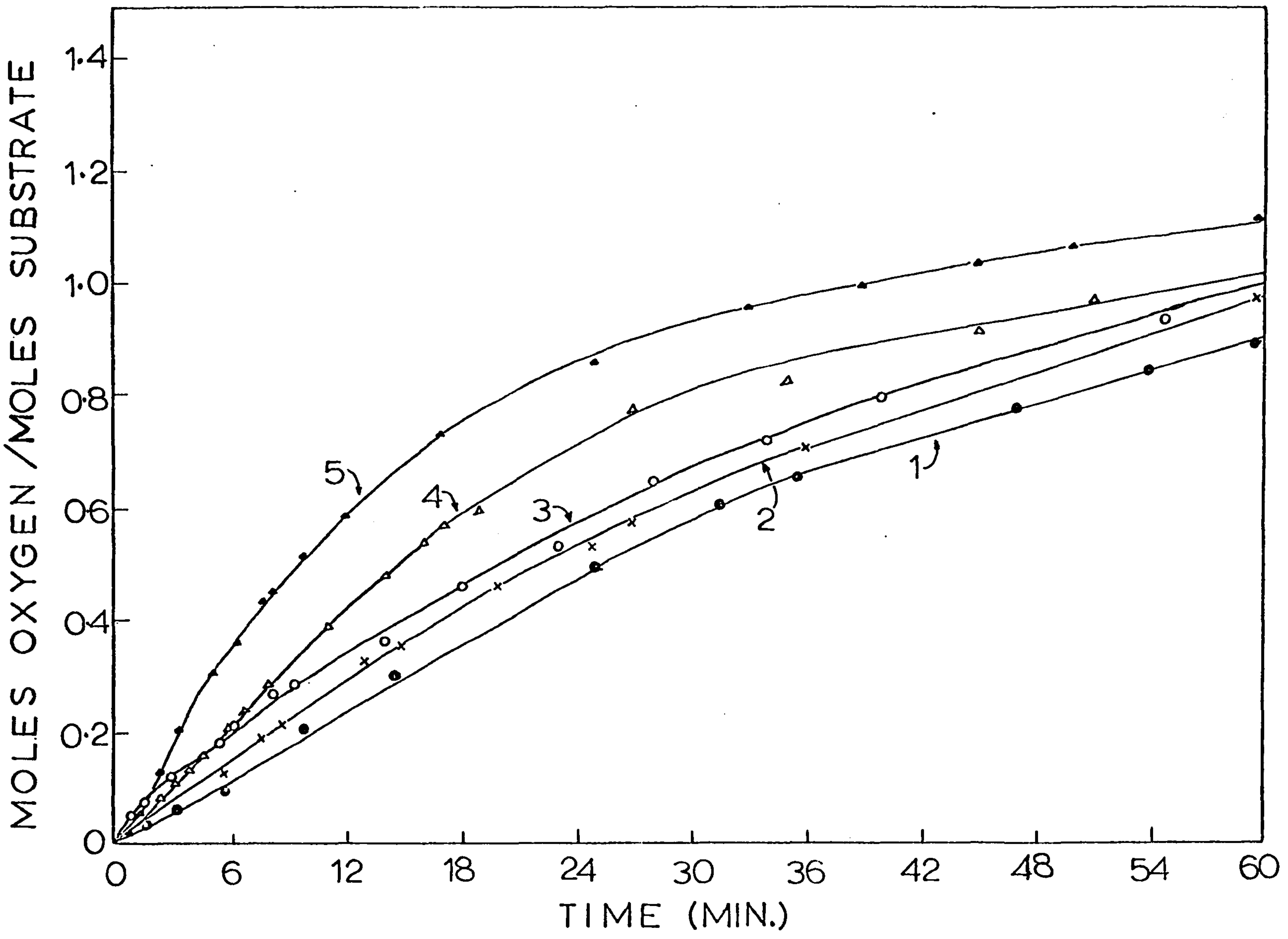
but the increase in rate of oxidation was too small to be significant.

Our search for other compounds which would affect the rate of oxidation of fluorene uncovered the catalytic effect exerted by nitrobenzene. This correlated with our findings that free radicals were spontaneously formed by p-nitrotoluene and derivatives in basic solution (100). Figure 32 shows the effect of added nitrobenzene to the oxidation of fluorene in t-butyl alcohol. In the presence of 3 and 8 mole % nitrobenzene the rate of oxidation was 1.5 and 2.5 times faster than the uncatalyzed oxidation. The initial rate in the presence of 3 mole % m-dinitrobenzene was at first faster than that observed for 3 mole % nitrobenzene but the rate slowed down rapidly to a rate similar to that of the uncatalyzed oxidation. Very little increase in rate was noticed in the presence of sym-trinitrobenzene. For the polynitro aromatic compounds the addition products of base to the nucleus are formed rapidly in this system of high excess base ($\sim$ 20 times that of the additive) and catalysis was relatively ineffective with these compounds.

The function of nitrobenzene in the catalyzed carbanion oxidation is thought to be that of an oxidizing agent or an electron acceptor like oxygen, the fluorenyl anion being oxidized by one electron, the

Figure 32. Catalyzed rates of oxidation of fluorene in *t*-butyl alcohol; effect of added nitroaromatic (6.05 mmoles potassium *t*-butoxide in 25 ml. solvent)

Curve 1	3.1 mmoles fluorene
Curve 2	2.99 mmoles fluorene, 3.06 mole % *sym*-trinitrobenzene
Curve 3	2.93 mmoles fluorene, 3.05 mole % *m*-dinitrobenzene
Curve 4	2.99 mmoles fluorene, 2.90 mole % nitrobenzene
Curve 5	3.04 mmoles fluorene, 8.20 mole % nitrobenzene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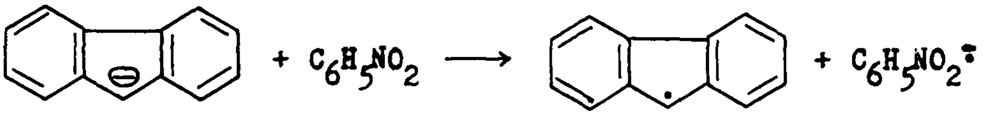
nitrobenzene molecule reduced by one electron.

(131)



This interpretation is substantiated by the observation that the nitrobenzene radical anion can be detected under these conditions in the absence of oxygen and its hyperfine spectrum resolved by E.S.R. techniques (see Electron transfer from carbanions). Since nitrobenzene radical ion is oxidized back to the parent compound by oxygen the described cycle of two steps is an initiation process generating fluorenyl free radicals. If this process is faster than the same sequence with oxygen a rate enhancement should be observed.

(132) $R^{\ominus} + O_2 \xrightarrow{k_1} R\cdot + \cdot O_2^-$

(133) $R^{\ominus} + C_6H_5NO_2 \xrightarrow{k_2} R\cdot + C_6H_5NO_2\cdot$

(134) $C_6H_5NO_2^{\overline{\cdot}} + O_2 \xrightarrow{k_3} C_6H_5NO_2 + \cdot O_2^-$ $\qquad k_2, k_3 > k_1$

The ease of electron transfer in general should parallel the redox potential of the couple, i.e., the reduction potential of the carbanion and the oxidation potential of the acceptor. With a given carbanion the more easily the acceptor is reduced the more readily electron transfer should take place and the faster should be the catalyzed rate of oxidation of the carbanion. The reduction potential of nitroaromatics decreases when electron-withdrawing substituents influence the nitro group as reported by Maki and Geske for para-substituted nitrobenzenes (38).

The rates of oxidation of fluorene in the presence of added substituted nitroaromatics follow the order p-CN $>$ p-Br $>$ p-Cl $>$ m-OCH_3 $>$ H $>$ m-CH_3 $>$ m-NH_2 (Figure 33, Table 8).

The logarithm of the ratio of the catalyzed rate of oxidation in the presence of 5% substituted nitrobenzene divided by the rate in the presence of 5% nitrobenzene (all in units of moles of oxygen/moles fluorene per minute) is plotted against Hammett's σ constant in Figure 34 (see Table 8). The rates catalyzed by the seven substituted nitrobenzenes mentioned above are known with better accuracy than the rates given for m-CN, m-NO_2 and p-NO_2 substituents. The oxidation curves of fluorene in the presence of these substituents are given in Figure 35. Since the extent of catalysis had to be estimated from the first point measured, because the slope of the curve decreased very rapidly, the values obtained were very approximate. The curve for nitrobenzene is included for comparison; it shows an almost linear initial slope including many observed points from which the initial rate was obtained. Good initial slopes were found for the rates of the other substituted nitrobenzenes (Figure 33).

The catalyzed rates plotted against Hammett's σ constant describe a reasonably good straight line (Figure 34). Since rates of oxidation of the bromo and chloro substituents are known with reasonable certainty this might be justification for drawing a curved line including these points reasoning that the more strongly electron-withdrawing groups have catalyzed the reaction to an extent greater than truly measured because some limiting factor such as maximum oxygen exposure or base decomposition of the catalyst has prevented the measurement of the true rates. However the fit to the straight line is remarkably good considering the

Figure 33. Catalyzed rates of oxidation of fluorene in *t*-butyl alcohol; effect of 4.75 mole % added substituted nitrobenzene (2.5 mmoles fluorene, 5.0 mmoles potassium *t*-butoxide, 25 ml. solvent)

Curve 1	uncatalyzed oxidation of fluorene
Curve 2	*m*-aminonitrobenzene (*m*-nitroaniline)
Curve 3	*m*-methylnitrobenzene (*m*-nitrotoluene)
Curve 4	*m*-methoxynitrobenzene (*m*-nitroanisole)
Curve 5	nitrobenzene
Curve 6	*p*-chloronitrobenzene
Curve 7	*p*-bromonitrobenzene
Curve 8	*p*-cyanonitrobenzene (*p*-nitrobenzonitrile)

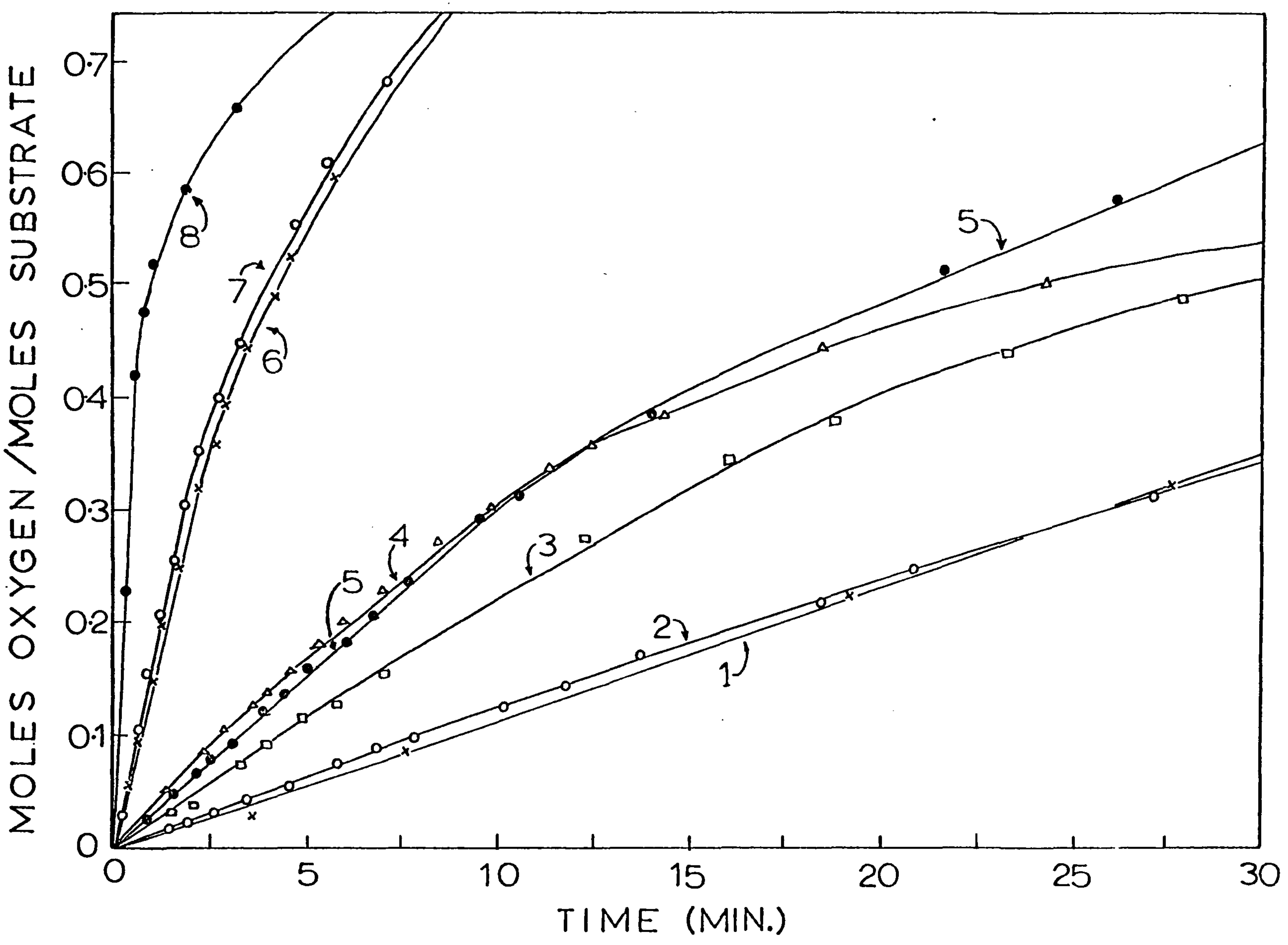

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Table 8. Rates of catalyzed oxidation of fluorene and Hammett's σ

Substituent	Rate[a]	Rate/rate$_o$[b]	Log$_{10}$ rate/rate$_o$	σ[c]	$\Delta E_{\frac{1}{2}}$[d]
p-NO_2	0.7	19.8	1.296	0.778	0.457
m-NO_2	.3	8.44	0.928	.710	.249
p-CN	.726	20.5	1.313	.660	.272
m-CN	.565	15.9	1.204	.56	.209
p-Br	.205	5.79	0.763	.232	.097
p-Cl	.157	4.32	.636	.227	.084
m-OCH_3	.0378	1.06	.025	.115	.0
H	.0355	1.00	.000	.00	.000
m-CH_3	.0272	0.766	- .115	- .069	- .033
m-NH_2	.0161	0.454	- .342	- .16	- .061
p-$N(CH_3)_2$	.12	3.38	.530	- .83	

[a] Catalyzed rate of oxidation of fluorene in the presence of substituted nitrobenzene

[b] Catalyzed rates of oxidation of substituted nitrobenzene over nitrobenzene

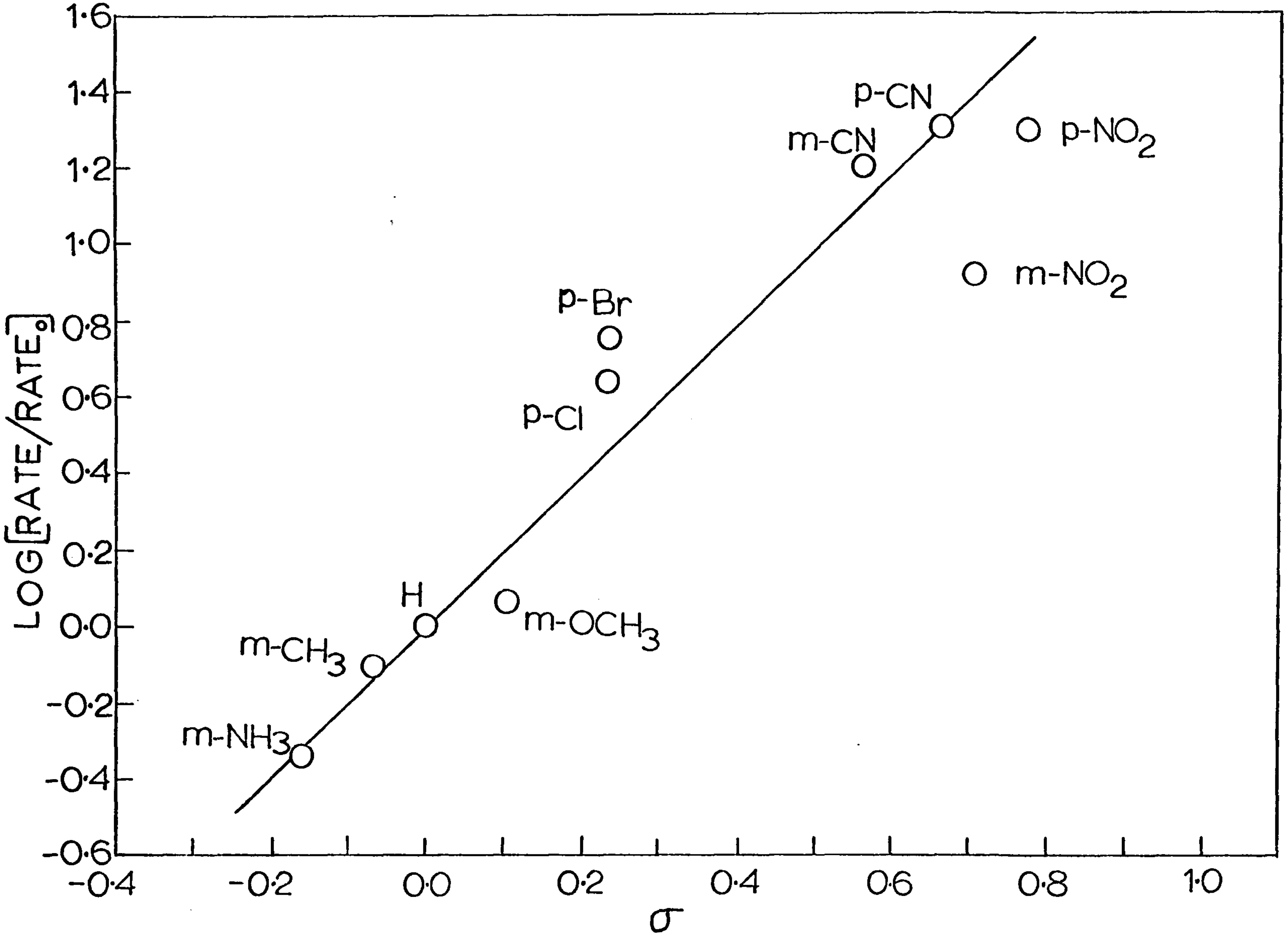
[c] Hammett's σ constant from Leffler and Grunwald (120)

[d] Reference 38

approximate nature of the rate determinations. The slope of 20 for this line seems very high.

A plot of $\Delta E_{\frac{1}{2}}$ for the substituted nitrobenzenes vs. the logarithm of the ratio of the catalyzed rates yields a reasonably good straight line (Figure 36). The para-nitro substituent falls far off the line as it does in Maki and Geske's (38) plot against the sigma values for the substituents.

Figure 34. Hammett σ^- plot of nitrobenzene-catalyzed rates of oxidation of fluorene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0·0
-0·2
-0·4
-0·6
LOG[RATE/RATE$_0$]
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-0·2
0·0
0·2
0·4
0·6
0·8
1·0
σ
p-CN
m-CN
p-NO$_2$
m-NO$_2$
p-Br
p-Cl
H
m-OCH$_3$
m-CH$_3$
m-NH$_3$

Figure 35. Catalyzed rates of oxidation of fluorene; effect of 4.75 mole % added substituted nitrobenzene unstable to base (2.5 mmoles fluorene, 5.0 mmoles potassium _t_-butoxide, 25 ml. solvent)

Curve 1	nitrobenzene
Curve 2	_m_-dinitrobenzene
Curve 3	_m_-cyanonitrobenzene
Curve 4	_p_-dinitrobenzene
Curve 5	_p_-(dimethylamino)-nitrobenzene

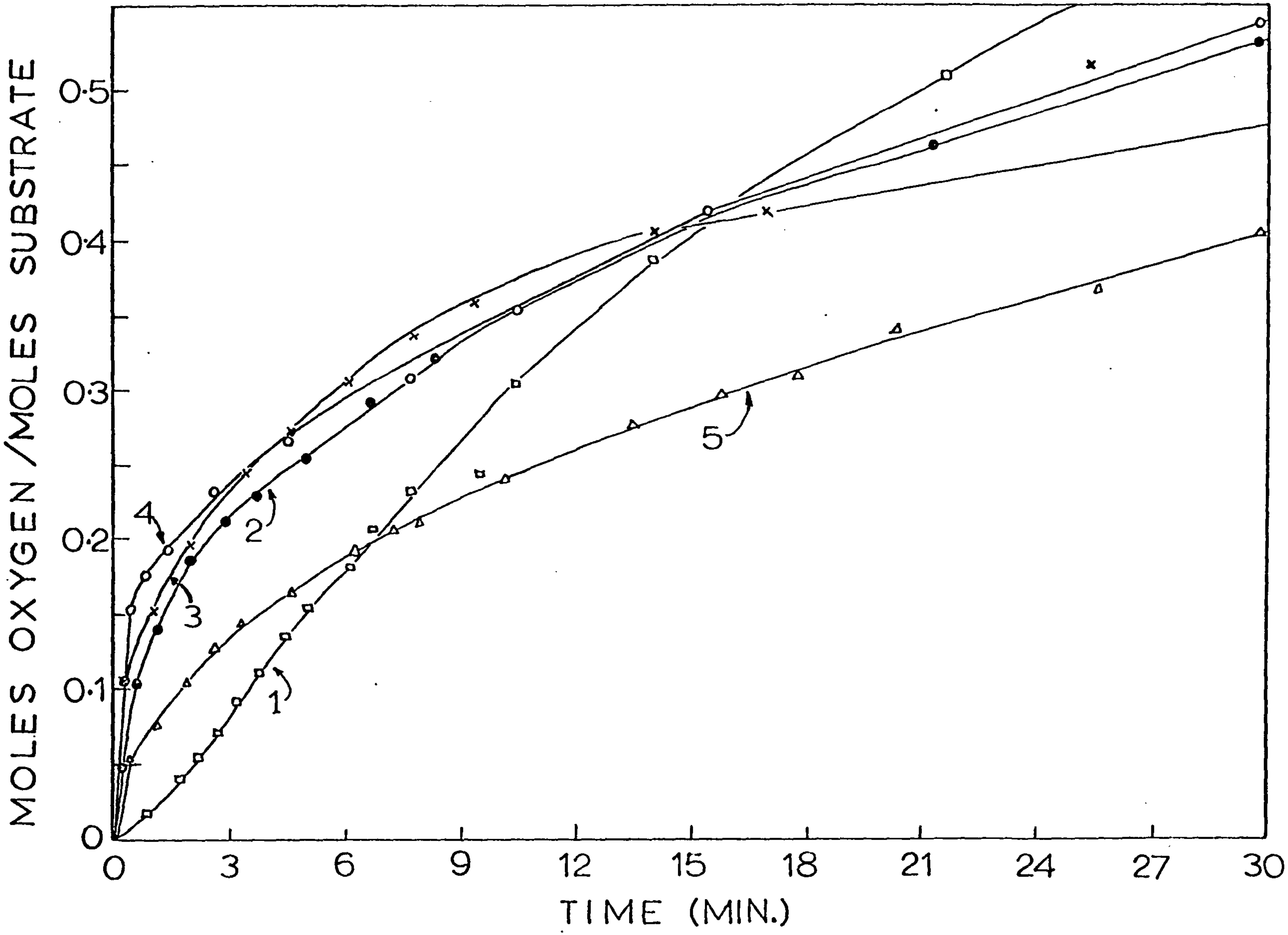
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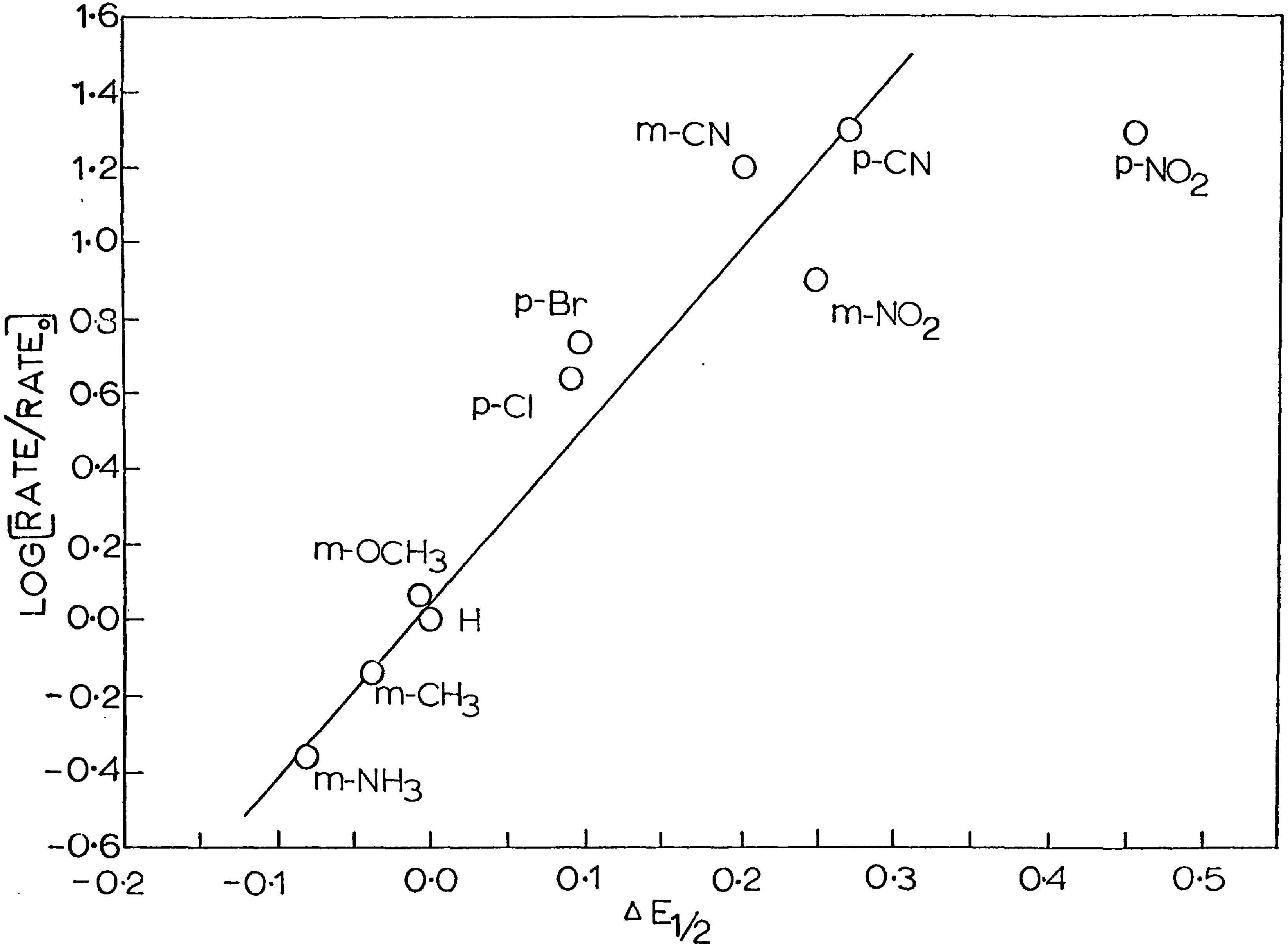
Figure 36. Plot of Maki and Geske's $\Delta E_{\frac{1}{2}}$ *vs.* the catalyzed rates of oxidation of fluorene (see Table 8)


LOG[RATE/RATE$_o$]
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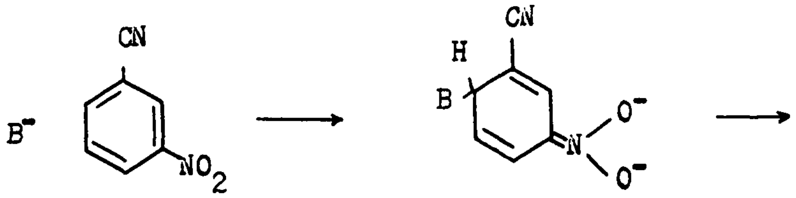
−0·4
−0·6
−0·2
−0·1
0·0
0·1
0·2
0·3
0·4
0·5
$\Delta E_{1/2}$
m-CN
p-CN
p-NO$_2$
m-NO$_2$
p-Br
p-Cl
m-OCH$_3$
H
m-CH$_3$
m-NH$_3$

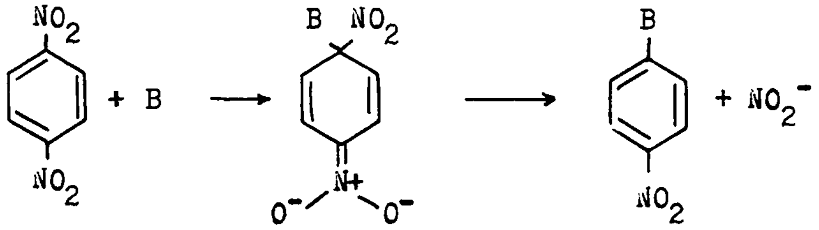
The choice of 4.75 moles % (5 equivalent per cent) was completely arbitrary and was simply a convenient concentration which gave reasonably good catalysis in the case of nitrobenzene so that electron-donating substituents could be used for the observation of slower rates, electron-withdrawing groups for faster rates. For a more accurate redetermination of the catalyzed rates a higher concentration of substituted nitrobenzenes with electron-donating groups should be used and a lower concentration for those with electron-withdrawing groups related by the determination of rates at the same concentrations, say for nitrobenzene. The relationship between concentration of electron acceptor and rate has not been investigated except that it was found as noted earlier that an increase of concentration for nitrobenzene from 3 to 8 mole % increased the catalyzed rate from 1.5 times to 2.5 times that of the uncatalyzed rate of oxidation of fluorene.

The decreasing catalytic effect by *m*-dinitrobenzene and *m*-cyanonitrobenzene is probably due to degradative oxidation of a base addition product.

(135) 

It was unexpected that *p*-dinitrobenzene should also be an unstable catalyst. Possibly the nitro group was displaced by potassium *t*-butoxide, and this may have brought about decomposition of the catalyst.

(136)



Because of these reactions which could have destroyed the catalyst the estimated rates for m-nitro, m-cyano and p-nitro are probably too low. The only very anamolous observation is that for the p-dimethylamino substituent.

The discovery of catalysis of oxidation of fluorene by nitrobenzene suggested numerous variants as a function of structure to be tried as catalysts. Of these only a few have been studied. 4-Nitropyridine-N-oxide proved to be the best electron acceptor although also the most unstable in the basic solution. Figure 37 shows the extremely fast initial oxidation of fluorene in the presence of 5% 4-nitropyridine-N-oxide; however the rate decreased rapidly with time. For comparison the oxygen absorption due to decomposition of catalyst under identical conditions in the absence of fluorene is also shown; although appreciable it does not account for the large amount of oxygen absorbed rapidly initially in the oxidation of fluorene. In view of the equations,

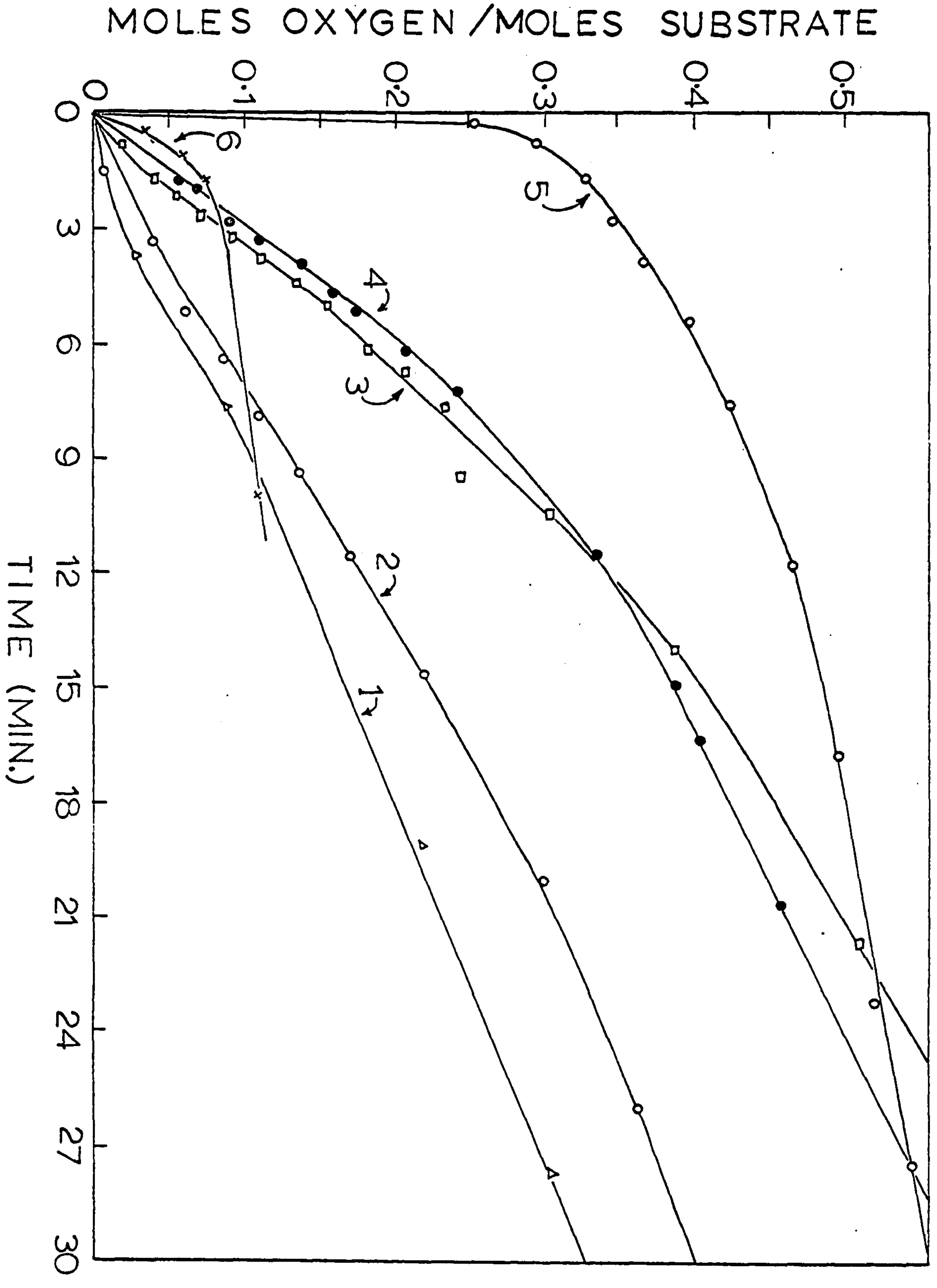
$$R^{\ominus} + O_2 \xrightarrow{k_1} R\cdot + O_2^{\overline{\cdot}} \qquad R^{\ominus} = \text{fluorenyl}$$

$$R^{\ominus} + A \xrightarrow{k_2} R\cdot + A^{\overline{\cdot}} \qquad A = \text{electron acceptor} \tag{137}$$

$$A^{\overline{\cdot}} + O_2 \xrightarrow{k_3} A + O_2^{\overline{\cdot}} \tag{138}$$

Figure 37. Catalyzed rates of oxidation of fluorene in *t*-butyl alcohol; effect of added nitroaromatic derivatives (2.5 mmoles fluorene, 5.0 mmoles potassium *t*-butoxide, 4.75 mole % added catalyst, 25 ml. solvent)

Curve 1	uncatalyzed rate
Curve 2	6-nitroquinoline
Curve 3	nitrobenzene
Curve 4	pentachlorobenzene
Curve 5	4-nitropyridine-N-oxide
Curve 6	4-nitropyridine-N-oxide in the absence of fluorene


MOLES OXYGEN /MOLES SUBSTRATE
0
0·1
0·2
0·3
0·4
0·5
TIME (MIN.)
0
3
6
9
12
15
18
21
24
27
30
1
2
3
4
5
6

for the catalysis to be effective both the rate of electron transfer from the carbanion to the acceptor and the oxidation of the acceptor radical ion by oxygen, must be faster than the oxidation of the carbanion by oxygen, $k_2 > k_1$ and $k_3 > k_1$. In the case of 4-nitropyridine-N-oxide possibly there is an advantageous relationship for both rates of electron transfer; i.e., 4-nitropyridine-N-oxide may be a very good electron acceptor but at the same time the resulting radical anion may not be as stable to oxygen as say nitrobenzene. A situation of this kind should show large rate enhancement as was observed.

It was thought that a polychloronitrobenzene should have a favorable reduction potential (a good electron acceptor) and at the same time be a stable oxidation catalyst. In fact pentachloronitrobenzene showed essentially no improvement over nitrobenzene in the oxidation of fluorene (Figure 37). Since p-chloronitrobenzene was considerably better than nitrobenzene in this regard it must be that steric interactions of the ortho-chloro substituents with the nitro group buttressed by the meta-chloro groups is causing significant non-planarity of the nitro group with the benzene ring. Non-planarity of the nitro group caused by ortho-methyl substituents increases the reduction potential (i.e., decreases the ease of reduction to the radical anion) as reported by Geske and Ragle (132). Apparently in the case of pentachloronitrobenzene there is a case of fortuitous cancellation of effects, namely a tendency to decrease the reduction potential of nitrobenzene caused by five chloro substituents and a tendency to increase the reduction potential caused by non-planarity of the nitro group with the benzene ring.

Little or no effect on the rate of oxidation of fluorene was observed in the presence of 3 mole % 2,4,6-trinitrotoluene indicating that a negatively charged catalyst is not a good electron acceptor. The effect, if any, of 6-nitroquinoline on the oxidation was small; instead of serving as an electronegative substituent[1] the ring nitrogen in 6-nitroquinoline apparently donates electrons like an p-amino group when in conjugation with the nitro group. Iodoxybenzene had little or no effect on the rate of oxidation of fluorene.

If the reaction between carbanions and nitroaromatics leads to electron transfer in general, the test of the occurrence of one-electron oxidation by oxygen in base-catalyzed oxidation should be the accelerating effect of added nitrobenzene to an oxidizing medium, provided the carbanion transfers more easily to nitrobenzene than to oxygen. A variety of oxidations in the presence of nitrobenzene have not been studied although the effect of nitrobenzene on the base-catalyzed oxidation of picolines has been investigated. The picolines were found to oxidize relatively slowly in 80% dimethyl sulfoxide - 20% t-butyl alcohol and it was thought that the rate of this oxidation might be increased in the presence of an electron acceptor like nitrobenzene. Small increases in rate were observed for the oxidations of all three picolines as shown in Figures 38 and 39 in the presence of 3,2,9 and 18 mole % nitrobenzene. Why the electron transfer from picolinic anion to radical, if that is the mechanism in the oxidation of the picolines, should be difficult is baffling.

---

[1] The substituent constant for $3,4\text{-}(CH)_3N$ (6-quinolyl) is quoted as +0.23 (133).

Figure 38. Catalyzed rates of oxidation of *γ*-picoline in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol (4 mmoles *γ*-picoline, 7.7 mmoles potassium *t*-butoxide, 40 ml. solvent)

Curve 1	uncatalyzed rate
Curve 2	9 mole % nitrobenzene
Curve 3	18 mole % nitrobenzene

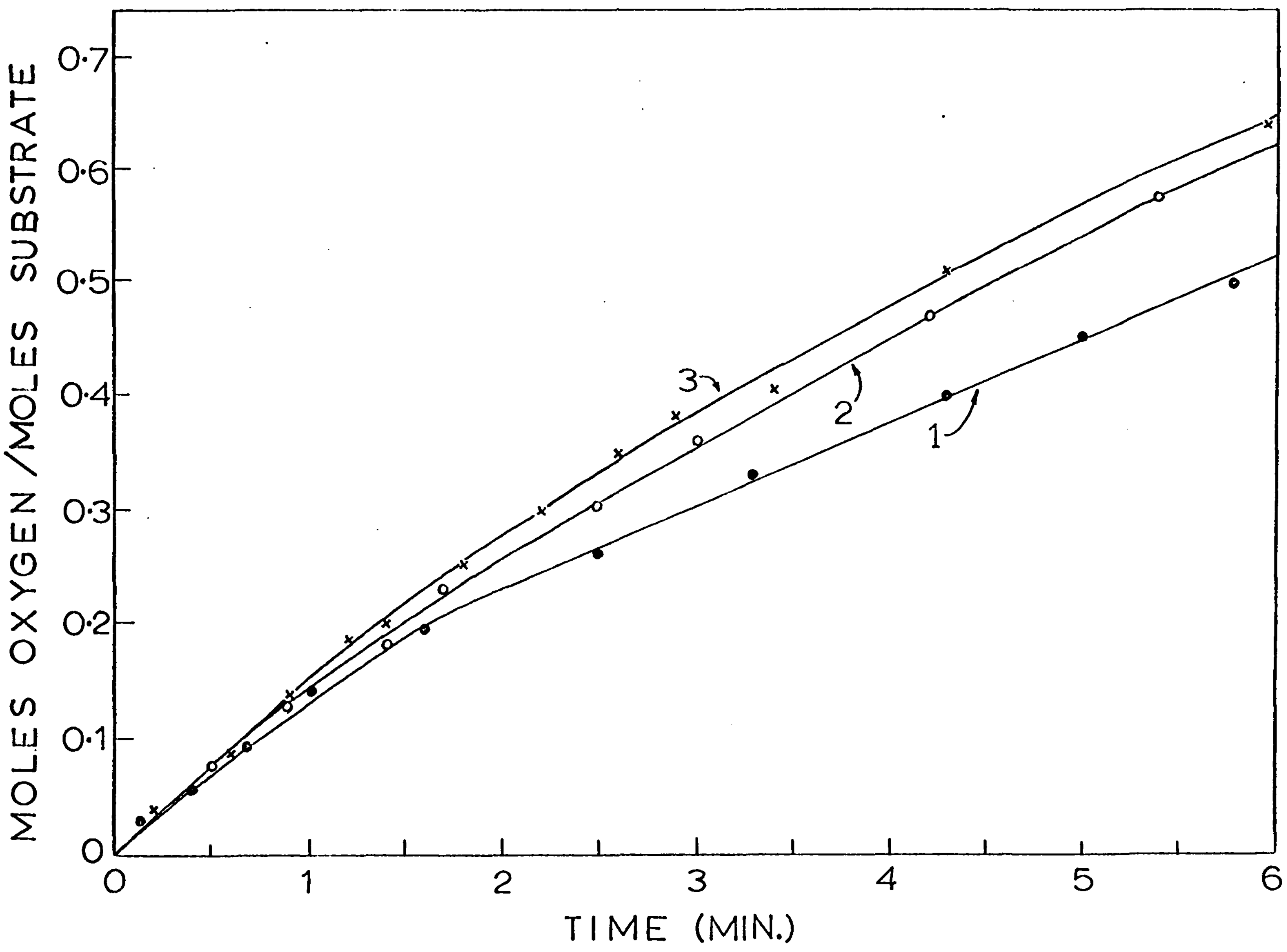
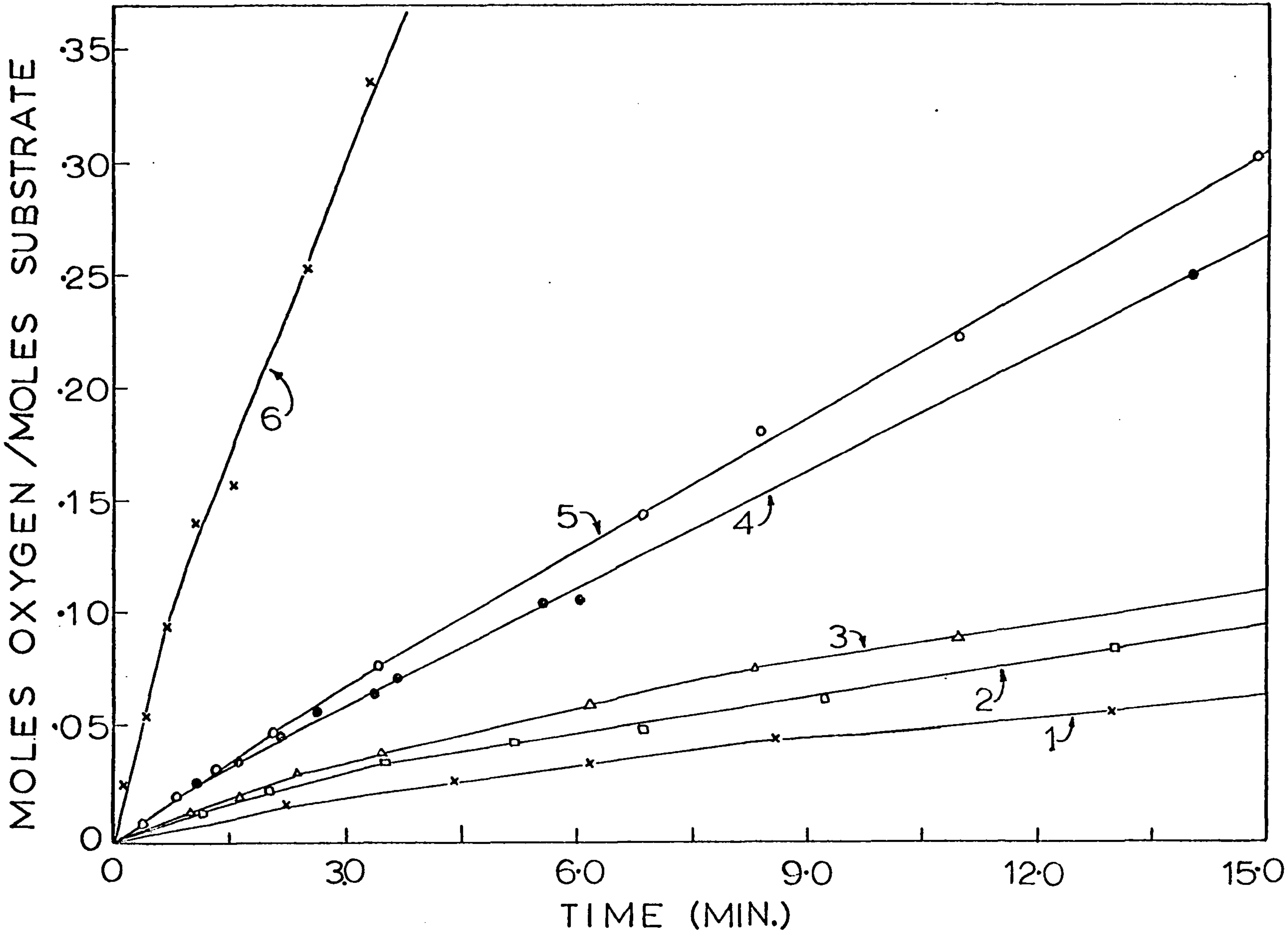

MOLES OXYGEN /MOLES SUBSTRATE
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
TIME (MIN.)
0
1
2
3
4
5
6
1
2
3

Figure 39. Catalyzed rates of oxidation of α- and β-picolines in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol (4 mmoles picoline, 20 mmoles potassium *t*-butoxide, 40 ml. solvent)

Curve 1	uncatalyzed rate of oxidation of β-picoline
Curve 2	oxidation of β-picoline in the presence of 3.2 mole % nitrobenzene
Curve 3	oxidation of β-picoline in the presence of 9 mole % nitrobenzene
Curve 4	uncatalyzed rate of oxidation of α-picoline
Curve 5	oxidation of α-picoline in the presence of 9 mole % nitrobenzene
Curve 6	uncatalyzed oxidation of γ-picoline for comparison (7.7 mmoles potassium *t*-butoxide)


MOLES OXYGEN /MOLES SUBSTRATE
TIME (MIN.)
0
·05
·10
·15
·20
·25
·30
·35
0
3.0
6·0
9·0
12·0
15·0
1
2
3
4
5
6

4. Rates as a function of base concentration

For carbanion autoxidation to occur relatively large concentrations of anion apparently are required and oxidations are usually performed under conditions of excess base. The discovery that nitroaromatics could increase the rate of oxidation of carbanions, specifically fluorene, and the observation made by Moye (3) that tris-(p-nitrophenyl)-methane oxidized faster under weakly basic conditions (e.g., in ethanol containing potassium hydroxide) than in the presence of strong base (e.g., in t-butyl alcohol containing potassium t-butoxide) prompted the suggestion that in the latter case as well as in others, oxidation might be faster in deficient base than in excess base due to more extensive electron transfer between the carbanion and the unionized nitroaromatic.

$$RH + B^{-} \longrightarrow R^{\ominus} + BH$$

$$R^{\ominus} + O_2 \longrightarrow R\cdot + O_2^{\overset{-}{\cdot}}$$

$$R^{\ominus} + RH \longrightarrow R\cdot + RH^{\overset{-}{\cdot}} \qquad \text{(A = RH, see equations 137, 138)}$$

$$R\cdot + O_2 \longrightarrow ROO\cdot$$

$$RH^{\overset{-}{\cdot}} + O_2 \longrightarrow RH + O_2^{\overset{-}{\cdot}}$$

This occurrence was in fact demonstrated by the observation that tris-(p-nitrophenyl)-methane oxidized faster in t-butyl alcohol containing equimolar concentrations of potassium t-butoxide than in the presence of 3-fold excess potassium t-butoxide (Figure 40). Oxidation also was faster in the presence of deficient base in 80% dimethyl sulfoxide - 20% t-butyl alcohol (Figure 41). If electron transfer from the carbanion to the unionized nitroaromatic was important the addition of nitrobenzene should

Figure 40. Autoxidation of tris-(p-nitrophenyl)-methane in t-butyl alcohol as a function of potassium t-butoxide (1.0 mmole tris-(p-nitrophenyl)-methane, 30 ml. solvent)

Curve 1	1.0 mmole potassium t-butoxide
Curve 2	3.0 mmoles potassium t-butoxide
Curve 3	3.0 mmoles potassium t-butoxide, 10 mmoles nitrobenzene

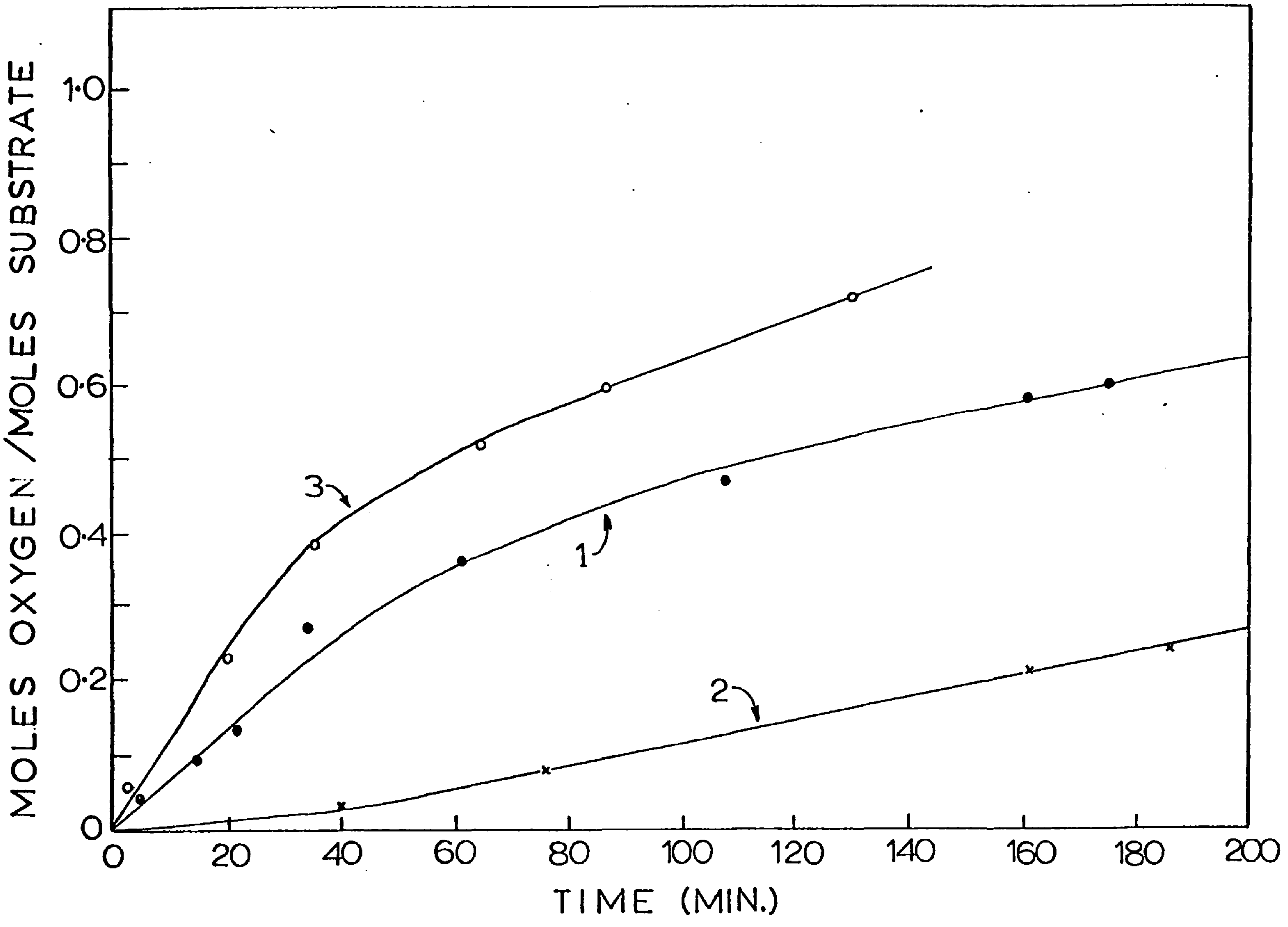
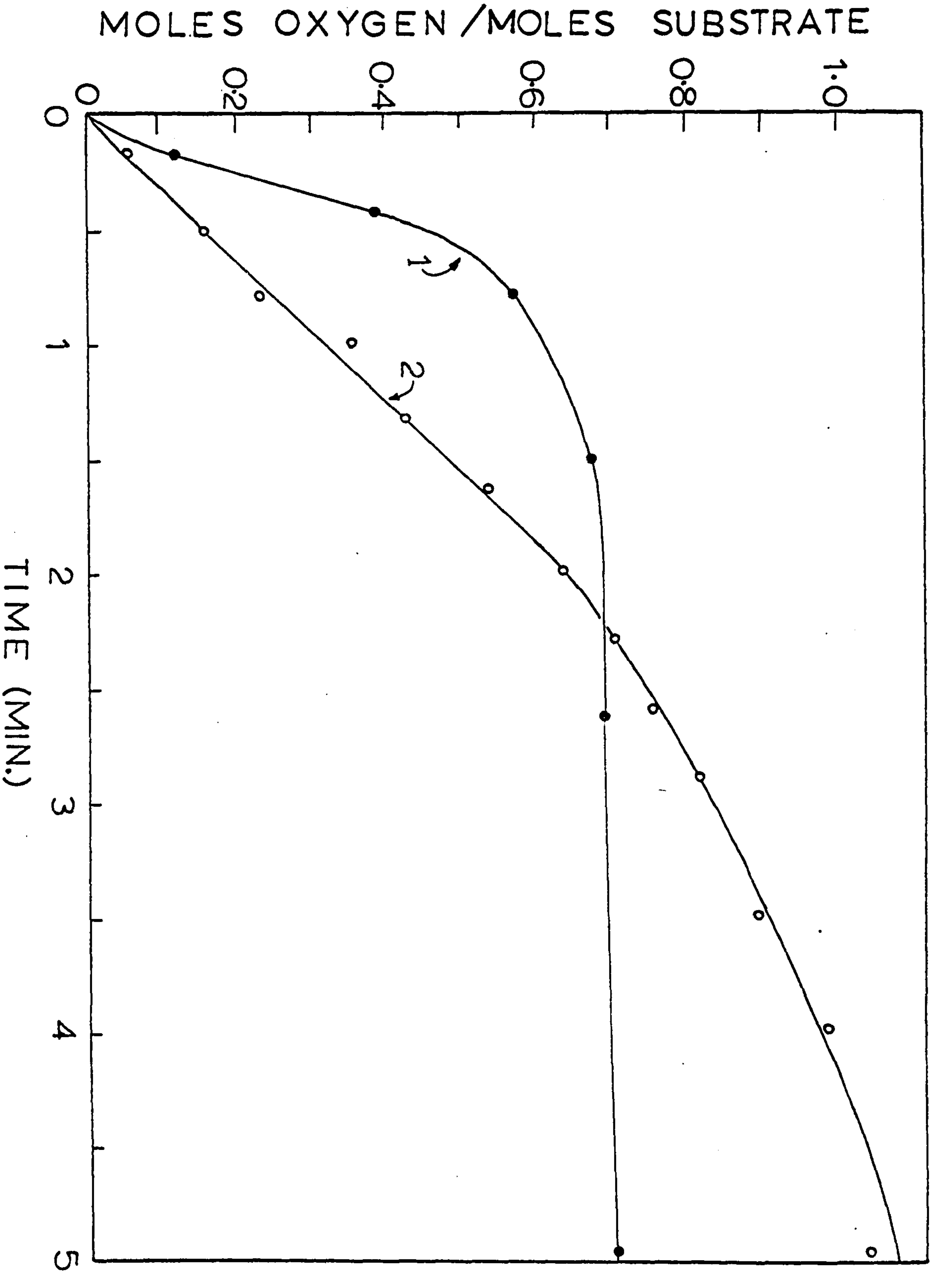

MOLES OXYGEN /MOLES SUBSTRATE
1·0
0·8
0·6
0·4
0·2
0
0
20
40
60
80
100
120
140
160
180
200
TIME (MIN.)
3
1
2

Figure 41. Autoxidation of tris-(p-nitrophenyl)-methane in 80% dimethyl sulfoxide - 20% t-butyl alcohol as a function of potassium t-butoxide (4 mmoles tris-(p-nitrophenyl)-methane, 40 ml. solvent)

Curve 1	2.0 mmoles potassium t-butoxide
Curve 2	7.8 mmoles potassium t-butoxide


MOLES OXYGEN/MOLES SUBSTRATE
0
0·2
0·4
0·6
0·8
1·0
TIME (MIN.)
0
1
2
3
4
5
1
2

serve the purpose of the electron acceptor in a solution of excess base. Figure 40 shows the effect of added nitrobenzene to a solution containing a 3-fold excess of potassium *t*-butoxide in *t*-butyl alcohol. This effect is in agreement with the electron transfer mechanism suggested for the catalyzed oxidation of fluorene.

$$(139)\quad (NO_2C_6H_4)_3C^{\ominus}\begin{array}{l} + \ (NO_2C_6H_4)_3CH \longrightarrow (NO_2C_6H_4)_3C\cdot + \ (NO_2C_6H_4)_3CH^{\overset{-}{\cdot}} \\ \\ + \ NO_2C_6H_5 \ \longrightarrow \ (NO_2C_6H_4)_3C\cdot + NO_2C_6H_5^{\overset{-}{\cdot}} \end{array}$$

An additional interesting possibility involves *tris*-(*p*-nitrophenyl)-methylhydroperoxide studied by Hawthorne and Hammond (102). In our solvents decomposition of the hydroperoxide by base must be rapid but in ethanol where this reaction is slow the nitrophenyl groups in the hydroperoxide could serve as the electron acceptors and not only increase the rate of oxidation over that in *t*-butyl alcohol (in excess base) but also decompose spontaneously to give the carbinol. A mechanism for this reaction has been suggested in the literature section.

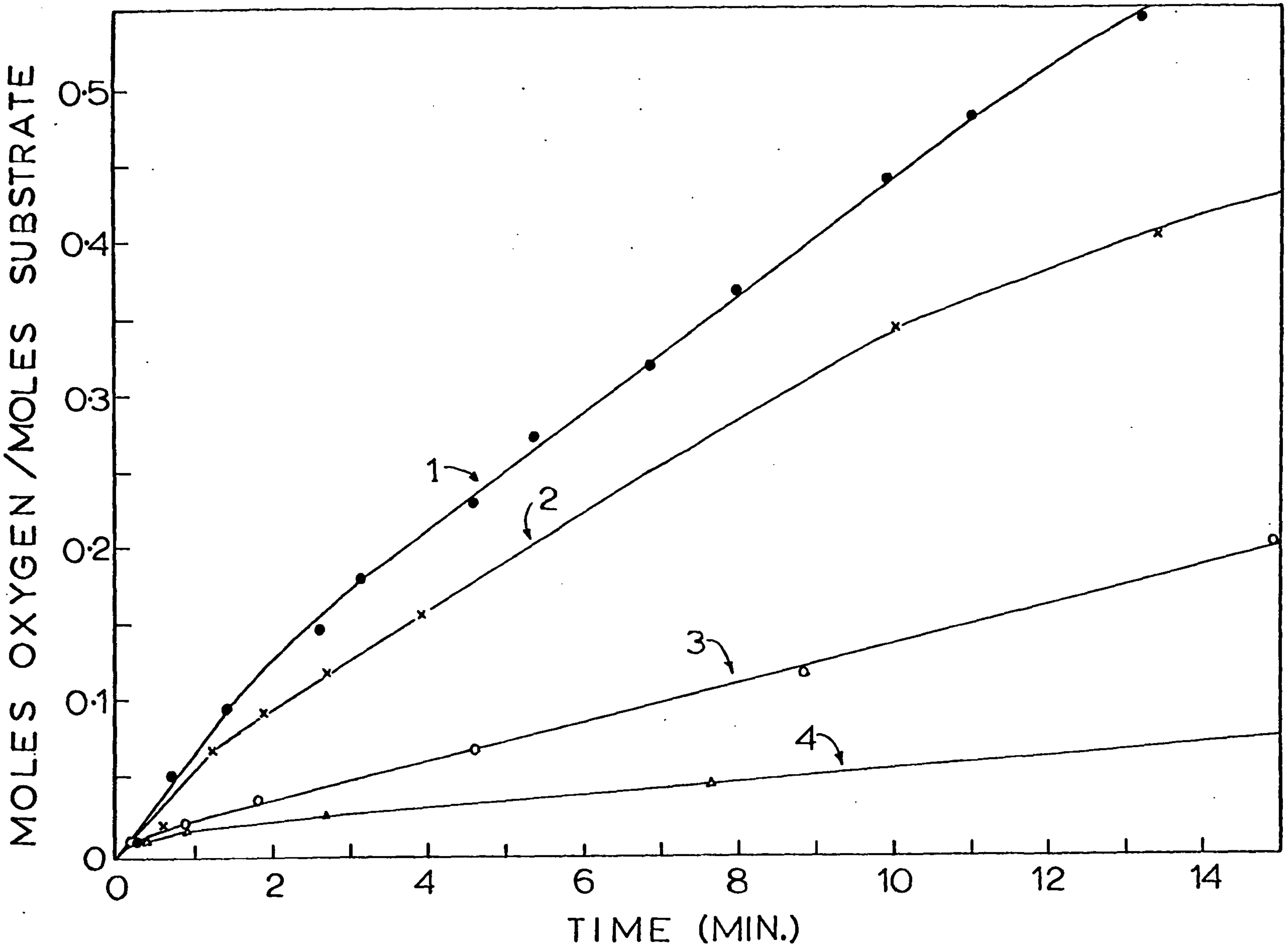
The rates oxidation of the *tris*-(*p*-nitrophenyl)-methide anion were faster in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol than in pure *t*-butyl alcohol. The increase in rate was found to be 137 times at a 1:1 ratio of base to substrate concentration obtained by extrapolating between the rates determined in dimethyl sulfoxide since experiments with exactly the same concentrations were not performed. A specific solvent effect has not been obtainable for the other carbanions studied since comparisons of rates always included the extent of ionization. In the case of *tris*-(*p*-nitrophenyl)-methane in equimolar base, ionization should be complete and the difference in rate should be due to a solvent effect on the electron transfer reaction with oxygen or with nitroaromatics.

The products of the oxidation in dimethyl sulfoxide were isolated in 85% yield (assuming the product to be carbinol). Of this, upon recrystallization from absolute ethanol 71% precipitated first and had a melting point of 194-6°; 7.5% of the remaining product was subsequently obtained with melting point 183-5°. The carbinol isolated by Hawthorne and Hammond (102) had a melting point of 190-1°, the hydroperoxide 186.5-7.5° and *p*,*p*'-dinitrobenzophenone 189-190°. From an oxidation performed in *t*-butyl alcohol solution in the presence of nitrobenzene, a yield of only 34% (assuming the product to be carbinol) with melting point of 178-180° was obtained after recrystallization from ethanol. The I.R. spectrum could be well reconciled with that expected and reported for the carbinol; the peaks at 2.90 and 7.10 μ for tertiary alcohol observed by Hammond were present as well as the usual nitro bands at 6.6 and 7.43 μ. The remainder of the oxidation product was not soluble in ethanol, appeared salt-like, charred over 300° and had an I.R. spectrum with three broad absorptions at 11.5, 6.5-7.5 and 2.95 μ and a sharp peak at 2.70 μ. Apparently a nitro salt had been isolated.

Polynitrobenzyl carbanions were found by Moye (3) to be more stable towards oxygen than the *p*-nitrobenzyl carbanion. Since these trials were performed in excess base the possibility of these compounds oxidizing faster in lower base concentration was apparent. Figure 42 shows the oxidation plots of 2,4-dinitrotoluene in *t*-butyl alcohol containing potassium *t*-butoxide. Since the substrate was found to be relatively

Figure 42. Autoxidation of 2,4-dinitrotoluene in *t*-butyl alcohol as a function of potassium *t*-butoxide

Curve 1	1.5 mmoles 2,4-dinitrotoluene, 13.5 mmoles potassium *t*-butoxide, 45 ml. solvent
Curve 2	3.0 mmoles 2,4-dinitrotoluene, 9.0 mmoles potassium *t*-butoxide, 30 ml. solvent (only partially dissolved)
Curve 3	0.9 mmole 2,4-dinitrotoluene, 1.0 mmole potassium *t*-butoxide, 40 ml. solvent
Curve 4	0.9 mmole 2,4-dinitrotoluene, 1.0 mmole potassium *t*-butoxide, 1.0 mmole nitrobenzene, 40 ml. solvent


MOLES OXYGEN /MOLES SUBSTRATE
0
0·1
0·2
0·3
0·4
0·5
0
2
4
6
8
10
12
14
TIME (MIN.)
1
2
3
4

insoluble in this system lower concentrations had to be used to obtain complete dissolution. An increase in rate of oxidation was found with an increase in base concentration in t-butyl alcohol from one to nine times that of 2,4-dinitrotoluene. The same observation was made in 80% dimethyl sulfoxide - 20% t-butyl alcohol (Figure 43) in the range of base concentration. The conclusion had to be made that we had not found the right conditions if they existed, to demonstrate autocatalysis for the oxidation of 2,4-dinitrotoluene in basic solution.

As in the case of the oxidation of the relatively stable carbanion, tris-(p-nitrophenyl)-methide anion, oxidation was faster in dimethyl sulfoxide than in t-butyl alcohol for 2,4-dinitrotoluene under similar conditions. The electron-transfer solvent effect was found to be 14 at equimolar concentrations of potassium t-butoxide to 2,4-dinitrotoluene. Figure 44 gives the plots of the initial oxidation rates as a function of the ratio of base to substrate for both solvent systems. The increasing slope of the plot for dimethyl sulfoxide may give indication of undetermined side reactions of base with the polynitroaromatic nucleus. However Figure 42 also includes the rate of oxidation of m-dinitrobenzene in dimethyl sulfoxide under base-deficient conditions. A comparison shows that the oxidation of 2,4-dinitrotoluene under the same conditions is not due to the reactions of base with the polynitro nucleus but an actual oxidation of the 2,4-dinitrobenzyl carbanion. The effect of nitrobenzene was puzzling in that apparently the rate of oxidation in t-butyl alcohol was slower in a solution containing nitrobenzene for equimolar amounts of base to 2,4-dinitrotoluene.

In the case of the oxidation of 2,4,6-trinitrotoluene in 80% dimethyl

Figure 43. Autoxidation of 2,4-dinitrotoluene in 80% dimethyl sulfoxide - 20% t-butyl alcohol as a function of potassium t-butoxide (4 mmoles 2,4-dinitrotoluene, 40 ml. solvent)

Curve 1	20 mmoles potassium t-butoxide
Curve 2	7.8 mmoles potassium t-butoxide
Curve 3	3.9 mmoles potassium t-butoxide
Curve 4	1.96 mmoles potassium t-butoxide
Curve 5	4 mmoles dinitrobenzene, 1.96 mmoles potassium t-butoxide (no 2,4-dinitrotoluene)

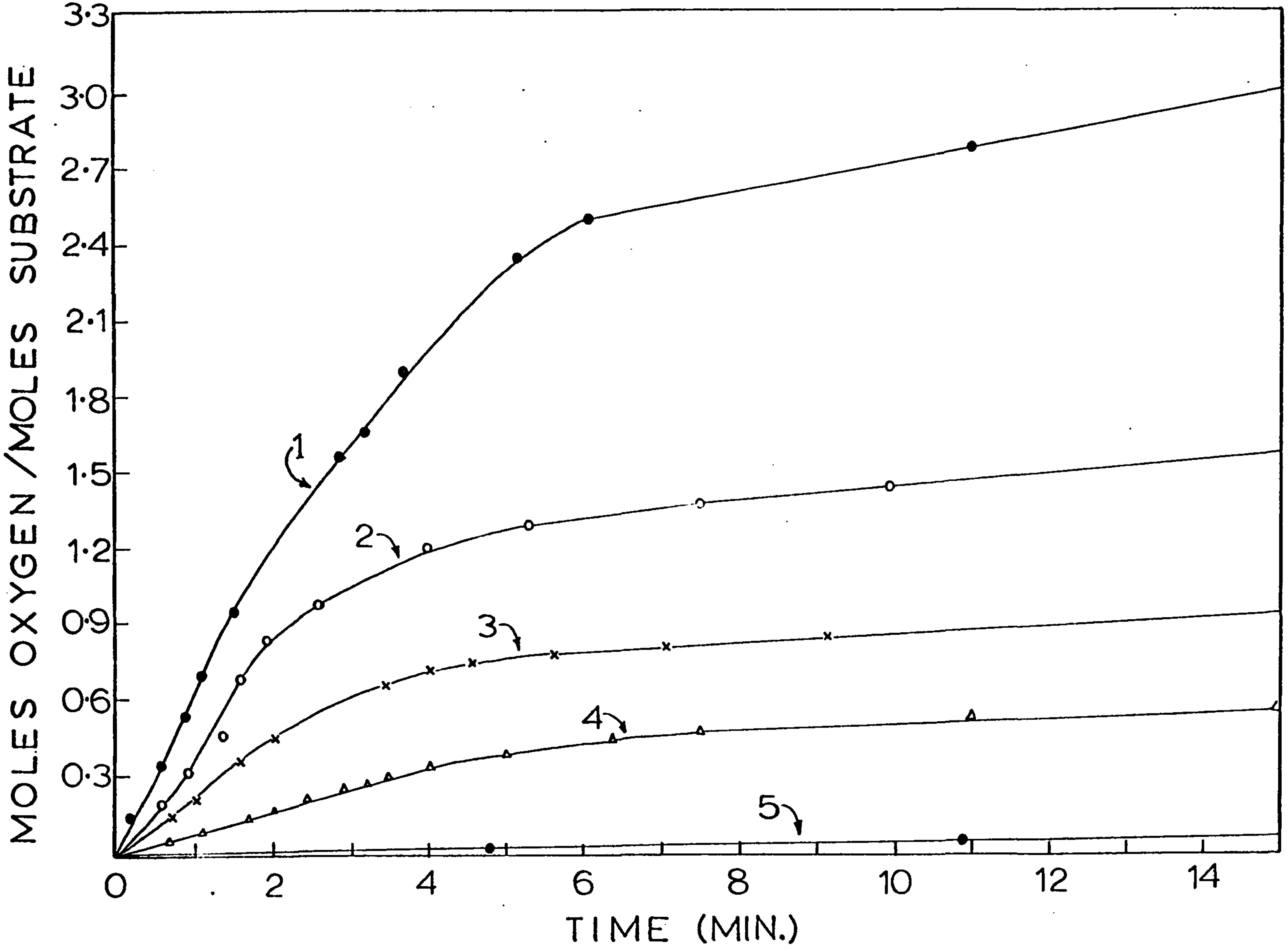
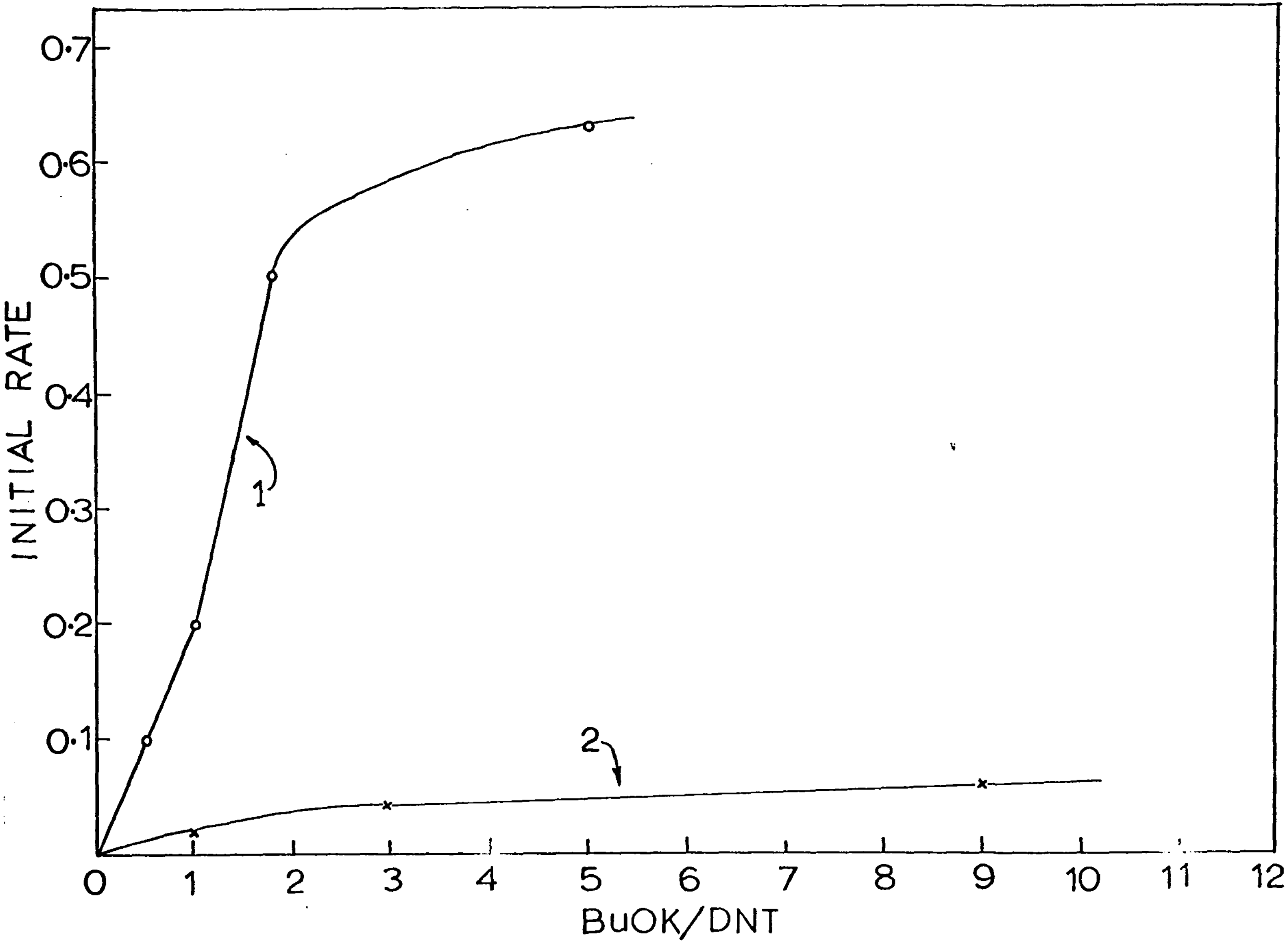

MOLES OXYGEN / MOLES SUBSTRATE
3·3
3·0
2·7
2·4
2·1
1·8
1·5
1·2
0·9
0·6
0·3
0
2
4
6
8
10
12
14
TIME (MIN.)
1
2
3
4
5

Figure 44. Plot of the initial rate of oxidation of 2,4-dinitrotoluene *vs.* potassium *t*-butoxide concentration

Curve 1 80% dimethyl sulfoxide - 20% *t*-butyl alcohol

Curve 2 *t*-butyl alcohol


INITIAL RATE
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
1
2
3
4
5
6
7
8
9
10
11
12
BuOK/DNT
1
2

sulfoxide - 20% *t*-butyl alcohol the rate of oxidation was found to be faster in deficient base than in equimolar or excess base concentrations (Figure 45), the fastest initial rate being that in a solution containing a ratio of 0.75 to 1 of potassium *t*-butoxide to 2,46-trinitrotoluene. Again a faster rate was observed in dimethyl sulfoxide than in *t*-butyl alcohol as indicated in Figure 45 which includes a run observed by Moye in *t*-butyl alcohol.

It was interesting that autocatalysis could be demonstrated for 2,4,6-trinitrotoluene but not for 2,4-dinitrotoluene. That electron transfer from carbanion to unionized nitro-aromatic in the case of 2,4-dinitrotoluene does occur was demonstrated by the observation that in the absence of oxygen in deficient base free radicals were spontaneously formed and could be detected by E.S.R. techniques (100) although the concentration of radical species decreased rapidly. Since autocatalysis was not found for dinitrotoluene but could be observed for trinitrotoluene a carbanion of somewhat greater stability towards oxygen than the 2,4-dinitrobenzyl anion seemed to be required for autocatalysis. *Tris*-(*p*-nitrophenyl)-methide anion apparently fulfills these requirements. Only a very narrow range in redox potential of the carbanion and nitroaromatic pair is permissible for autocatalysis to be observable.

Our search for compounds which oxidized faster in deficient than in excess base did not uncover more examples for which autocatalysis could be demonstrated. *Bis*-(*p*-nitrophenyl)-methane showed an increase in rate in the presence of increasing amounts of base in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol (Figure 46) as did the oxidation of ethyl *p*-nitrophenylacetate, *p*-nitrophenylacetic acid and *p*-nitrobenzyl alcohol

Figure 45. Autoxidation of 2,4,6-trinitrotoluene in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol as a function of potassium *t*-butoxide (4 mmoles 2,4,6-trinitrotoluene, 40 ml. solvent)

Curve 1	7.84 mmoles potassium *t*-butoxide
Curve 2	3.92 mmoles potassium *t*-butoxide
Curve 3	2.94 mmoles potassium *t*-butoxide
Curve 4	1.96 mmoles potassium *t*-butoxide
Curve 5	in *t*-butyl alcohol (Moye (3))

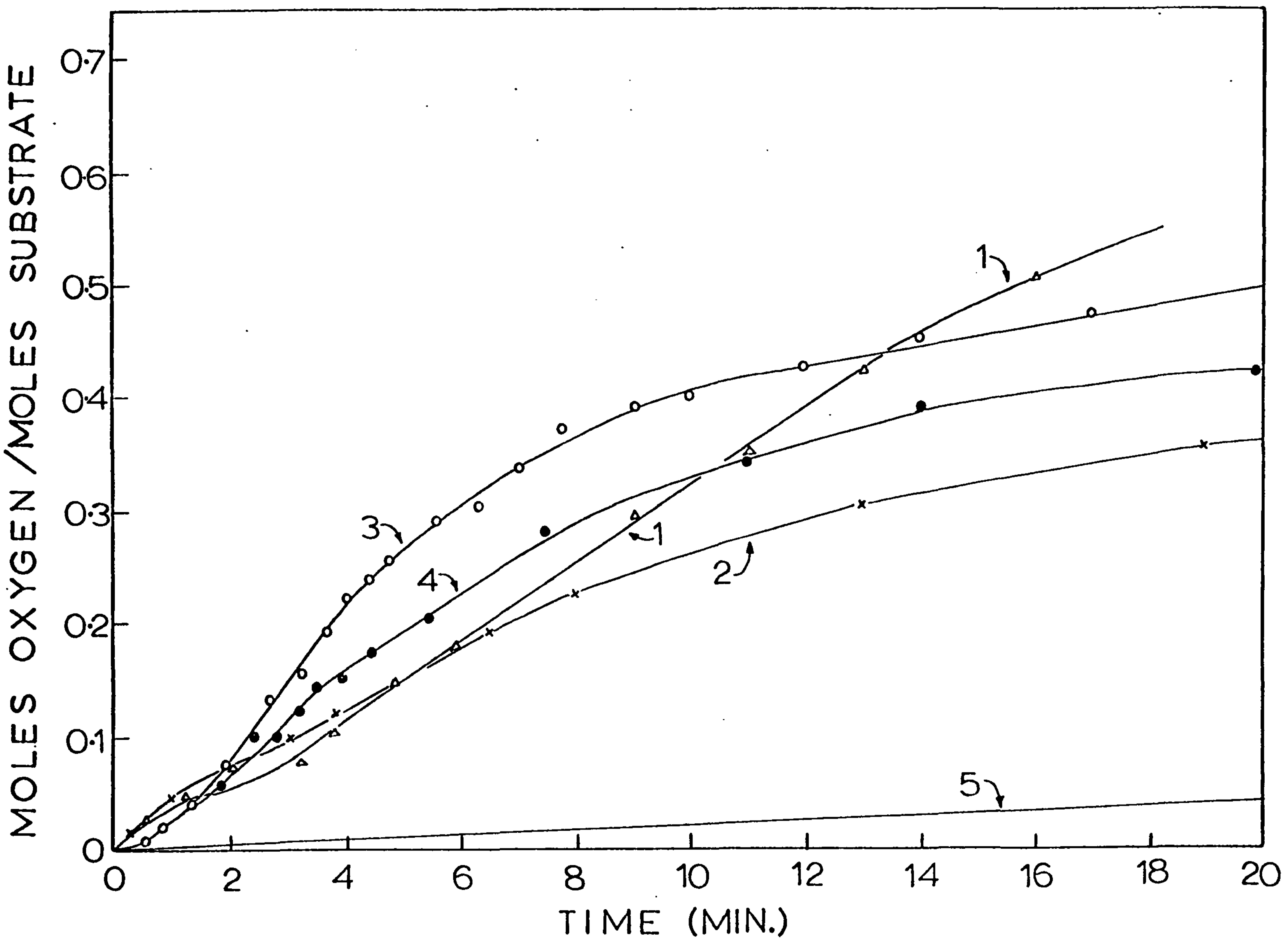
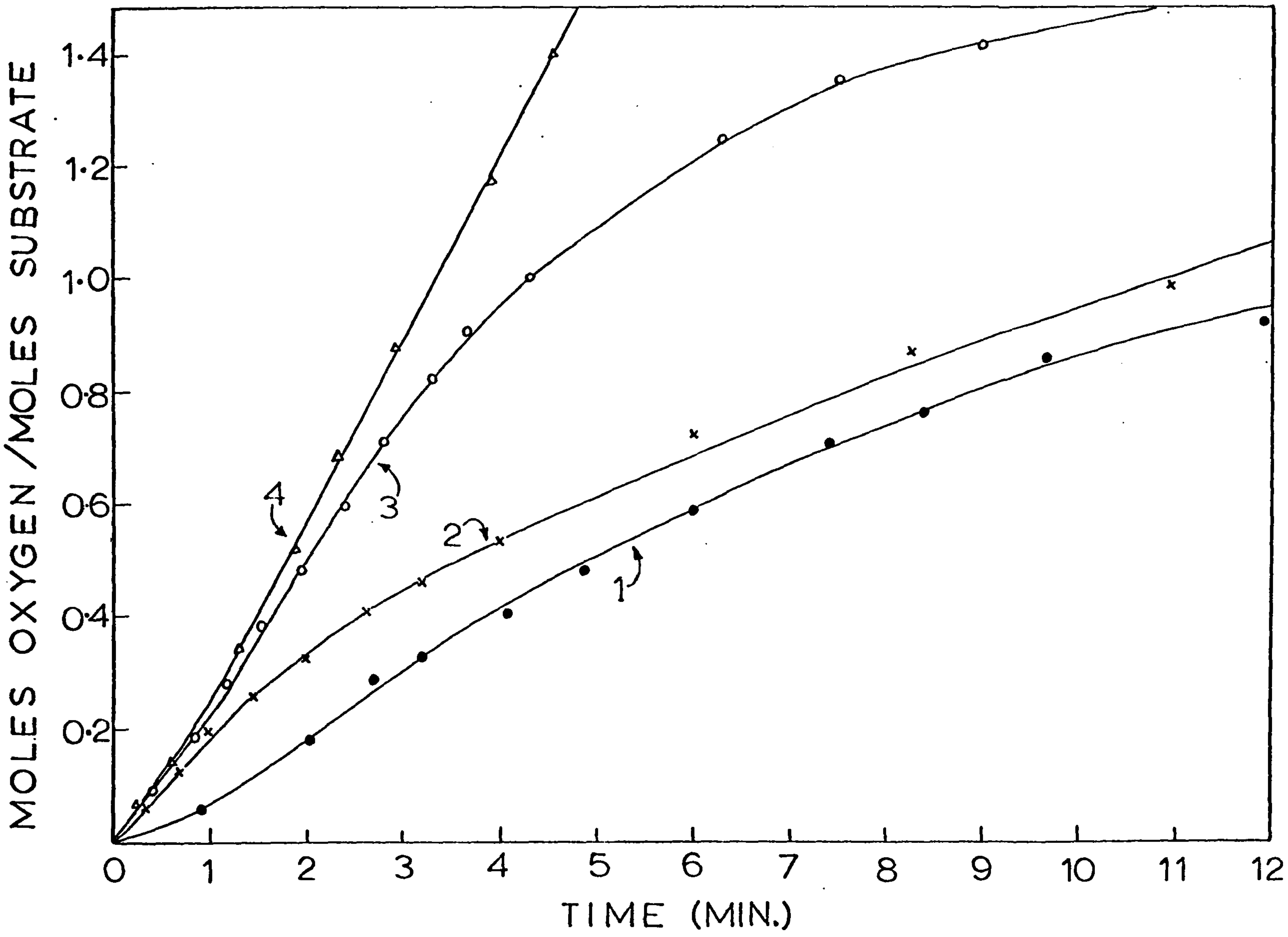

MOLES OXYGEN /MOLES SUBSTRATE
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
TIME (MIN.)
0
2
4
6
8
10
12
14
16
18
20
1
1
2
3
4
5

Figure 46. Autoxidation of bis-(p-nitrophenyl)-methane in 80% dimethyl sulfoxide - 20% t-butyl alcohol as a function of potassium t-butoxide (4 mmoles bis-(p-nitrophenyl)-methane in 40 ml. solvent)

Curve 1	3 mmoles potassium t-butoxide
Curve 2	4 mmoles potassium t-butoxide
Curve 3	8 mmoles potassium t-butoxide
Curve 4	20 mmoles potassium t-butoxide


MOLES OXYGEN /MOLES SUBSTRATE
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0
1
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6
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10
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12
TIME (MIN.)
1
2
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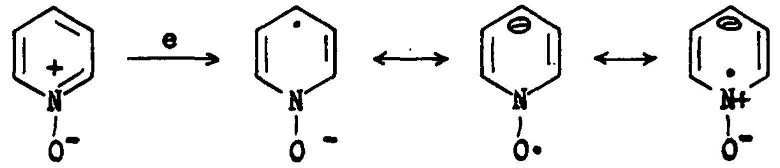
4

(Figures 47, 48, 49).

The effect of increasing the base to substrate ratio on the initial rates of oxidations of these examples is illustrated in Figure 50. The slopes of the lines give indications of the sensitivity of the rate of reaction to the change in base strength. The plot for tris-(p-nitrophenyl)-methane has the steepest slope of the compounds studied. In comparison the change in slope for 2,4,6-trinitrotoluene is small.

Because of the remarkably large catalytic effect exerted by 4-nitropyridine-N-oxide on the autoxidation of fluorene it was thought that possibly the pyridine-N-oxide grouping had the ability to function as an electron acceptor like a nitroaromatic group.

(140)



If the redox potential were favorable in the case of the picolinic-N-oxide anion, autocatalysis should be observable. In fact no evidence for this type of electron transfer could be obtained since the rate of oxidation of γ-picoline-N-oxide increased with increase in base concentration in 80% dimethyl sulfoxide - 20% t-butyl alcohol (Figure 51). Nor was oxidation observed in pure t-butyl alcohol whether potassium t-butoxide was 5, 1.3 or 0.8 times the concentration of γ-picoline-N-oxide. Oxidation could not be initiated by the addition of 3 equivalent per cent nitrobenzene to the first two of the above-mentioned solutions.

The rate of oxidation of α- and γ-picoline as a function of base was also investigated but again the rate increased with increase in base

Figure 47. Autoxidation of ethyl p-nitrophenylacetate in 80% dimethyl sulfoxide - 20% t-butyl alcohol as a function of potassium t-butoxide (4 mmoles ethyl p-nitrophenylacetate in 40 ml. solvent)

Curve 1	3 mmoles potassium t-butoxide
Curve 2	8 mmoles potassium t-butoxide

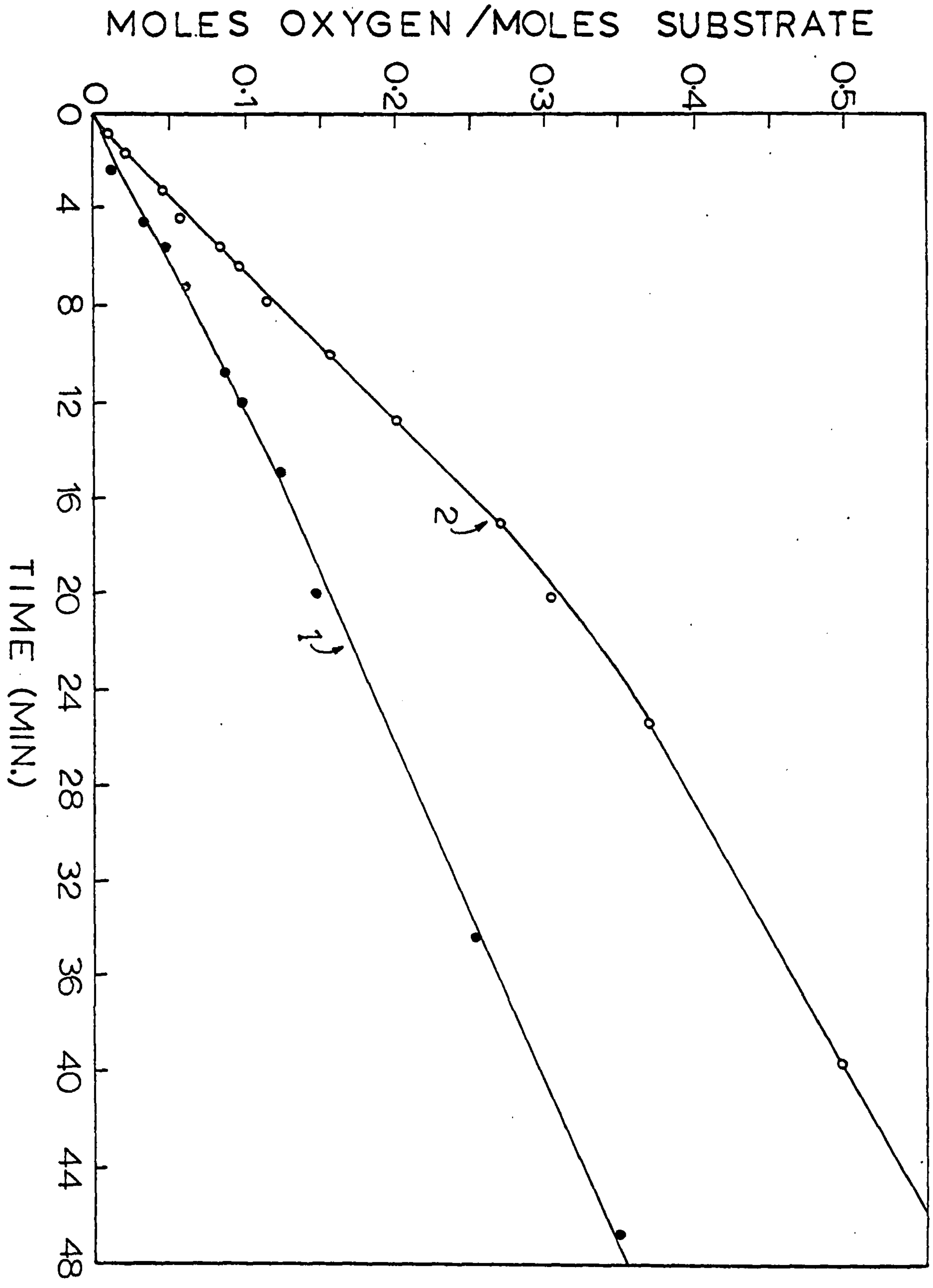

MOLES OXYGEN /MOLES SUBSTRATE
0
0·1
0·2
0·3
0·4
0·5
TIME (MIN.)
0
4
8
12
16
20
24
28
32
36
40
44
48
1
2

Figure 48. Autoxidation of potassium p-nitrophenylacetate in 80% dimethyl sulfoxide - 20% t-butyl alcohol as a function of potassium t-butoxide (4 mmoles p-nitrophenylacetic acid, 40 ml. solvent)

Curve 1	8 mmoles potassium t-butoxide
Curve 2	20 mmoles potassium t-butoxide

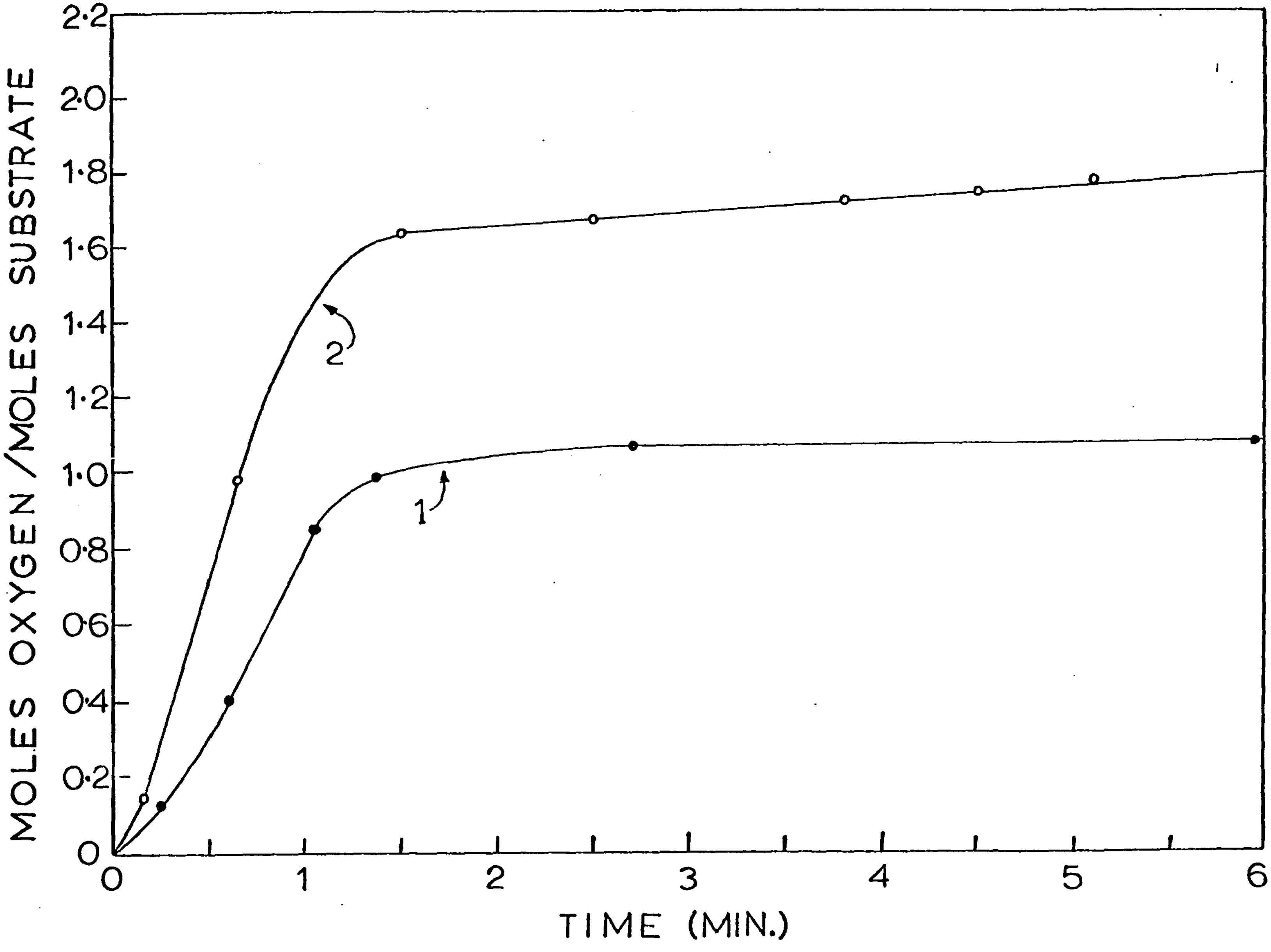

MOLES OXYGEN /MOLES SUBSTRATE
2·2
2·0
1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0
0
1
2
3
4
5
6
TIME (MIN.)
1
2

Figure 49. Autoxidation of potassium *p*-nitrobenzyl alcoholate in 20% dimethyl sulfoxide - 80% *t*-butyl alcohol as a function of potassium *t*-butoxide

Curve 1	4 mmoles potassium *t*-butoxide
Curve 2	8 mmoles potassium *t*-butoxide
Curve 3	12 mmoles potassium *t*-butoxide

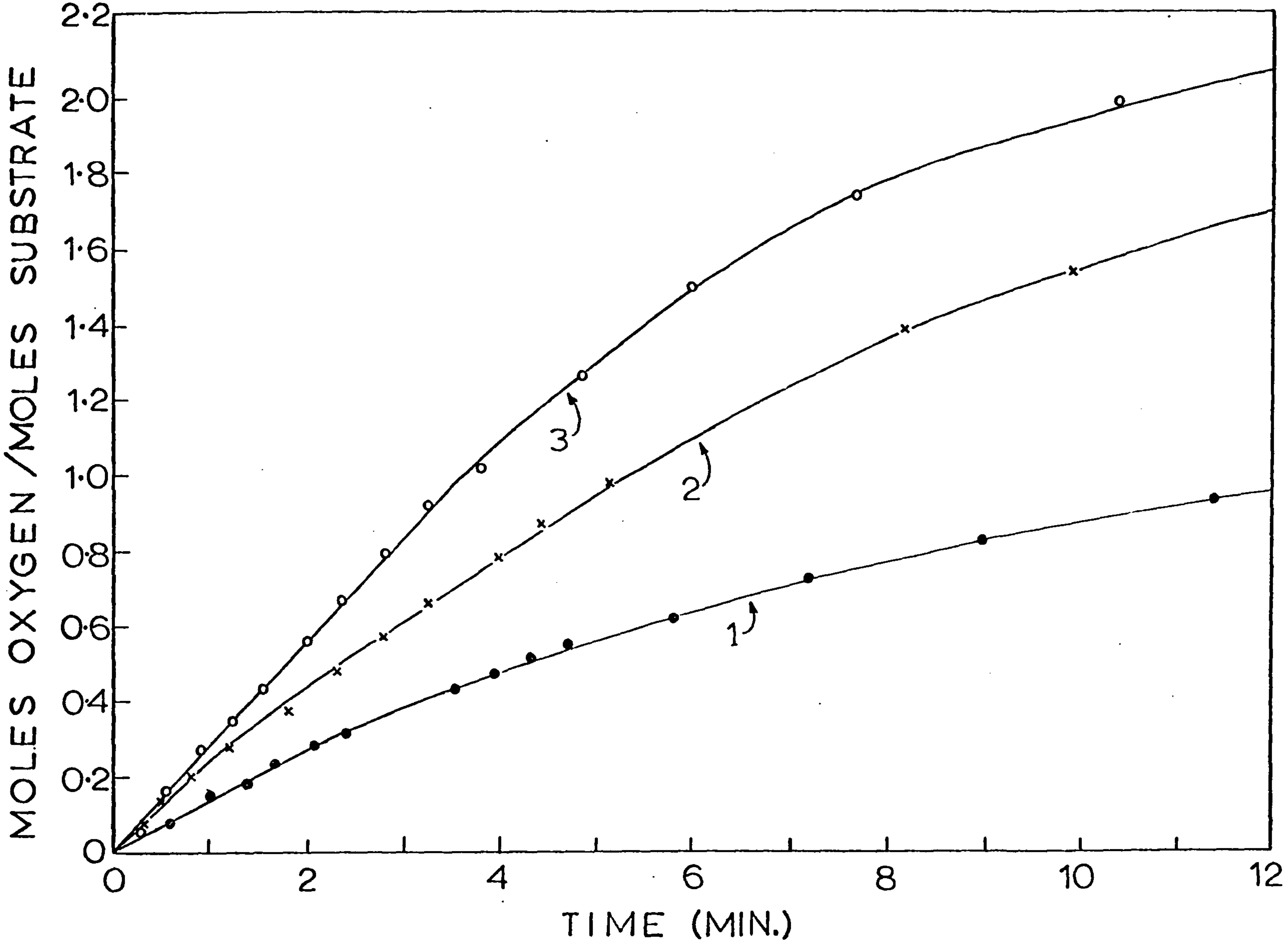

MOLES OXYGEN /MOLES SUBSTRATE
0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0
2·2
TIME (MIN.)
0
2
4
6
8
10
12
1
2
3

Figure 50. Plot of the initial rates of autoxidation of stable carbanions *vs*. potassium *t*-butoxide concentration

Curve 1	*tris*-(*p*-nitrophenyl)-methane
Curve 2	2,4-dinitrotoluene
Curve 3	*p*-nitrobenzyl alcohol
Curve 4	*bis*-(*p*-nitrophenyl)-methane
Curve 5	2,4,6-trinitrotoluene
Curve 6	ethyl *p*-nitrophenylacetate

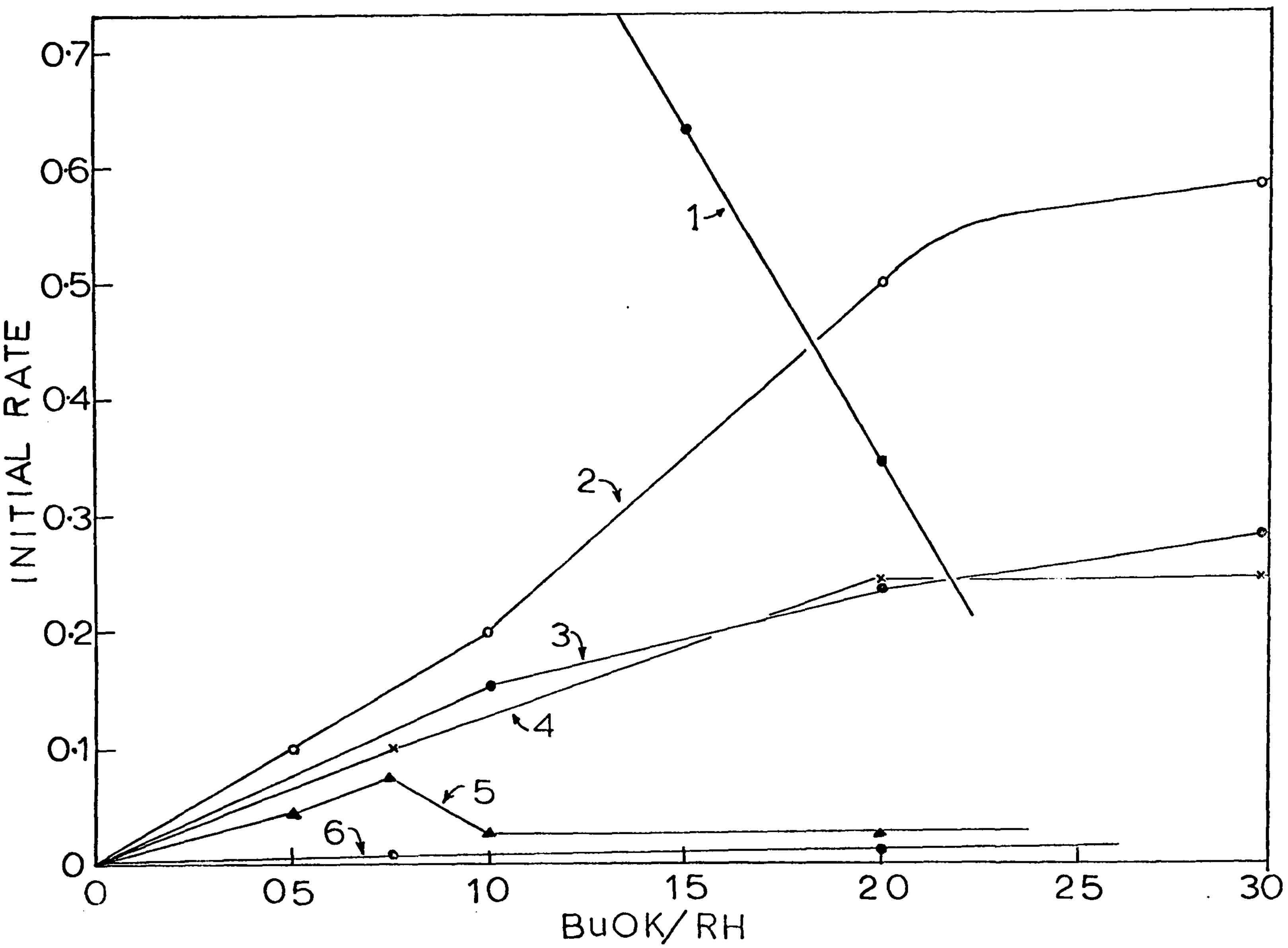
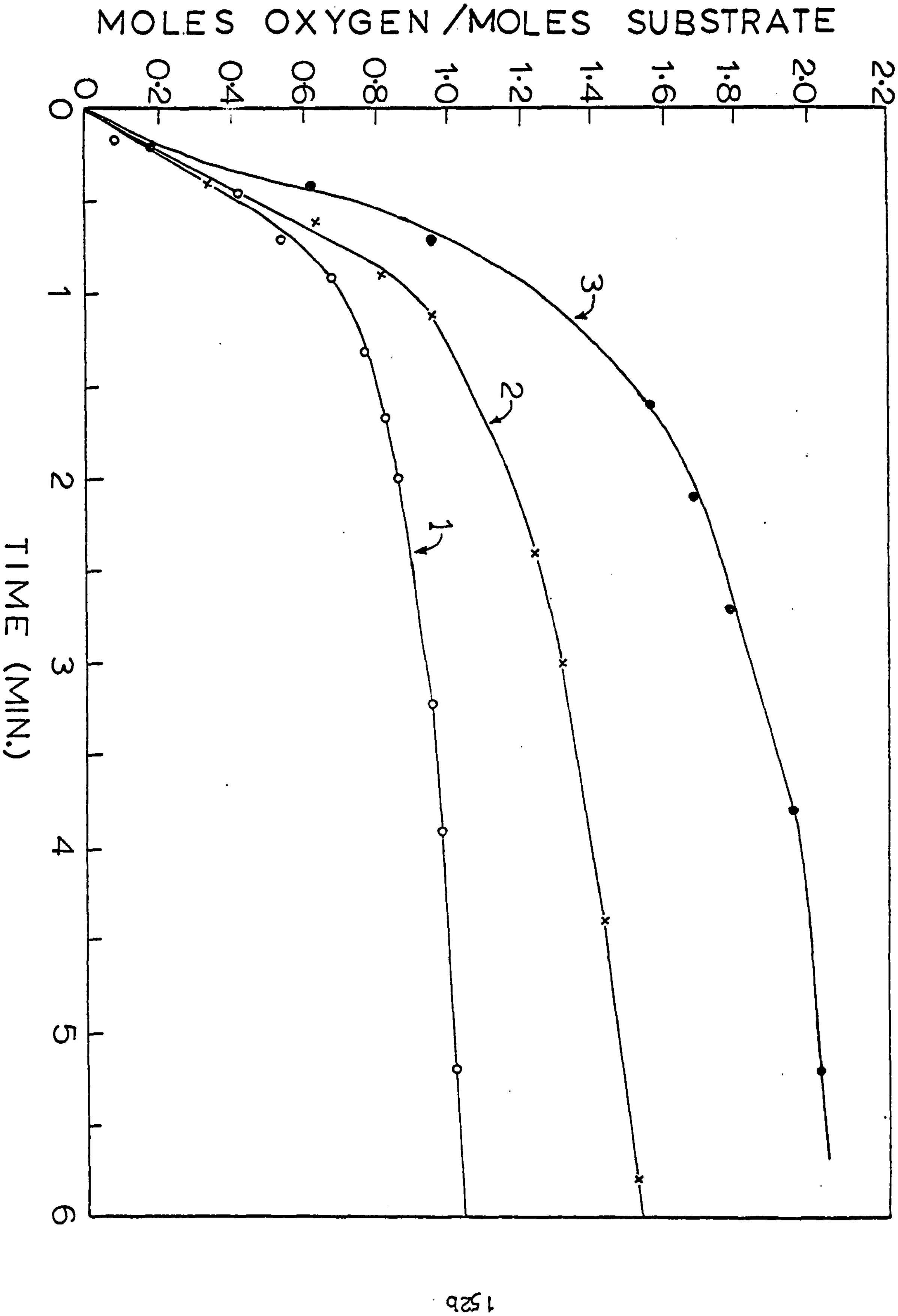

INITIAL RATE
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
BuOK/RH
0
0·5
1·0
1·5
2·0
2·5
3·0
1
2
3
4
5
6

Figure 51. Autoxidation of γ-picoline-N-oxide in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol as a function of potassium *t*-butoxide (4 mmoles γ-picoline-N-oxide in 40 ml. solvent)

Curve 1	3.1 mmoles potassium *t*-butoxide
Curve 2	6.0 mmoles potassium *t*-butoxide
Curve 3	20 mmoles potassium *t*-butoxide



MOLES OXYGEN /MOLES SUBSTRATE
0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0
2·2
TIME (MIN.)
0
1
2
3
4
5
6
1
2
3

concentration (Figures 52,53). A plot of the initial or fastest rate of oxidation for the picolines expressed as the logarithms of the rate [1] are presented in Figure 54 . The slopes are remarkably similar. After a base concentration of approximately 0.5 times excess the sensitivity of the rate to changes in base is approximately the same and constant for all three picolines.

D. Spontaneous Dimerization

Because free radicals were spontaneously formed in strongly basic solutions of p-nitrotoluene (100) a reinvestigation of the fate of the p-nitrobenzyl anion in the absence of oxygen by the isolation of products was necessary. Since a large amount of oxidation data had been collected by Moye (3) in t-butyl alcohol the reaction was first investigated in this solvent. In these experiments the p-nitrobenzyl anion was formed by adding potassium t-butoxide to p-nitrotoluene completely dissolved in t-butyl alcohol. After neutralization and exposure to air the products obtained were unreacted p-nitrotoluene and p,p'-dinitrobibenzyl in varying degrees of purity. Data on the color changes, yields of products and extent of catalysis by nitrobenzene as a function of time was obtained.

In a first series of experiments, qualitative information was obtained regarding color changes, precipitation, effect of the addition of water, acid or air on the color of the solution and purity of products (Table 10).

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[1] Since the rates vary by several orders of magnitude between the compounds the logarithms of the rates were used to allow mutual presentation (see Table 9).

Figure 52. Autoxidation of $\underline{\alpha}$-picoline in 80% dimethyl sulfoxide - 20% _t_-butyl alcohol as a function of potassium _t_-butoxide (4 mmoles $\underline{\alpha}$-picoline, 40 ml. solvent)

Curve 1	10.2 mmoles potassium _t_-butoxide
Curve 2	20 mmoles potassium _t_-butoxide

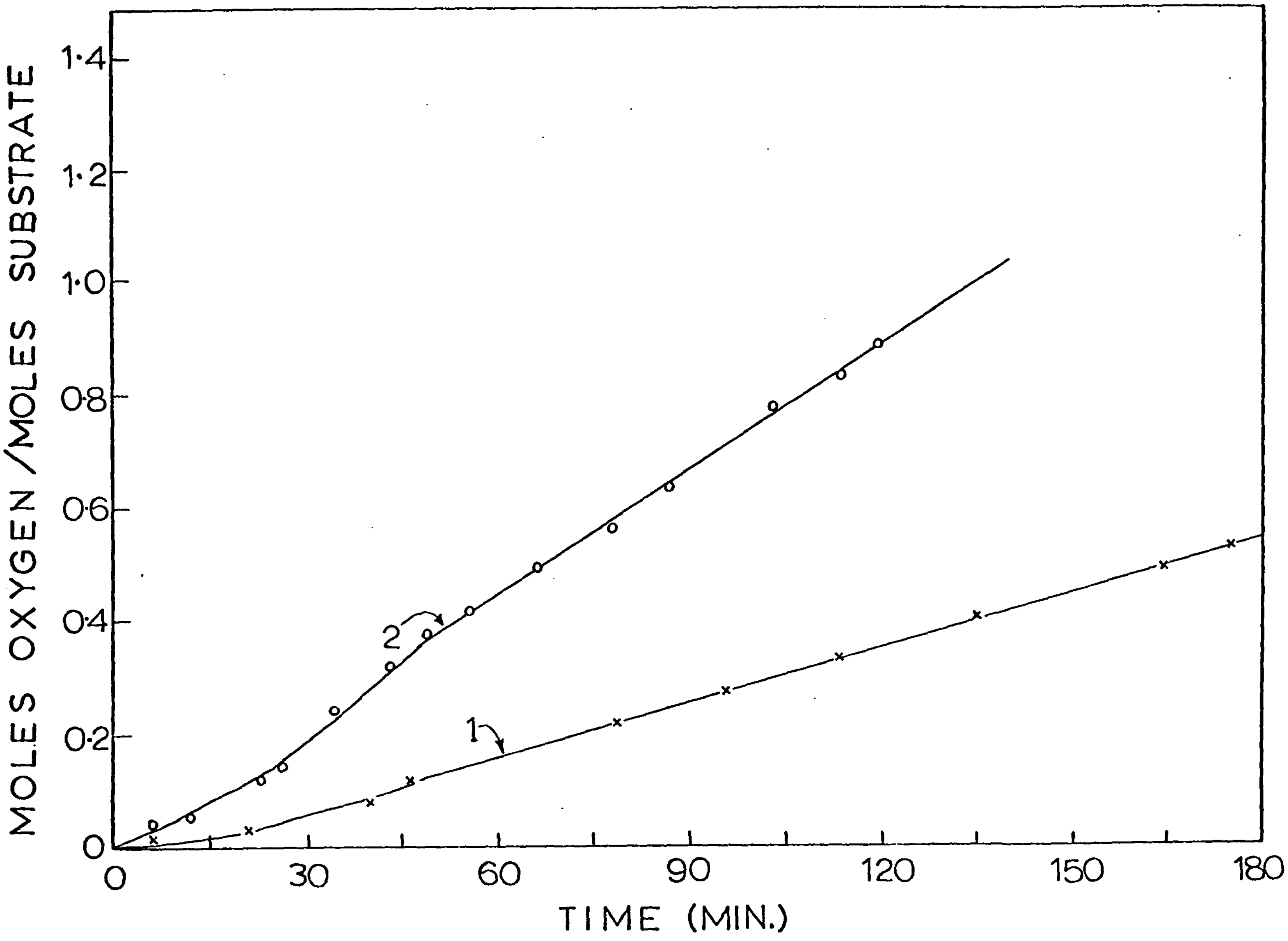
MOLES OXYGEN /MOLES SUBSTRATE
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0
2
1
0
30
60
90
120
150
180
TIME (MIN.)

Figure 53. Autoxidation of _γ_-picolines in 80% dimethyl sulfoxide - 20% _t_-butyl alcohol as a function of potassium _t_-butoxide (4 mmoles _γ_-picoline in 40 ml. solvent)

Curve 1	3.6 mmoles potassium _t_-butoxide
Curve 2	5.6 mmoles potassium _t_-butoxide
Curve 3	10.4 mmoles potassium _t_-butoxide
Curve 4	20 mmoles potassium _t_-butoxide

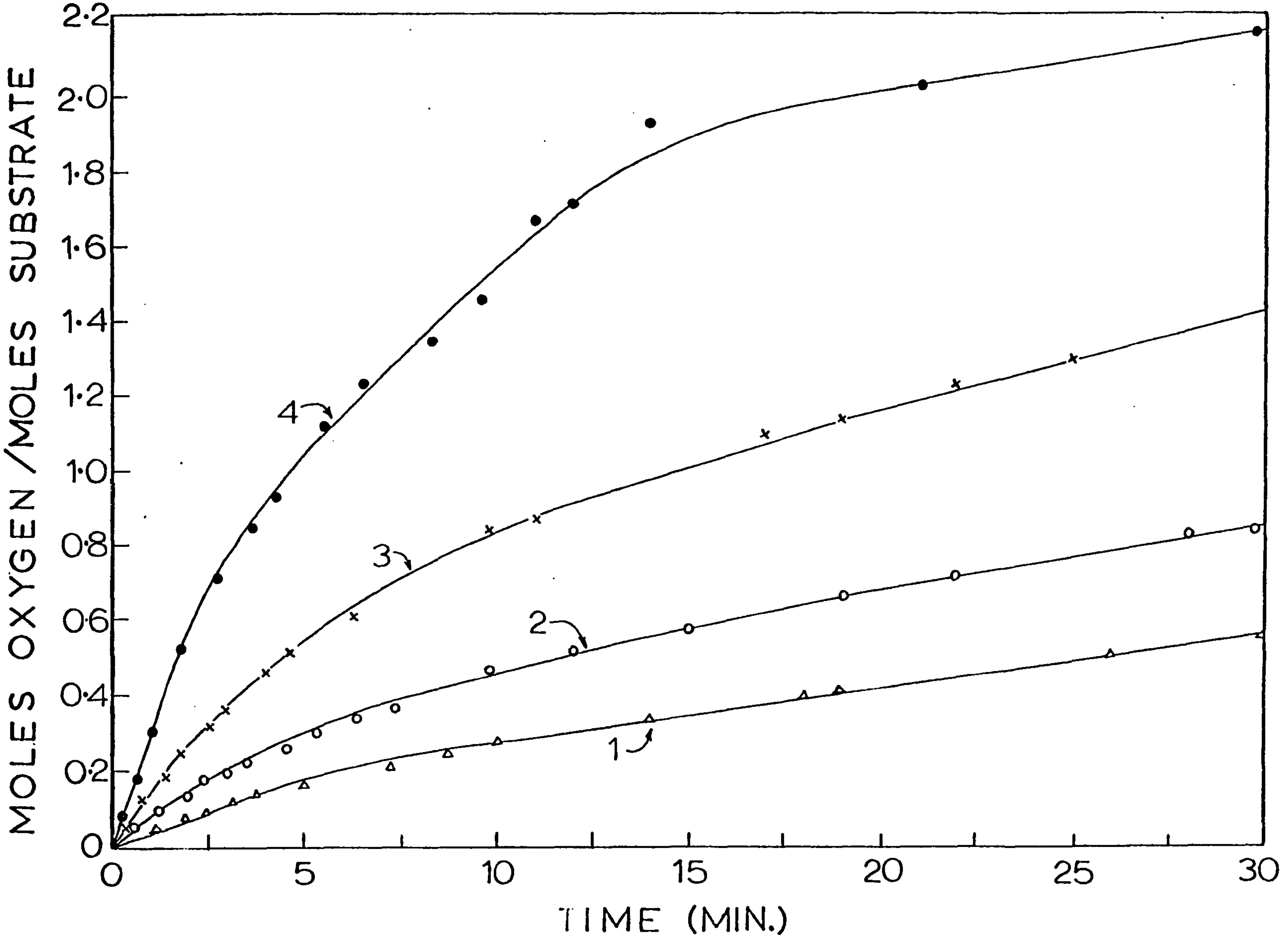
MOLES OXYGEN /MOLES SUBSTRATE
0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0
2·2
0
5
10
15
20
25
30
TIME (MIN.)
4
3
2
1

Table 9. Initial rates of oxidation of picolines as a function of base concentration

Run	Picoline	B^-/RH^a	Initial (or fastest) rate	Log_{10} rate
92_2-B	$\underline{\gamma}$-N-oxide	5	2.15	0.333
92_1-B	$\underline{\gamma}$-N-oxide	1.5	1.5	.178
93_1-B	$\underline{\gamma}$-N-oxide	0.78	1.25	.099
97_1-B	$\underline{\gamma}$-	5	0.275	- .56
97_2-B	$\underline{\gamma}$-	2.6	.110	- .956
96_1-B	$\underline{\gamma}$-	1.4	.061	-1.214
96_2-B	$\underline{\gamma}$-	0.9	.034	-1.467
95-B	$\underline{\alpha}$-	5	.0085	-2.070
94-B	$\underline{\alpha}$-	2.6	.0037	-2.43

$^a B^-/RH$ = potassium t-butoxide/picoline concentrations

The reaction was started by the addition of potassium t-butoxide to the p-nitrotoluene solution while the solution was stirred with a magnetic stirring bar. Immediately the solution turned very pale yellow-green; after 0.5 min. an orange color developed which by 1.0 min. had deepened into a clear cherry red; at 1.4 min. the solution became turbid and shortly after, precipitation of a dark red precipitate began which continued for 5 min. as evidenced by the deepening of the color and increasing turbidity of the solution. After 0.5-1.0 hr. stirring, water was added to the solution to neutralize any carbanion present. The flask was then opened to air and oxygen bubbled through the solution.

Figure 54. Plot of the initial rates of autoxidation of picolines *vs*. potassium *t*-butoxide concentration

Curve 1	*γ*-picoline-N-oxide
Curve 2	*γ*-picoline
Curve 3	*α*-picoline

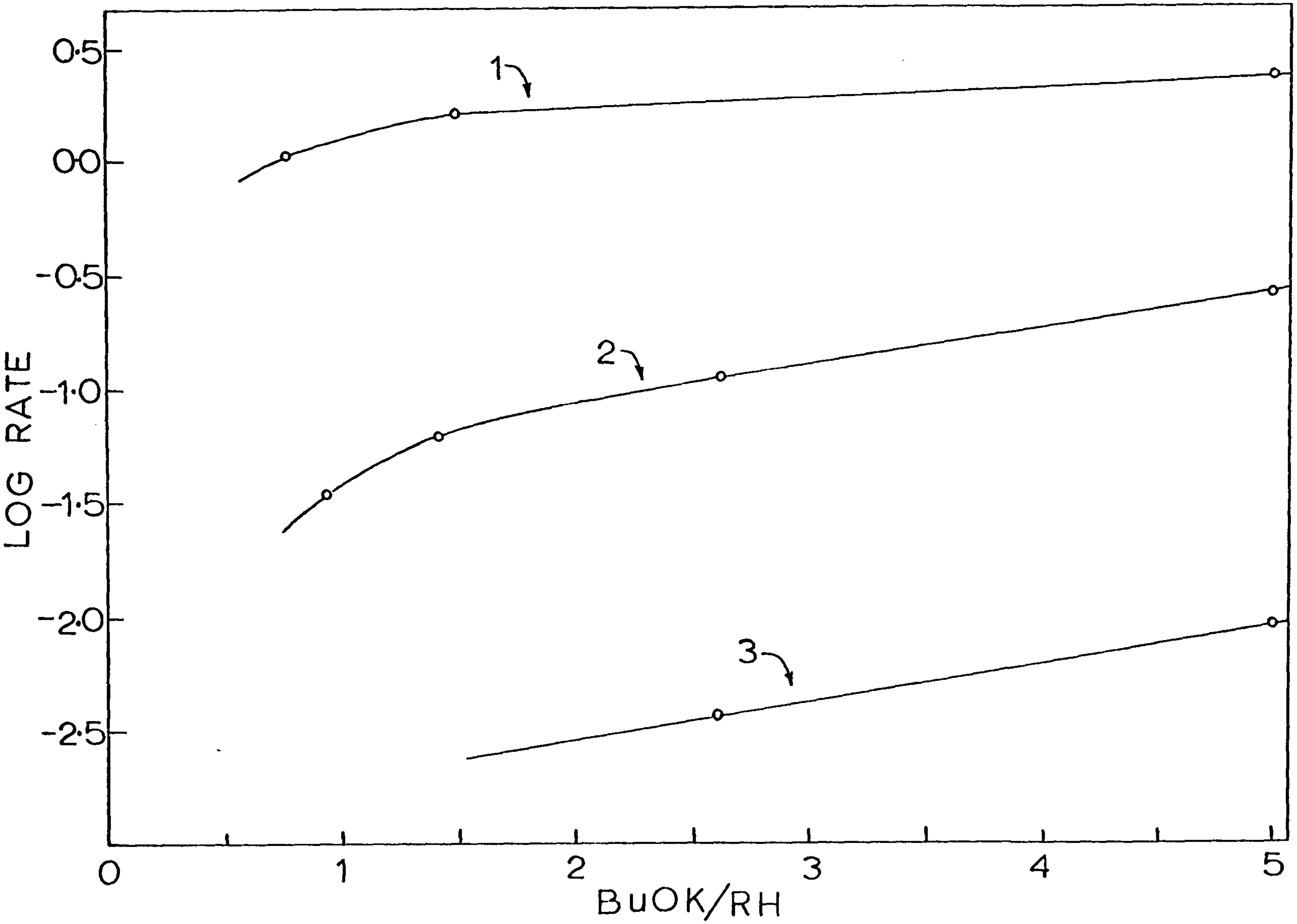
0·5
0·0
-0·5
-1·0
-1·5
-2·0
-2·5
LOG RATE
0
1
2
3
4
5
BuOK/RH
1
2
3

Table 10. Spontaneous dimerization of p-nitrotoluene in 50 ml. t-butyl alcohol

Run	PNT[a] (g.)	t-BuOK[b] / PNT	Time[c] (min.)	Quencher[d]	Dimer[e] (g.)	PNT[f] (g.)
263-A[g]	0.42	3	60	1 ml. H_2O	0.23 (155-180°)	
265-A	.66	1.8	60	2 ml. H_2O	.40 (170°)	0.10 (49-52°)
266-A	.66	1.8	30	3 ml. H_2O	.31 (160-170°)	
264-A	.66	2	60	2 ml. H_2SO_4	.38 (170-172°)	
267-A	.66	1.8	30	10 ml. HAc	.31 (165-175°)	.14 (49-51°)

[a] PNT = p-nitrotoluene

[b] t-BuOK = potassium t-butoxide

[c] Reaction time from time of mixing to quenching

[d] H_2O = water; H_2SO_4 = 1:1 sulfuric acid-water mixture; HAc = acetic acid

[e] p,p'-Dinitrobibenzyl, melting point 179-181°; yields are not optimal

[f] Melting point, 50.5-51°

[g] Total volume 25 ml.

When a small amount of wet t-butyl alcohol was added to the reaction mixture (Run 263-A, Table 10) the red precipitate merely settled to the bottom of the flask with no marked change in color visible. Upon addition of a larger amount of water (Run 266-A) the precipitate turned slightly brown, the color darkening until finally after 1.5 hr. stirring in the absence of air the solution was chocolate-brown in color. The addition of sulfuric or acetic acid (Runs 264-A and 267-A) to the reaction mixture dispelled the red color immediately leaving a yellow precipitate and a clear solution.

In all cases when the reaction was quenched with water the reddish-brown precipitate and solution turned yellow on exposure to oxygen; where acid was added no color change appeared on contact with oxygen. In one instance (Run 266-A) after opening the flask aerated water was squirted into the solution and a bright pink color appeared which could be dispelled by evacuation and introduction of nitrogen. The products were isolated by pouring the solution into a large excess of water and filtering. Unreacted p-nitrotoluene could be recovered by extraction with benzene. The precipitate obtained by filtration contained the dimer p,p'-dinitrobibenzyl but in an impure form as indicated by a large and indefinite melting point range. Since boiling benzene dissolved the dimer but left behind a brown unidentified material it was used as a recrystallizing solvent.

The experiments just described suggested an investigation into the yield of dimer produced as a function of time. Essentially the same method was used (see Experimental) except that larger amounts of reactants were used to facilitate recovery of material. The results of these experiments are given in Table 11.

The same color changes were observed as described for the earlier experiments. However when the water was added in quantity approximately equal to the volume of t-butyl alcohol, the solution was homogeneous although not clear and transparent. This solution was pale orange-yellow in color but turned red-brown on exposure to air. While bubbling air through the solution a yellow precipitate formed which was identified as p,p'-dinitrobibenzyl. The purity and identity of the isolated products

Table 11. Spontaneous dimerization of p-nitrotoluene as a function of reaction time; 0.10 M p-nitrotoluene, 0.21 M potassium t-butoxide, and 175 ml. t-butyl alcohol

Run	Time[a] (min.)	Dimer[b] yield (%)	PNT[c] yield (%)	Unidentified yield[d] (%)	Total recovery (%)
273-A	5	21.0 (176-180°)	69.4 (49-51°)	0	90.4
272-A	10	36.6 (170-5°)	56.1 (48-50°)	0.4	93.1
271-A	20	40.7 (170-5°)	50.9 (45-6°)	1.5	93.1
269-A[e]	10	9.6 (173-5°)	78.0 (48-50°)		

[a] Reaction time from time of mixing to quenching by water

[b] p,p'-Dinitrobibenzyl, melting point 178-181°; melting points are that of crude material; after recrystallization from benzene M.P. 179-181° (Run 272-A)

[c] PNT = p-nitrotoluene, melting point 50.5-51°

[d] Brown unidentified material insoluble in benzene found in precipitate filtered from water

[e] p-Nitrotoluene added as a solid to basic solution

were checked by melting points and I.R. The dimer isolated from longer reaction times was darker in color and had a larger melting point range. It contained small amounts of a brown unidentified material which could be removed by recrystallization from hot benzene.

The extent of catalysis by nitrobenzene on the spontaneous dimerization of p-nitrotoluene was investigated by the same method except that the reaction was performed in the presence of nitrobenzene. The results of these experiments are given in Table 12. The dimer p,p'-dinitrobibenzyl obtained by evaporation of the benzene extracts gave I.R. spectra which agreed very well with a spectrum of authentic dimer and had

Table 12. Spontaneous dimerization of p-nitrotoluene in the presence of nitrobenzene; 0.1 M p-nitrotoluene, 500 ml. t-butyl alcohol

Rx.[a]	B^-[b] / PNT	$C_6H_5NO_2$ (moles)	Time[c] (min.)	Dimer[d] (%)	Unidentified product (%)	Reaction[e] extent (%)
3	1	0.06	15	25 (179-180.5°)[f]	2.2 (197-205°)	27.2
4	3	.06	15	67 (171-3°)	9.3 (210-5°)	76.3
12	3	.06	30	66.3 (177-9°)	18.8	85.1
11[g]	3	.50	15	29 (179.5-181°)		83.7
5[h]	1.2	.06	15	24.4 (158-160°)	22.6	
20[i]	1.2	.50	15	27.4 (141-164°)	33.6 (260-280°)	61.0
22[j]	3	.06	15	48.5 (182-5°)	15.8 (>250° d.)	64.3
21[k]	3	.06	15	67.5 (182-5.5°)	8.2 (190-291°)	75.7
23[k]	3	.06	60	72.6 (173-7°)	5.6 (185-350°)	88.2
28	3	.50	60	22.8 (192-239°)	64.2 (279-283°)	87

[a] Reaction number

[b] B^- = potassium t-butoxide; PNT = p-nitrotoluene

[c] Time = reaction time from time of mixing to quenching

[d] Dimer = p,p'-dinitrobibenzyl, M.P. 178-181°; p,p'-dinitrostilbene, M.P. 304-6° (trans), separated from the isolated solid filtered from water by repeated treatments with boiling benzene;

[e] Calculated from weight of crude solid filtered from water

[f] Mixed melting point with p,p'dinitrobibenzyl 179.2-180.2°

[g] Only 51% recovery after benzene treatment

[h] Total volume, 200 ml. 20% dimethyl sulfoxide - 80% t-butyl alcohol

[i] Total volume, 570 ml. 75% dimethyl sulfoxide - 20% t-butyl alcohol

[j] Reaction quenched with aerated water

[k] Reaction treated with oxygen after stated time by bubbling for 5 min.

melting points as given in Table 12. In Reactions 5 and 20 where dimethyl sulfoxide was used as solvent, p,p'-dinitrostilbene was present in the isolated dimer as indicated by the appearance of a broad doublet absorption at 10.25-10.52 μ (975-950 cm.$^{-1}$). No evidence for the presence of p,p'-dinitrostilbene in the reaction product isolated by dissolving the crude precipitate in hot benzene was found for Reaction 3 and 4 which were run in t-butyl alcohol. In all cases a red-brown material was formed to a lesser or greater extent which remained unidentified and was separated from p,p'-dinitrobibenzyl because of its insolubility in hot benzene[1]. This material was always noncrystalline, usually gave poorly resolved I.R. spectra and had broad melting point ranges. The I.R. absorption peaks which characterized the material are given in the experimental section.

The nature of the red precipitate observed in t-butyl alcohol formed from the reaction of p-nitrotoluene and potassium t-butoxide was a puzzling question. From the observations described it had to be concluded that it was not the p-nitrobenzyl carbanion since it should have been neutralized rapidly even in the presence of traces of water whereas the red precipitate apparently reacted slowly with small amounts of water (Run 263-A). It appeared that the color of the p-nitrobenzyl carbanion was pale yellow-green as observed immediately upon mixing the solutions of base and p-nitrotoluene. Although large amounts of water had the effect of changing the red color to brown the color could be dispelled instantly with acid to yield to all indications p,p'-dinitrobibenzyl. The red

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[1] This unidentified material was more soluble in hot chlorobenzene (see Reaction 28).

precipitate may have contained the precursor of the dimer since on exposure to oxygen this precipitate turned yellow to yield p,p'-nitrobibenzyl.

Figure 55 is a plot of the per cent dimer (by weight) isolated from the spontaneous dimerization of p-nitrotoluene in t-butyl alcohol as a function of time. From the three points obtained the conclusion can be made that the spontaneous dimerization proceeds rapidly until approximately 38-40% of the initial p-nitrotoluene has been consumed. Since the reaction slows down drastically at this point the amounts of reactants must be depleted and converted into an unusable form. If this is so the recovered p-nitrotoluene must have arisen from something which was unable to produce the precursor of the dimer, and which yielded p-nitrotoluene on treatment with water and air. The proportions of products isolated (40% by weight bibenzyl) correspond to three molecules of p-nitrotoluene precursors and 1 molecule of bibenzyl precursor.

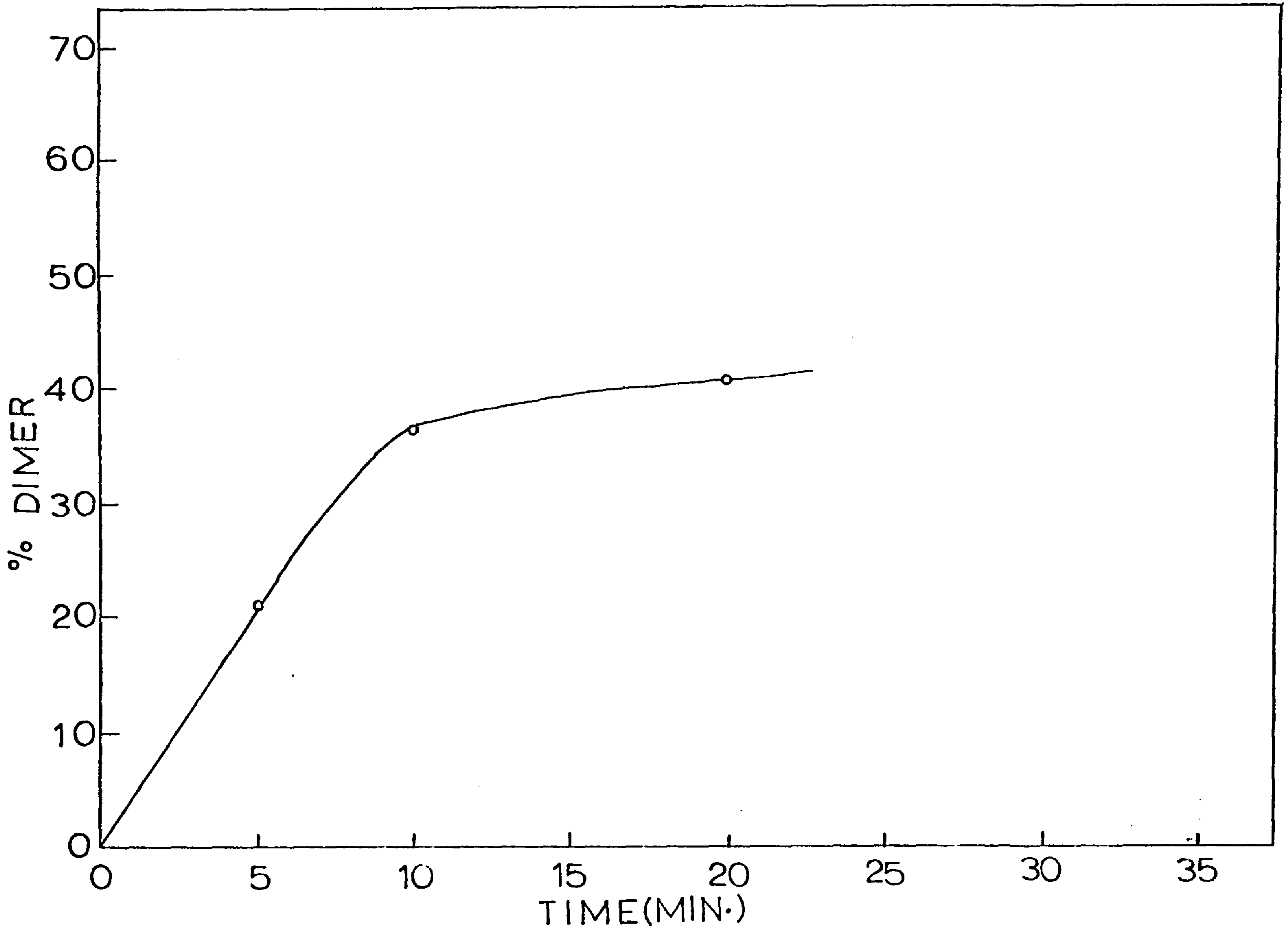
Initial PNT = $(B\text{-}B)_p + 3(PNT)_p$ after 15 min.

where $(B\text{-}B)_p \xrightarrow{H_2O, O_2}$ p,p'-dinitrobibenzyl

$(PNT)_p \xrightarrow{H_2O, O_2}$ p-nitrotoluene

In anticipation of data to be presented on the spontaneous formation of free radicals in basic solutions of p-nitrotoluene a mechanism including radical anions can be written which is most consistent with all the information known for the reaction.

Figure 55. Yield p,p'-dinitrobibenzyl (by weight) isolated as a function of time from the spontaneous dimerization reaction of p-nitrotoluene in t-butyl alcohol (see Table 11)


% DIMER
70
60
50
40
30
20
10
0
0
5
10
15
20
25
30
35
TIME(MIN·)

Steps

1 $\mathrm{PNT} + \mathrm{B}^{-} \longrightarrow \mathrm{PNT}^{\ominus} + \mathrm{BH}$

2 $\mathrm{PNT}^{\ominus} + \mathrm{PNT} \longrightarrow \left[\mathrm{PNT} \rightarrow \mathrm{PNT}\right]^{-}$

3 $\left[\mathrm{PNT} \rightarrow \mathrm{PNT}\right]^{-} \_\ \mathrm{PNT} + \mathrm{B}^{-} \longrightarrow \mathrm{B\text{-}B}^{\overset{-}{\cdot}} + \mathrm{PNT}^{\overset{-}{\cdot}} + \mathrm{BH}$

where $\left[\mathrm{PNT} \rightarrow \mathrm{PNT}\right]^{-}$ = charge-transfer complex

Since the final yield of bibenzyl isolated was 40% by weight, it follows that by the time 40% of starting p-nitrotoluene has been converted to the bibenzyl precursor, all the free p-nitrotoluene has been consumed either in charge-transfer complex formation with p-nitrobenzyl carbanion or in an electron transfer reaction with the charge-transfer complex. For this explanation to hold it must also be postulated that the charge-transfer complex is stable and not formed in a reversible reaction.

In the presence of approximately equimolar amounts of nitrobenzene to p-nitrotoluene (Table 12) yields of 66-67% of p,p'-dinitrobibenzyl were isolated, after a reaction time of 15 min. but did not increase by 30 min. (Reactions 4 and 12). Higher yields of dimer, possibly 100% were anticipated. However if a stable charge-transfer complex can form between the p-nitrobenzyl carbanion and nitrobenzene as well as with unionized p-nitrotoluene the yield of dimer might be reduced by an amount equivalent to the concentration of p-nitrobenzyl carbanion complexed with nitrobenzene.

The data to be presented on the determination of the order of the reaction leading to spontaneous formation of free radicals is also consistent with the presented mechanism. The fact that p,p'-dinitrostilbene is not formed in the spontaneous dimerization of p-nitrotoluene in t-butyl alcohol suggests that the bibenzyl may be completely precipitated out of solution as the radical anion. E.S.R. observations to be presented agree with this possibility since a solid radical was detected in these solutions which formed shortly after the appearance of the p-nitrotoluene radical ion.

Small amounts of the dimer, 2,3-bis-(p-nitrophenyl)-butane, were spontaneously formed with p-nitroethylbenzene in basic solution (see Table 13). In Reaction 6 the crystals were simply removed from the aqueous solution which had been set aside for later study. The residues of Reactions 7 and 9 had I.R. spectra almost identical to the dimer and may be the double-bonded dimer. The bulk of the product from Reaction 24 was a sticky brown material and only a trace of dimer could be obtained by treating it with acetone and decolorizing charcoal and recrystallization from benzene. A small amount of what apparently was o,o'-dinitrobibenzyl was obtained from the reaction with o-nitrotoluene. A solid unidentified product was isolated from the reaction with o-nitroethylbenzene. No reaction product was obtained from p-nitrocumene in pure t-butyl alcohol or 5% dimethyl sulfoxide - 95% t-butyl alcohol although unreacted starting material was isolated in Reaction 15.

E. Electron Transfer

1. Free radicals from carbanion oxidation

It had been known for a long time that a number of species of stable free radicals could be produced in basic solution by the action of oxygen on a carbanion. The best known example is the semiquinone radical anion

Table 13. Spontaneous dimerization of *p*-nitrotoluene derivatives; 0.1 M substrate, 0.3 M potassium *t*-butoxide, 0.12 M nitrobenzene in 500 ml. *t*-butyl alcohol

Rx.[a]	Substrate[b]	Time[c] (min.)	Dimer yield[d] (%)	Unidentified product (M.P.)	Reaction extent (%)
8[e]	DNBB	15	20.5 (277-283.5°)	235-252°	89.7
6	PNEB	15	3.3 (248°)		3.3
9	PNEB	30	3.0 (243-7°)		10.2
7	PNEB	60	3.0 (252.5-5°)	244-249.5°	21
24[f]	PNEB	15	0.1 (232-7°)	97-106°	>100
25	ONEB	15	2.3 (152-172°)	261-273°	
27	ONT	15	15 (119-122°)		15
13	PNC	10.5 hr.			0
15[g]	PNC	30			0

[a] Reaction number

[b] DNBB = *p,p'*-dinitrobibenzyl; PNEB = *p*-nitroethylbenzene; ONEB = *o*-nitroethylbenzene; ONT = *o*-nitrotoluene; PNC = *p*-nitrocumene

[c] Time = reaction time from time of mixing to quenching

[d] *p,p'*-Dinitrostilbene, M.P. 304-6° (*trans*); *bis*-2,3-(*p*-nitropheny)-butane, M.P. 254-6° (3); *o,o'*-dinitrobibenzyl, M.P. 121-2° (134)

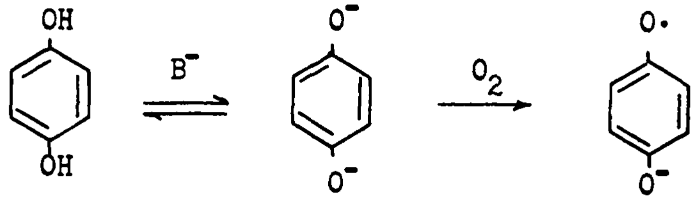
[e] DNBB, 0.025 moles; potassium *t*-butoxide, 0.055 moles; solvent 200 ml. 80% dimethyl sulfoxide - 20% *t*-butyl alcohol; reaction extent was total recovery with 69.2% unidentified product insoluble in hot benzene

[f] Total volume, 330 ml. 60% dimethyl sulfoxide - 40% *t*-butyl alcohol

[g] 5% dimethyl sulfoxide - 95% *t*-butyl alcohol

made by oxidation of hydroquinone in basic solution (26).

(147)



Our early efforts in the use of electron spin resonance techniques for the detection of stable free radicals were directed towards searching for more examples of this reaction. We tested numerous compounds in dimethyl sulfoxide - t-butyl alcohol containing potassium t-butoxide for the presence of free radicals generated by air oxidation. It was during these queries that we discovered that free radicals were formed spontaneously in basic solutions of p-nitrotoluene and in general in solutions containing carbanions and nitroaromatics. This section will include non-nitroaromatic radical anions produced in basic solutions in the presence of a small amount of oxygen.

It was found that by simply dissolving fluorenol in air in basic solutions of dimethyl sufloxide - t-butyl alcohol a bright red color immediately developed and the solutions contained large concentrations of free radicals. On low resolution five major peaks of the E.S.R. spectrum shown in Figure 56 could easily be resolved. The same spectrum could be obtained with fluorenone in solutions of dimethyl sulfoxide - t-butyl alcohol containing small amounts of potassium t-butoxide in the presence of glucose[1]. A solution of fluorenone in tetrahydrofuran to which

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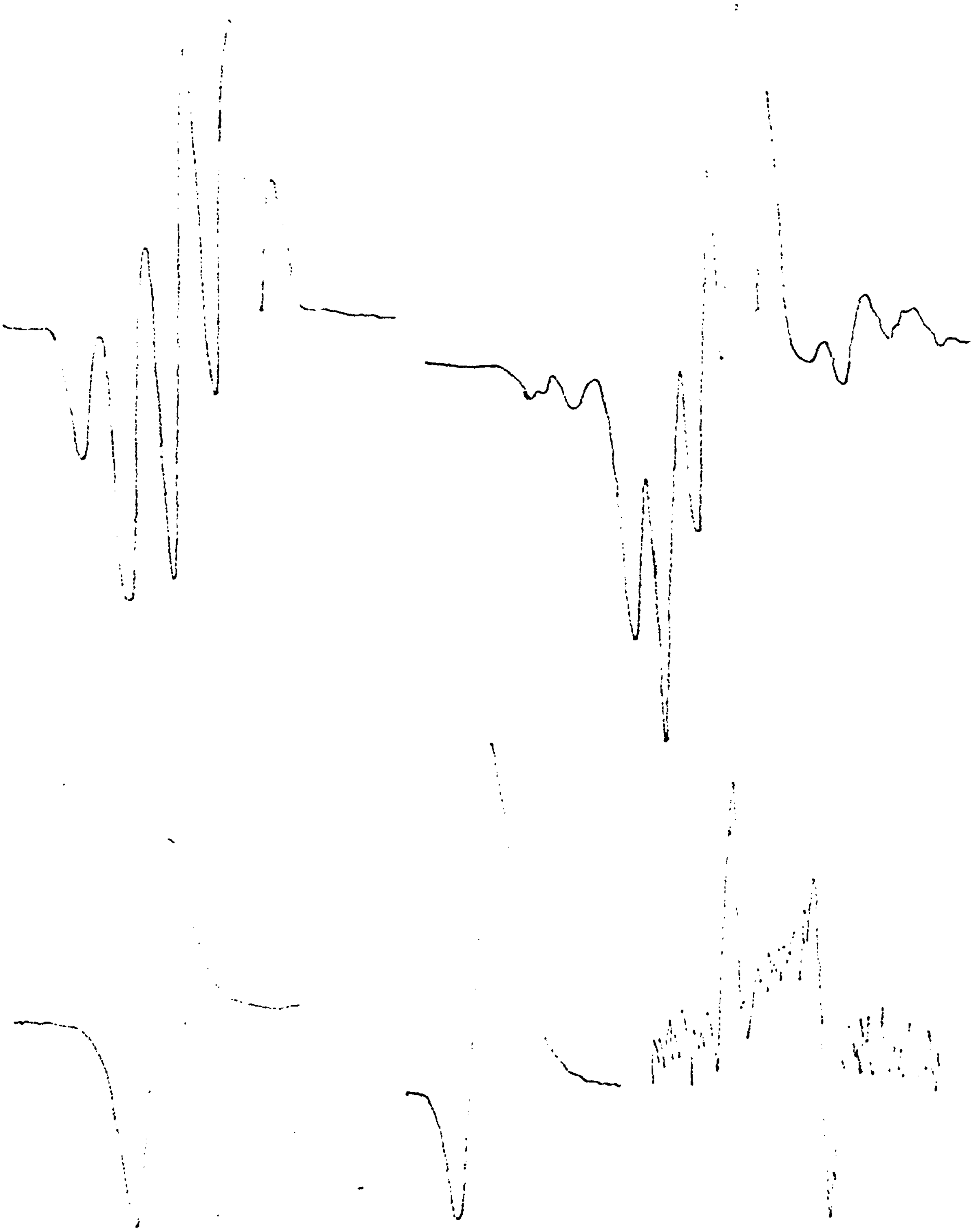
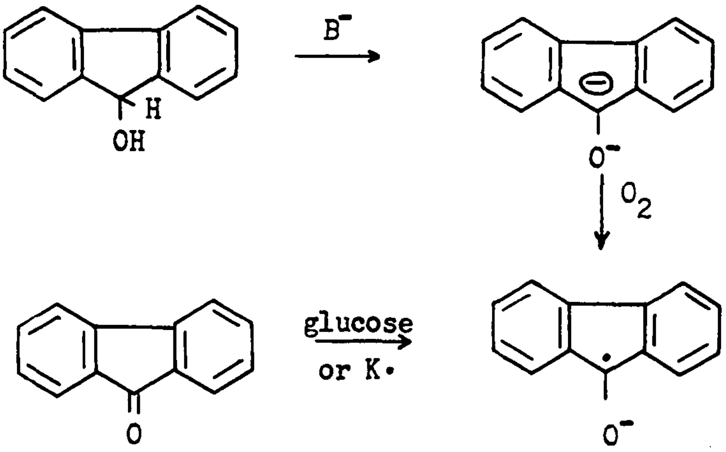
[1] Glucose in base is a commonly used reducing agent for the preparation of radical anions (26).

Figure 56. E.S.R. spectra of fluorenone ketyl radical anion generated from fluorenol (top left) or fluorenone (top right) in the presence of potassium _t_-butoxide in dimethyl sulfoxide - _t_-butyl alcohol and radical species observed in solutions of base-catalyzed oxidations of indene (bottom left) in dimethyl sulfoxide - _t_-butyl alcohol containing potassium _t_-butoxide after 1 day (middle) and after 3 days (right)



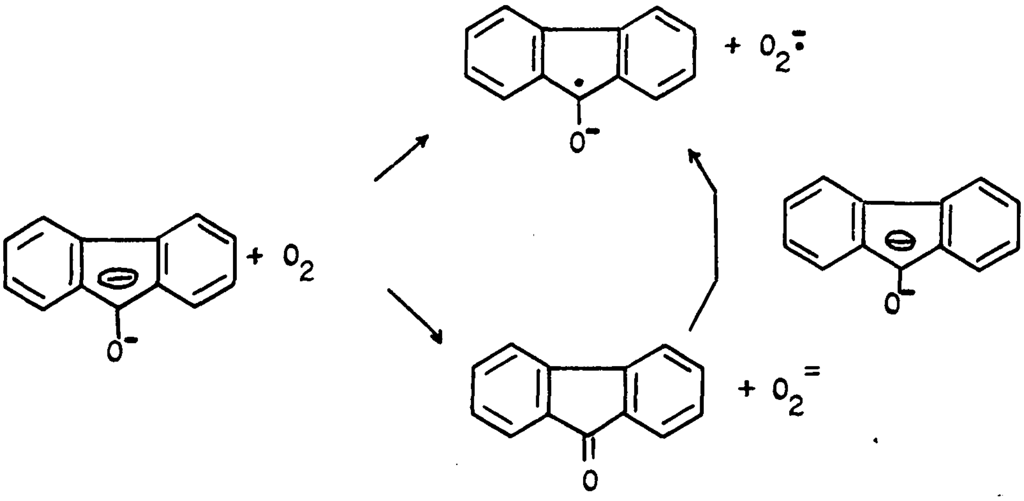
potassium metal had been added gave a strong signal which on dilution could be resolved to give the same 5-peak spectrum. These observations allowed the conclusion to be made that the ketyl radical anion of fluorenone was readily formed by the air oxidation of fluorenol in basic solution.

(142)



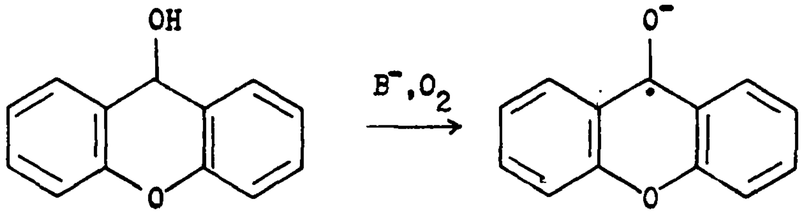
Since it was found that the fluorenone ketyl radical anion could be formed by the symmetrical electron exchange reaction between fluorenone and fluorenol in basic solution (see Electron exchange) the pathway for the formation of the ketyl in the air oxidation of fluorenol could not be ascertained.

(143)



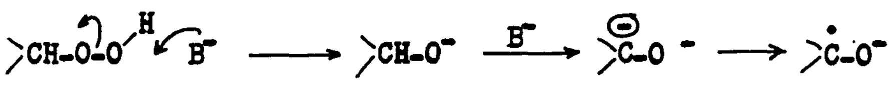
For a free radical to be detected by E.S.R. it must be a reasonably long-lived species; a free radical produced and detected in the presence of air must be particularly stable, *i.e.*, the rate of reaction of the radical with oxygen must be relatively slow. The fluorenone ketyl seems to be such an example. The xanthone ketyl radical anion was also made by a similar reaction of oxygen in a basic solution.

(144)



The 5-peak spectrum of this radical was very similar to that of fluorenone ketyl under low resolution (Figure 56). It was not possible to make the benzophenone ketyl from a similar reaction starting with benzhydrol.

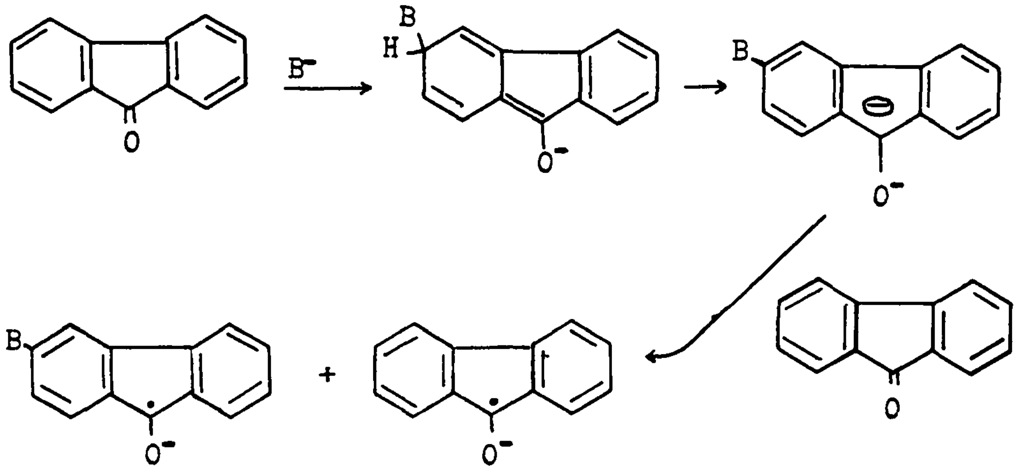
The fluorenone ketyl spectrum could also be obtained from a solution of fluorene which had been oxidized in the normal fashion and from which the dimethyl sulfoxide adduct could be isolated (see Products as a function of solvent). The same spectra has since been obtained when base was added to a solution of dimethyl sulfoxide containing fluorene which had been allowed to stand in air for a long period of time. Moreover, solutions of fluorenone in dimethyl sulfoxide - *t*-butyl alcohol gave a similar spectrum although a few additional peaks appeared on the edges (Figure 56). In the oxidation of fluorene the fluorenone ketyl radical anion could be formed as the result of the following reaction:



$$>CH\text{-}O\text{-}O\overset{H}{\,}\;B^- \longrightarrow\; >CH\text{-}O^- \xrightarrow{B^-}\; >\overset{\ominus}{C}\text{-}O^- \longrightarrow\; >\dot{C}\text{-}O^-$$

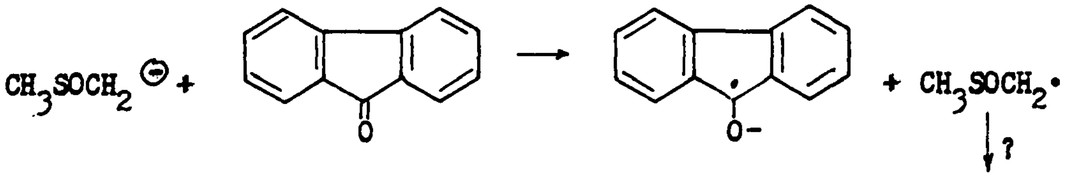
The radical from fluorenone and base can be considered the result of nucleophilic addition to the ring followed by electron transfer

(145)



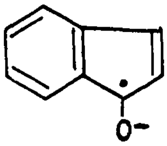
or the result of electron transfer from the methylsulfinyl anion to fluorenone.

(146)



It is not known how the dimethyl sulfoxide adduct influences these solutions containing free radicals.

The base-catalyzed oxidations of indene gave E.S.R. signals although not resolvable. Figure 56 shows the signal obtained immediately after an oxidation of indene in 80% dimethyl sulfoxide - 20% t-butyl alcohol containing potassium t-butoxide. Signals were also recorded 1 and 3 days after the oxidation experiment on aliquots of the solution kept under nitrogen. The unresolved and unsymmetrical spectra gave no information as to the nature of the radical species but reasoning by analogy, the ketyl of indenone (itself an unknown compound) might be expected.



XXVIII

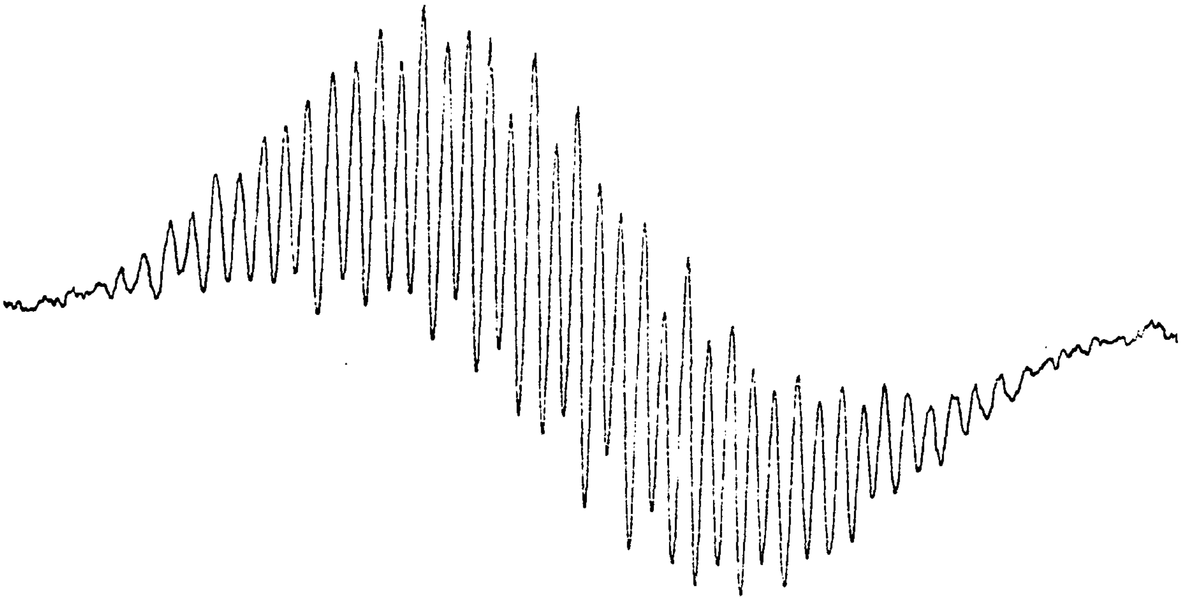
The ketyl of 2,3-diphenylindenone was synthesized by reduction of the ketone but no fine structure could be resolved (see Ketyls in Appendix).

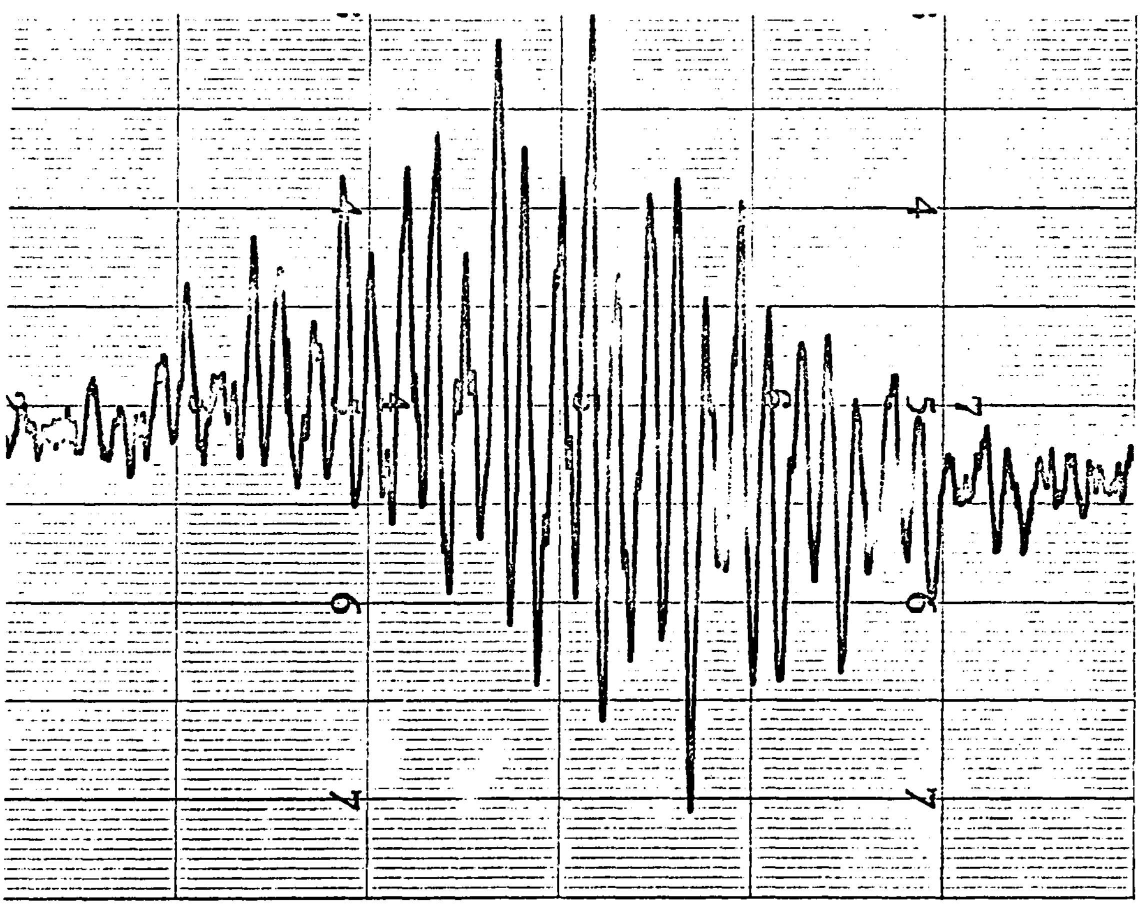
The tris-(p-nitrophenyl)-methyl radical was another example of a free radical which could be formed by the action of oxygen on the carbanion (Figure 57).

$$(147)\quad (NO_2C_6H_5)_3C^{\ominus} \xrightarrow{O_2} (NO_2C_6H_5)_3C\cdot$$

In dimethyl sulfoxide - t-butyl alcohol containing potassium t-butoxide the solution was initially blue presumably due to the tris-(p-nitrophenyl)-methide anion but turned slowly dark green on exposure to air which is the reported color of the tris-(p-nitrophenyl)-methyl radical (102). The total line width as reported by Jones (135) is 26 gauss for the tris-(p-nitrophenyl)-methyl radical in dimethoxyethane (also see Reference 66). The spectrum we obtained looked very similar to that reported by Jones but the total line width was approximately 32 gauss. If this difference in line width between the reported spectrum and ours was due to a solvent effect or to an inaccuracy in our line width estimation or even because our radical was not in fact the tris-(p-nitrophenyl)-methyl radical was not ascertained.

Figure 57. E.S.R. spectra of tris-(p-nitrophenyl)-methyl radical (top) and azobenzene radical anion (bottom) in dimethyl sulfoxide - t-butyl alcohol




4
4
5
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7
7

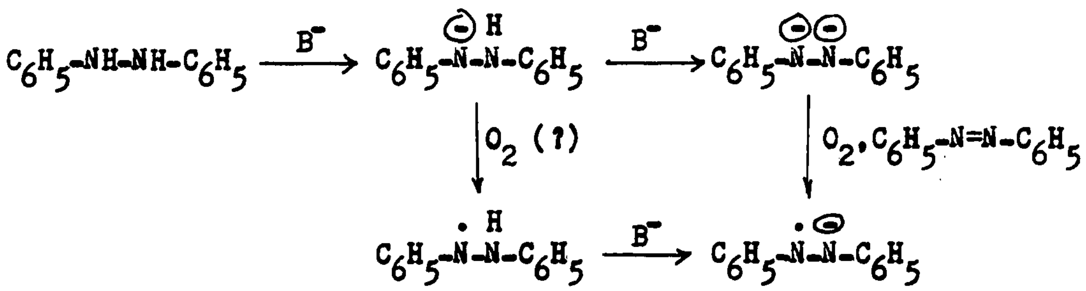
It is known that the tris-(p-nitrophenyl)-methyl radical reacts slowly with oxygen and in a crystal this reaction is reversible; the tris-(p-nitrophenyl)-methyl peroxy radical within a crystal of tris-(p-nitrophenyl)-methyl decomposes under vacuum to yield the radical and oxygen (136). Like the fluorenol dianion the tris-(p-nitrophenyl)-methide anion reacts faster with oxygen to produce radicals than the radical reacts with oxygen, i.e.,

$$(148)\qquad R^{=}\ (\text{or } R^{-}) \xrightarrow[k_1]{O_2} R^{\dot{-}}\ (\text{or } R\cdot) \xrightarrow[k_2]{O_2} R\ (\text{or } ROO\cdot) \qquad k_1 > k_2$$

However attempts to make the triphenylmethyl radical by a similar reaction using triphenylmethane in a basic solution of dimethyl sulfoxide was not successful. It seems for fluorenol, xanthydrol and tris-(p-nitrophenyl) methane $k_1 > k_2$ in Equation 148 but for benzhydrol and triphenylmethane $k_2 > k_1$.

Free radicals were formed readily from hydrazobenzene in basic solutions in the presence of air (Figure 57). The same radical could also be formed in the presence of azobenzene in the absence of air (52). This radical was assigned the structure of the azobenzene radical anion.

(149)



$$\begin{tikzcd} C_6H_5\text{-}NH\text{-}NH\text{-}C_6H_5 \arrow[r, "B^-"] & C_6H_5\text{-}\overset{\ominus\,H}{N\text{-}N}\text{-}C_6H_5 \arrow[r, "B^-"] \arrow[d, "O_2\ (?)"] & C_6H_5\text{-}\overset{\ominus\ominus}{N\text{-}N}\text{-}C_6H_5 \arrow[d, "{O_2,\,C_6H_5\text{-}N=N\text{-}C_6H_5}"] \\ & C_6H_5\text{-}\overset{\cdot\ H}{N\text{-}N}\text{-}C_6H_5 \arrow[r, "B^-"] & C_6H_5\text{-}\overset{\cdot\ \ominus}{N\text{-}N}\text{-}C_6H_5 \end{tikzcd}$$

Solutions of hydrazobenzene and base containing radicals were yellow-brown in color. The spectrum from air oxidation contained approximately 35 peaks but better resolution provided by an electron transfer experiment indicated 41 peaks (52). By the method of deuterium substitution in the benzene rings all the splitting constants for the radical anion have been obtained by Russell and Konaka[1]; the best fit is obtained by assuming a non-linear structure for the radical anion.

We further attempted to synthesize in basic solutions of dimethyl sulfoxide - t-butyl alcohol the nitrogen analogues of the semiquinone by the air oxidation of p-aminophenol, p-phenylenediamine, benzidine and N,N'-diphenylbenzidine. None of these gave free radicals as readily as the before mentioned compounds although weak signals were obtained suggestive of the feasibility of studying the oxidation of these species in basic solution. A weak unresolved signal was obtained from p-aminophenol which formed a dark brown solution. Similarly p-phenylenediamine gave a weak unresolved signal but formed a dark purple solution.

Better resolved spectra were obtained for both benzidine and N,N'-diphenylbenzidine (Figure 58). It was found that benzidine dissolved slowly in solutions of dimethyl sulfoxide - t-butyl alcohol but much faster after the addition of potassium t-butoxide to the solution. The color of the solution was dark blue-green particularly intense on the surface in contact with air. A strong signal was produced initially but weakened quickly and gave a different spectrum on standing (Figure 58). N,N'-diphenylbenzidine dissolved in dimethyl sulfoxide - t-butyl alcohol containing potassium t-butoxide to give an orange-yellow solution which

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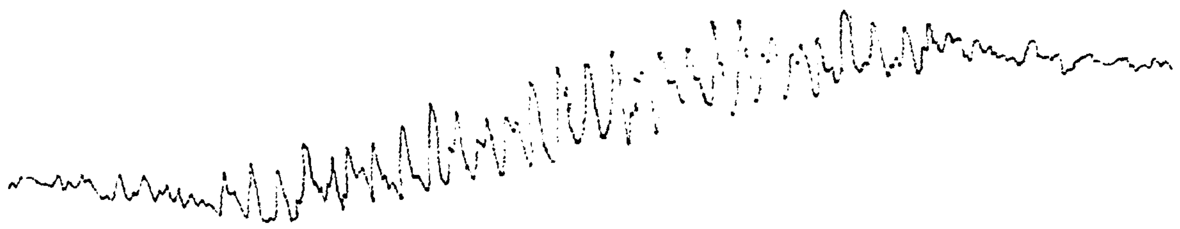
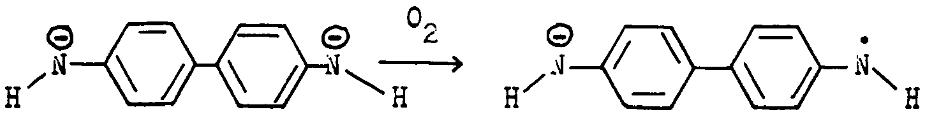
[1] G. A. Russell and R. Konaka, Dept. of Chemistry, Iowa State University, Ames, Iowa. Private communication concerning azobenzene radical anion, May, 1963.

Figure 58. E.S.R. spectra obtained from benzidine (initial, top left; on standing, top right), N,N'-diphenyl-*p*-phenylenediamine (middle) and acridan (bottom) in dimethyl sulfoxide - *t*-butyl alcohol containing potassium *t*-butoxide exposed to air



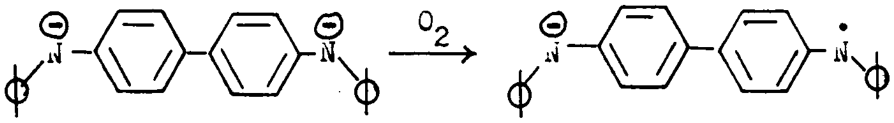
turned red in contact with air. The signal obtained was fairly strong initially although not as strong as that obtained from benzidine (Figure 58). The semiquinone analogues expected were the following,

(150)



XXIX

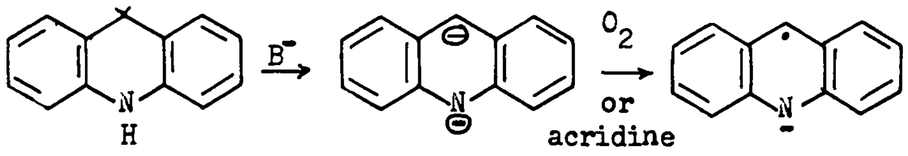
(151)



XXX

It was of interest to see if radical anions could be made by ionization of the dihydroderivatives of polycyclic aromatic compounds followed by air oxidation. Acridan dissolved in a solution of dimethyl sulfoxide - t-butyl alcohol containing potassium t-butoxide which turned pink on prolonged exposure to air and gave the E.S.R. spectrum shown in Figure 58.

(152)



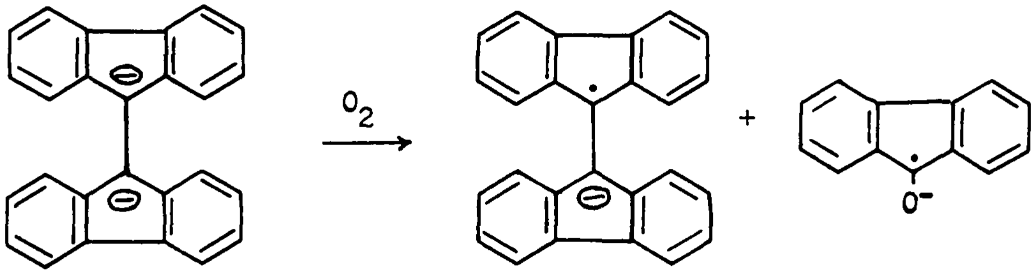
Acridone did not give a free radical under these conditions.

Dihydroanthracene in basic solution turned pink on exposure to air and produced a radical species which has since been shown to be the anthraquinone semiquinone radical rather than the anthracene radical anion.

Presumably this was another case where the rate of oxidation of the free radical by oxygen to anthracene was as fast or faster than the rate of production of the radical anion. The oxidation leading to anthraquinone may have been largely due to the oxygenation of the dihydroanthracene monoanion.

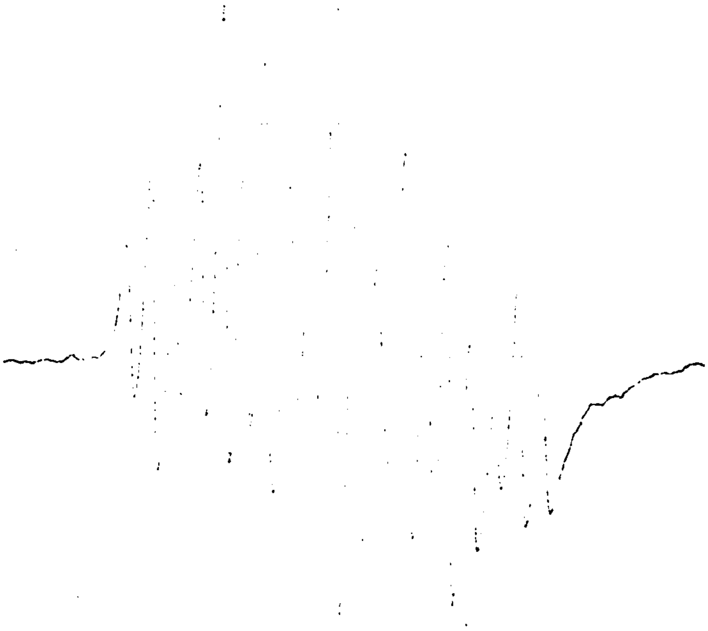
9,9'-Bifluorene gave a very strong signal in a basic solution of dimethyl sulfoxide exposed to air (Figure 59). Some spectra under high resolution indicated the presence of more than one radical species. Since our oxidations of 9,9'-bifluorene produced fluorenone (see Rates and products as a function of structure) it was felt that the fluorenone ketyl could have also been present along with the radical anion of △-9,9'-bifluorene.

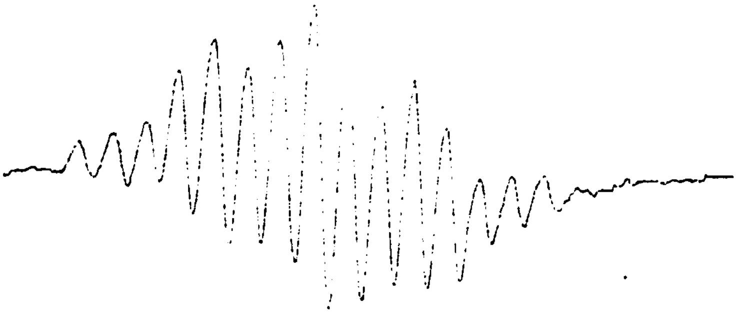
(153)



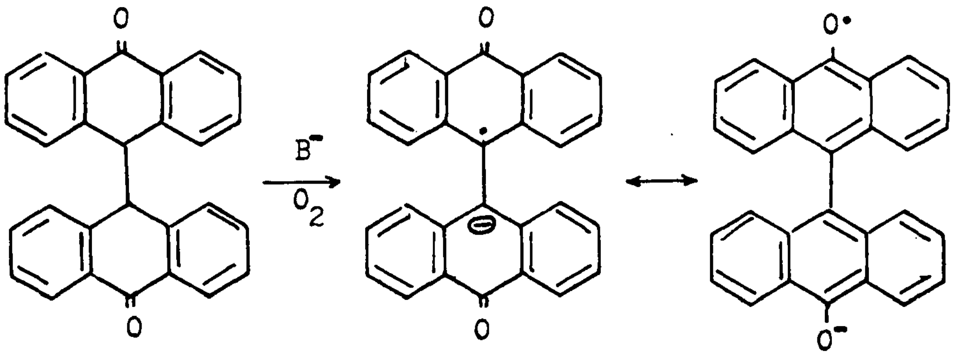
The color of the solution of bifluorene in dimethyl sulfoxide was initially pink but turned to yellow-brown. Under similar conditions 9,9'-bianthrone gave a bright reddish-orange solution with a strong signal (Figure 59). Anthrone and 9-nitroanthrone gave no radicals under these conditions. The radical we had hoped to obtain from bianthrone was

Figure 59. E.S.R. spectra obtained in a basic solution of dimethyl sulfoxide - <u>t</u>-butyl alcohol from 9,9'-bifluorene (top, 1 cm. = 2.38 gauss) and 9,9'-bianthrone (bottom, 1 cm. = 0.876 gauss) exposed to air





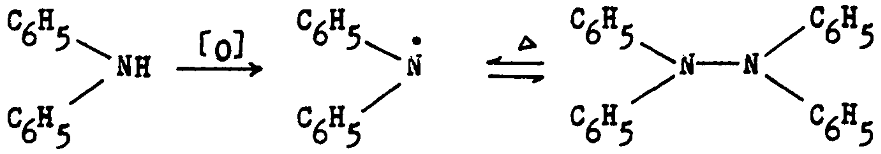
(154)



but the splitting constants from the hyperfine components of the spectrum were not determined. Although the 15 peaks obtained separated by 2.86 gauss could be assigned to 16 equivalent hydrogens (17 peaks, 2 lost) the intensities of lines did not agree with the expected values.

The diphenyl amine radical has been known for some time and can be synthesized from diphenylamine by lead peroxide, iodine or permanganate oxidation (137) or by heating tetraphenylhydrazine (138).

(155)



It was of interest to investigate the possibility of forming this radical from the diphenyl nitranion by air oxidation.

(156)

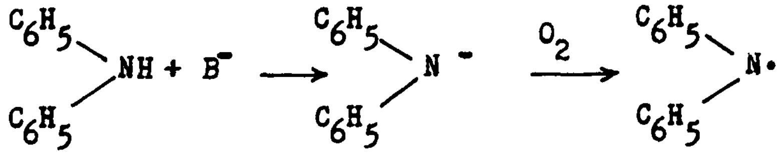


Figure 60 shows the E.S.R. spectrum obtained from such a reaction. The study of this radical species was continued and the conclusion has been

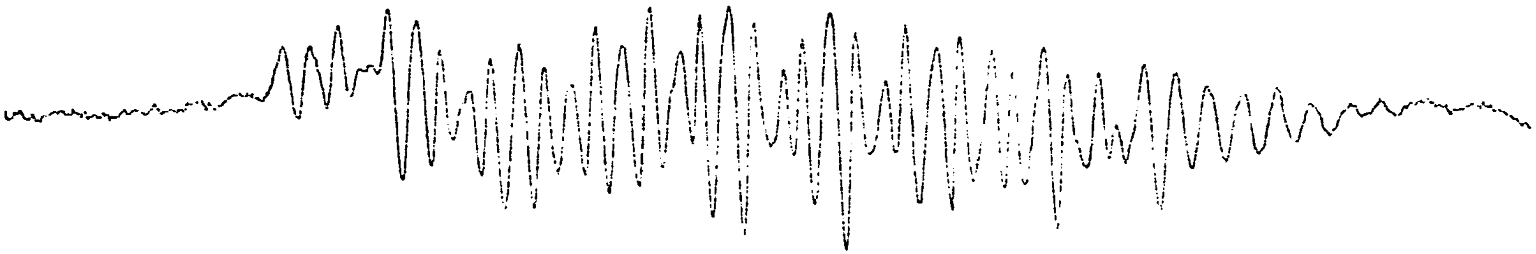
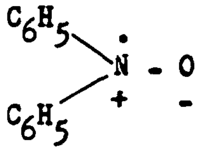


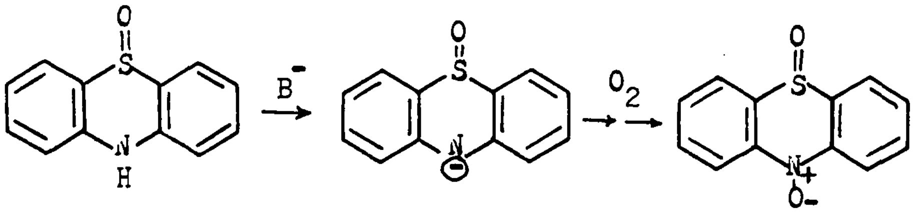
Figure 60. E.S.R. spectrum obtained by the air oxidation of diphenyl amine in dimethyl sulfoxide - t-butyl alcohol containing potassium t-butoxide

made by Russell and Smentowski[1] that the predominant radical species probably was the previously reported diphenylamine oxide (47).

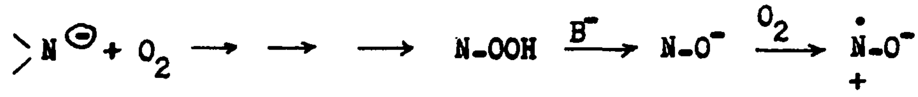


XXXI

A number of other derivatives of diphenyl amine were tried under similar conditions. Both phenothiazine and phenothiazine-S-oxide gave strong radical signals and in the latter case a well resolved spectrum could be obtained (Figure 61). The spectrum of phenothiazine indicated the presence of more than one radical species possibly because the starting compound was of practical grade and needed purification. By analogy these radical species were thought to be the nitrogen oxides.

(157) 

The mechanism of the base-catalyzed oxidation of nitranions is not known, although it is possible to suggest one analogous to that of carbanions.

(158) 

$$>N^{\ominus} + O_2 \longrightarrow \longrightarrow \longrightarrow N\text{-}OOH \xrightarrow{B^-} N\text{-}O^- \xrightarrow{O_2} \overset{\bullet}{\underset{+}{N}}\text{-}O^-$$

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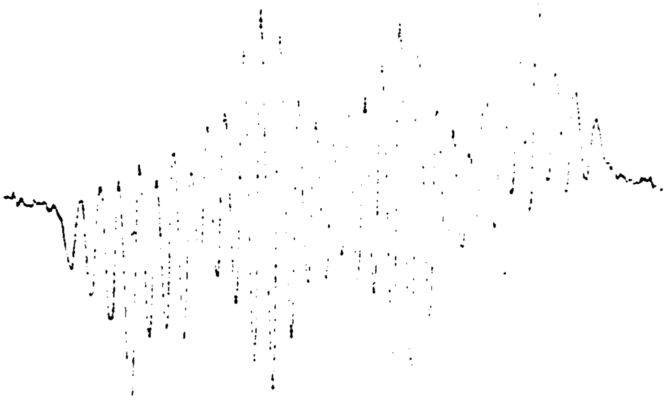
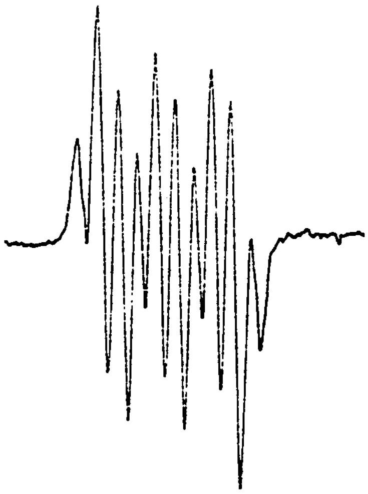
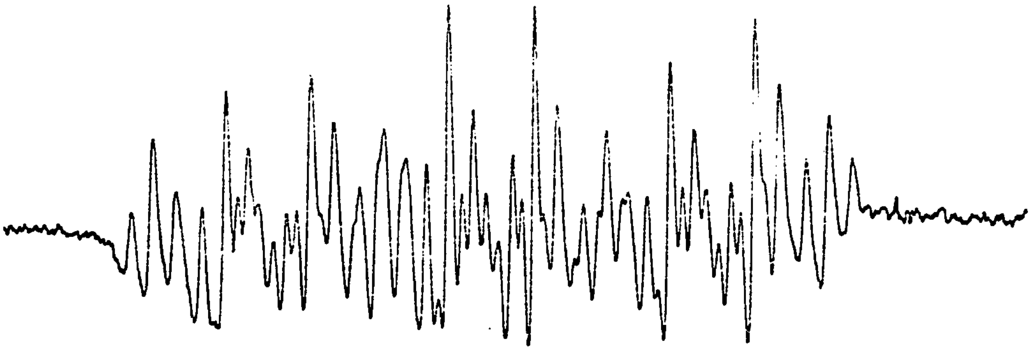
[1] G. A. Russell and F. J. Smentowski, Dept. of Chemistry, Iowa State University of Science and Technology. Private communication regarding radical formation from diphenyl amine oxidation, 1962.

Figure 61. E.S.R. spectra obtained from secondary amines exposed to air in dimethyl sulfoxide - t-butyl alcohol containing potassium t-butoxide; phenothiazine (top, 1 mm. = 0.32 gauss), phenothiazine-S-oxide (middle left, 1 mm. = 0.32 gauss), 1,2,*N*,*N*'-tetraphenylethylenediamine (low resolution, middle right; high resolution, bottom)

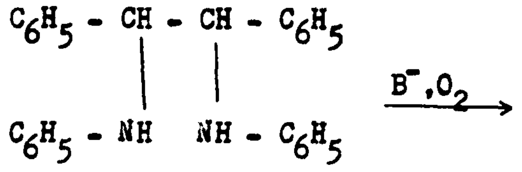






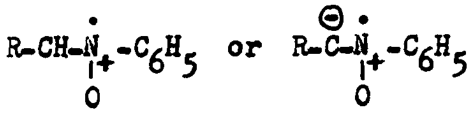
Probably another example of radical formation by nitranion oxidation was the stable radical formed from the action of base and air on tetraphenylethylenediamine (Figure 61).

(159)



$$\begin{array}{l} C_6H_5-\underset{|}{CH}-\underset{|}{CH}-C_6H_5 \\ C_6H_5-NH\qquad NH-C_6H_5 \end{array} \xrightarrow{B^-,O_2}$$

It was thought the observed radical was the N-benzyl aniline radical anion produced by homolytic cleavage of a dinegatively charged molecule by analogy to the pinacols (52) but it was found that larger concentrations of radicals were produced in air indicating nitrogen oxide radical formation. A similar spectrum was obtained from N-benzyl aniline although the signal obtained indicated a very low concentration of free radicals. The structure of these radical species may be,



$$R\text{-}CH\text{-}\underset{O}{\overset{\bullet}{N}}{}^{+}\text{-}C_6H_5 \quad \text{or} \quad R\text{-}\overset{\ominus}{C}\text{-}\underset{O}{\overset{\bullet}{N}}{}^{+}\text{-}C_6H_5$$

XXXII

since it has been subsequently found that it is difficult to ionize N-benzylaniline to the dianion and its radical ion has not been obtained in attempted electron exchange experiments between N-benzylaniline and benzaldehyde anil[1]

(160) $C_6H_5\text{-}CH_2\text{-}NH\text{-}C_6H_5 + C_6H_5\text{-}CH{=}N\text{-}C_6H_5 + B^- \not\rightleftharpoons C_6H_5\text{-}CH\text{-}\overset{\bullet\,\ominus}{N}\text{-}C_6H_5$

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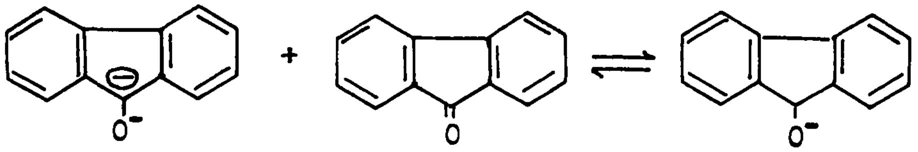
[1] G. A. Russell and E. T. Strom, Dept. of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Private communication regarding electron exchange experiments, 1963.

2. Electron exchange

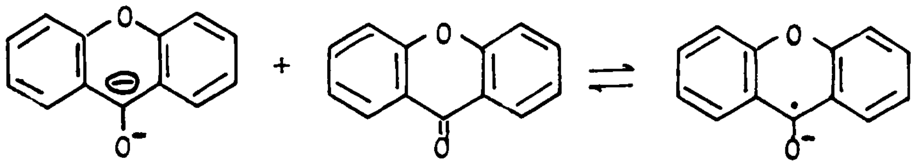
The oxidation by air of fluorenol to fluorenone ketyl radical anion in basic solution was an analogous reaction to the oxidation of hydroquinone to semiquinone. Since the semiquinone radical anion can also be produced by electron exchange between hydroquinone and quinone in basic solution in the absence of air it seemed likely that fluorenol and fluorenone would undergo the same electron exchange in strongly basic solution. In 80% dimethyl sulfoxide - 20% t-butyl alcohol in the absence of air the electron exchange was found to be essentially quantitative (Table 14).

(161)



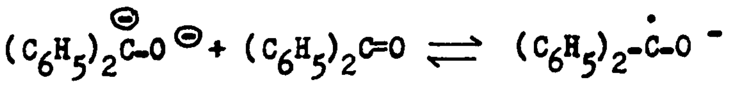
The same reaction went very readily for xanthydrol and xanthone,

(162)



but less readily for benzhydrol and benzophenone (Figure 62).

(163)



$$(C_6H_5)_2\overset{\ominus}{C}\text{-}O^{\ominus} + (C_6H_5)_2C{=}O \rightleftharpoons (C_6H_5)_2\text{-}\overset{\bullet}{C}\text{-}O^{-}$$

The same bright red color developed for the electron exchange experiment between fluorenol and fluorenone in 80% dimethyl sulfoxide - 20% t-butyl alcohol as was observed in the air oxidation of fluorenol in base. In t-butyl alcohol - potassium t-butoxide a dark green color

Table 14. Symmetrical electron transfer between alcohols and ketones in 80% dimethyl sulfoxide - 20% t-butyl alcohol

Substrate	R_2CHOH[a]	$R_2C{=}O$[b]	t-BuOK[c]	DPPH[d]		R•[e]		Transfer (%)
				$M\times10^2$	Age[f]	$M\times10^2$	(mmoles)	
fluorenone	0.397	0.416	0.291	1.11	1	1.22	0.366	126
fluorenone	.215	.207	.262	1.11	1	2.08	.520	199
fluorenone	.187	.200	.194	1.11	2	1.11	.610	315
fluorenone	.095	.094	.200	1.4	0	1.05	.210	112
xanthone	.087	.085	.175	1.4	0	1.05	.210	124
xanthone	.094	.096	.200	1.12	0	3.36	.672	358
benzophenone	2.29	2.24	4.5	0.00185	0	0.0026	0.0052	.0043

[a] R_2CHOH = fluorenol, xanthydrol or benzhydrol in mmoles

[b] $R_2C{=}O$ = fluorenone, xanthone or benzophenone in mmoles

[c] t-BuOK = potassium t-butoxide in mmoles

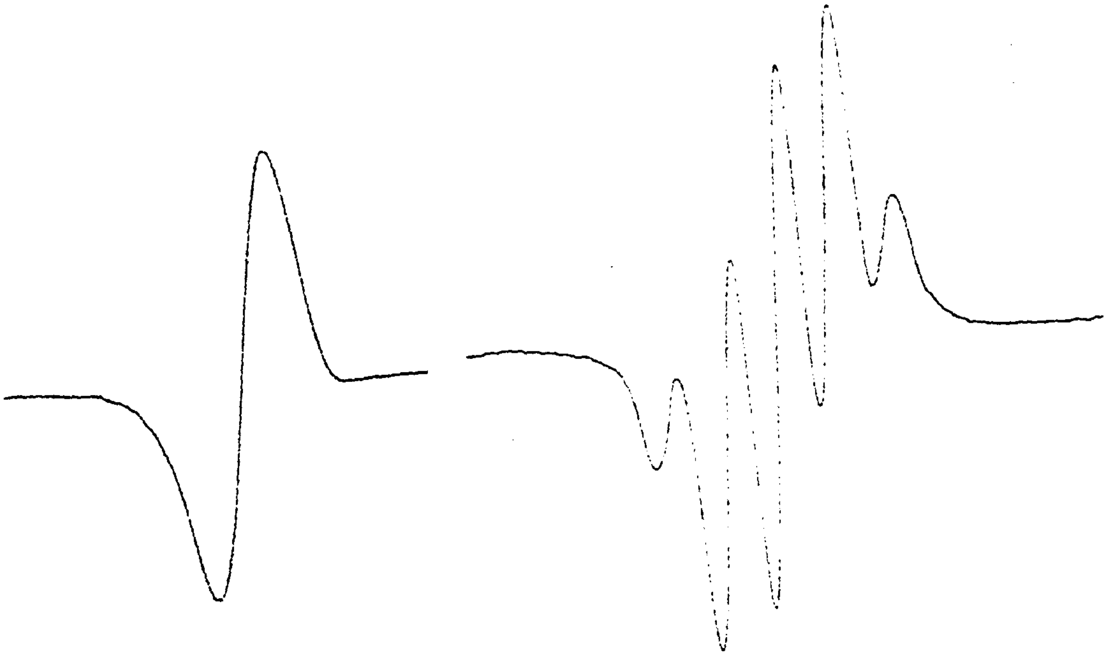
[d] DPPH = solution of diphenylpicrylhydrazyl in the same solvent

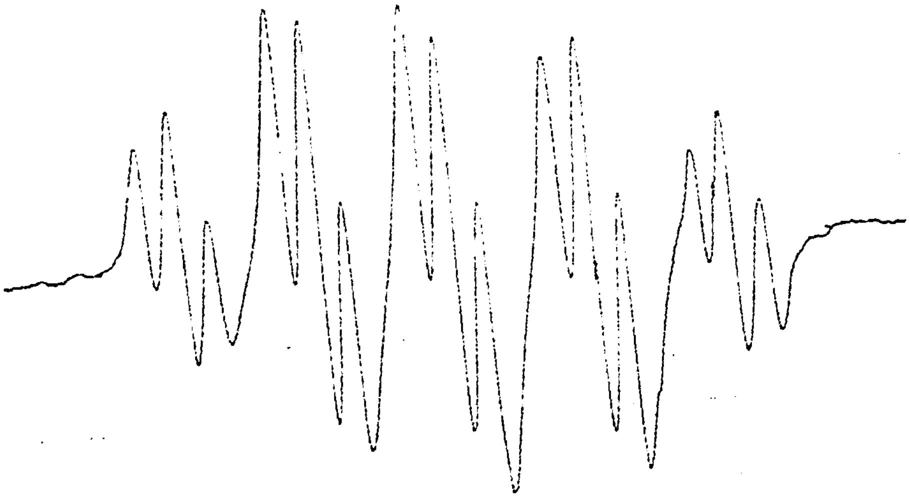
[e] R• = ketyl radical anion

[f] Age = age of diphenylpicrylhydrazyl in days

appeared and the usual 5-peak E.S.R. spectra was observed. The xanthydrol - xanthone solution in 80% dimethyl sulfoxide - 20% t-butyl alcohol turned blue quickly upon addition of potassium t-butoxide. With Triton B the same color appeared more slowly and did not become as intense. A faint blue color appeared in the solution of benzhydrol - benzophenone 10-15 min.

Figure 62. E.S.R. spectra of radicals obtained from the symmetrical electron transfer reaction between alcohols and ketones in 80% dimethyl sulfoxide - 20% t-butyl alcohol containing potassium t-butoxide; benzhydrol-benzophenone (top left, 1 cm. = 8.18 gauss) and xanthydrol-xanthone (top right, low resolution, 1 cm. = 5.78 gauss; bottom, high resolution, 1 cm. = 1.56 gauss)



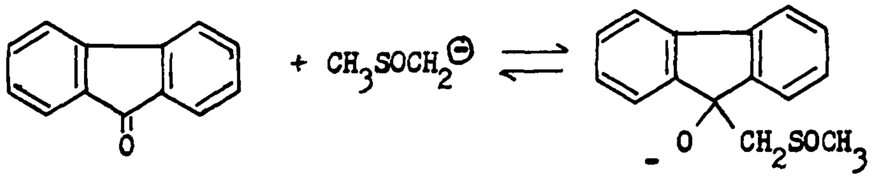


after the addition of potassium *t*-butoxide in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol. After 25 min. the solution was blue-green and green after 50 min. at which time the quantitative E.S.R. experiment was run (Table 14) indicating approximately $4 \times 10^{-3}\%$ transfer.

Table 14 serves to show the large inaccuracy inherent in our method of obtaining concentration measurements which involved a comparison of the area under the first derivative trace obtained for the radical under question and diphenylpicrylhydrazyl (DPPH) in the same solvent. The error can be attributed mainly to decomposition of DPPH on standing in the solvent since a freshly prepared solution gave the most reasonable electron exchange value.

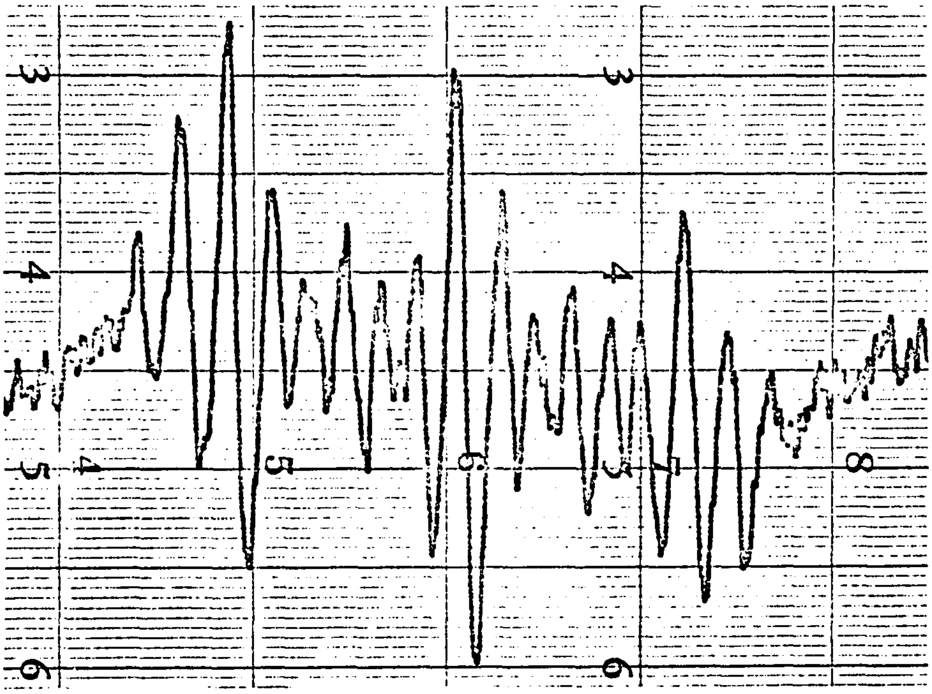
Dimethyl sulfoxide addition products form readily with fluorenone and benzophenone but not for xanthone. It seems surprising to find extensive electron exchange occurring in solutions containing fluorenone which produce mainly adducts upon treatment with water in the absence of fluorenol. These observations suggest that electron exchange is faster or the preferred reaction and that adduct formation might be a reversible reaction.

(164)



Electron exchange between *p*,*p*'-dinitrobibenzyl and *p*,*p*'-dinitrostilbene in dimethyl sulfoxide - *t*-butyl alcohol containing potassium *t*-butoxide gave the radical spectrum shown in Figure 63.

Figure 63. E.S.R. spectra of radical species from electron exchange experiments with p,p'-dinitrobibenzyl and p,p'-dinitrostilbene in 50% dimethyl sulfoxide - 50% t-butyl alcohol containing potassium t-butoxide (top) and bis-1,2-(4-methylpyridinium iodide)-ethane, bis-1,2-(4-methylpyridinium iodide)-ethylene in 80% dimethyl sulfoxide - 20% t-butyl alcohol containing 0.1 M piperidine (bottom, 1 cm. = 3.89 gauss)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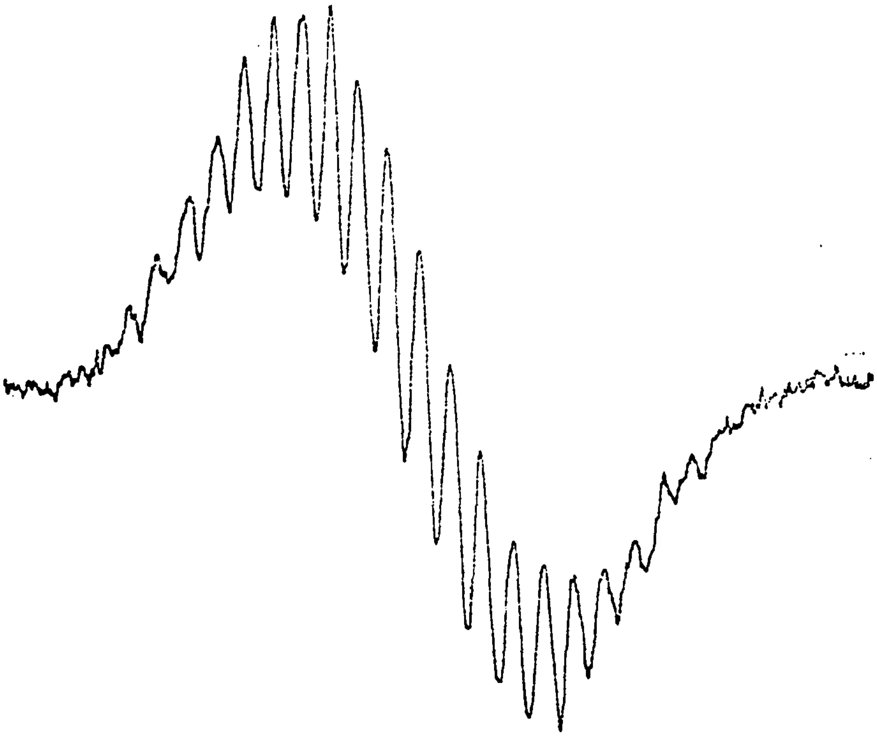
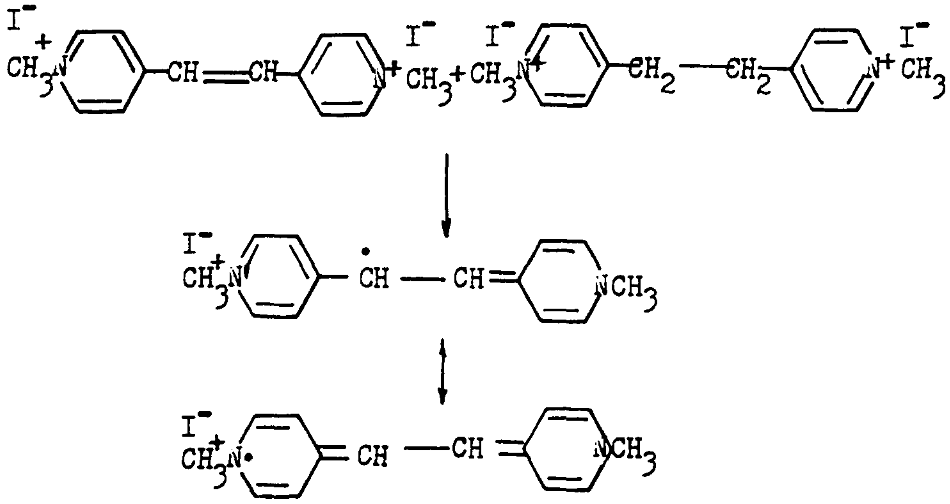


An example of a neutral free radical obtained by electron exchange was the radical of reduced bis-1,2-(4-methylpyridinium iodide)-ethylene. In 80% dimethyl sulfoxide - 20% t-butyl alcohol containing 0.1 M piperdine the spectrum in Figure 63 was obtained.

(165)



The quaternary amines were not stable in more strongly basic solutions.

3. Spontaneous free radical formation

a. Alkyl nitroaromatics During a series of scouting experiments in the formation of free radicals in basic solution in the presence of a trace of air, the formation of large concentrations of free radicals was observed in basic solutions of p-nitrotoluene and other alkyl nitroaromatic compounds (100). Although these radicals could be produced in air the radical signal was more easily resolved and completely stable in the absence of air. In fact air was not necessary for radical formation; by simply dissolving 2.5 x 10^{-3} M p-nitrotoluene in 0.6 M potassium t-butoxide in t-butyl alcohol approximately 2 x 10^{-3} M free radical species were produced by 0.5-1.0 hr. The signal obtained from this solution after 67 min. is given in Figure 64 which also shows the signal of 2×10^{-3} M diphenylpicrylhydrazyl[1] in t-butyl alcohol for comparison. By double integration of both spectra Russell and Janzen (100) estimated the concentration of the unpaired spins in the p-nitrotoluene - t-butyl alcohol solution to be 2.6×10^{-3} moles, assuming 80% radical purity of the diphenylpicrylhydrazyl used.

In dimethyl sulfoxide - t-butyl alcohol[2] a large number of alkyl nitroaromatic compounds were tried without rigorous exclusion of air in the presence of potassium t-butoxide. Some of these were subsequently repeated more carefully under specified conditions under nitrogen. Most of the initial spectra obtained could not be solved merely by inspection, i.e., the splitting constants derivable from the hyperfine components were not determined and more work was required under controlled conditions to obtain this information. Examples of the best spectra obtained under these conditions are recorded in this section and the splitting constants given where available.

The spectrum produced from p-nitrotoluene in the presence of potassium t-butoxide in dimethyl sulfoxide - t-butyl alcohol under unspecified conditions is given in Figure 65. It is very similar to the published

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[1] Diphenylpicrylhydrazyl is a commercially available stable free radical.

[2] In this section, unless otherwise stated, dimethyl sulfoxide - t-butyl alcohol solution describes a mixture of predominantly dimethyl sulfoxide (over 90% by volume); since the potassium t-butoxide added to these solutions was dissolved in t-butyl alcohol an undetermined amount of alcohol was added to the solution of the nitroaromatic in dimethyl sulfoxide.

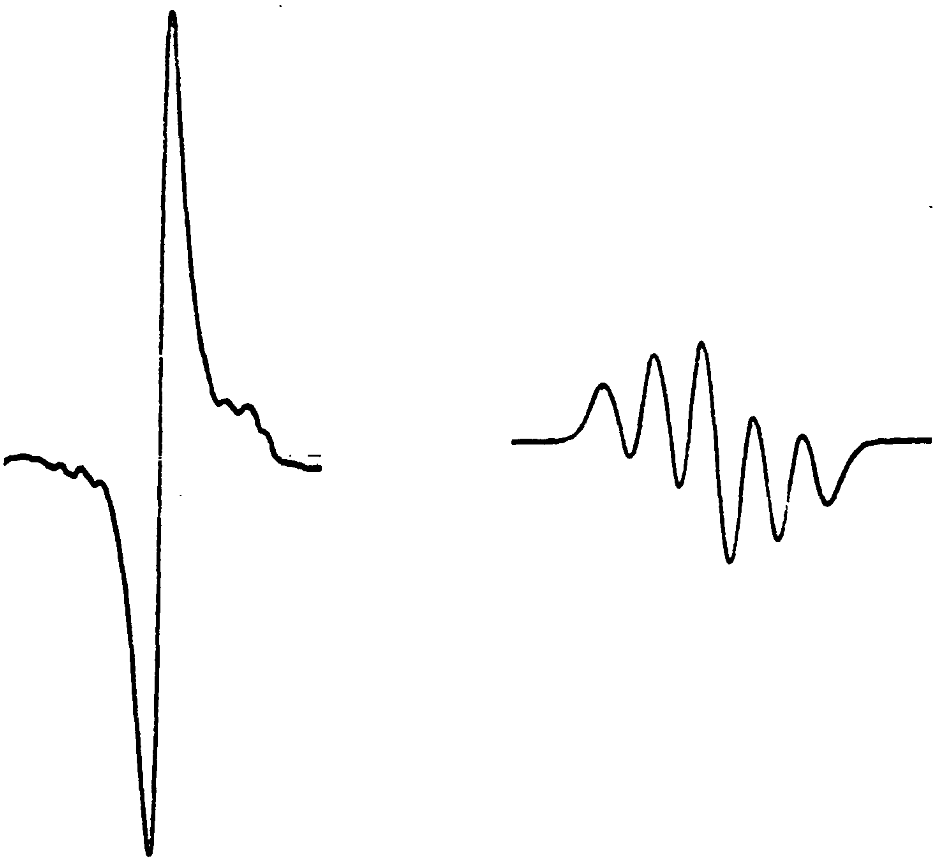


Figure 64. E.S.R. signal of spontaneously formed radical from p-nitrotoluene in t-butyl alcohol containing potassium t-butoxide (left) and diphenylpicrylhydrazyl under identical conditions (right, see text for concentrations)

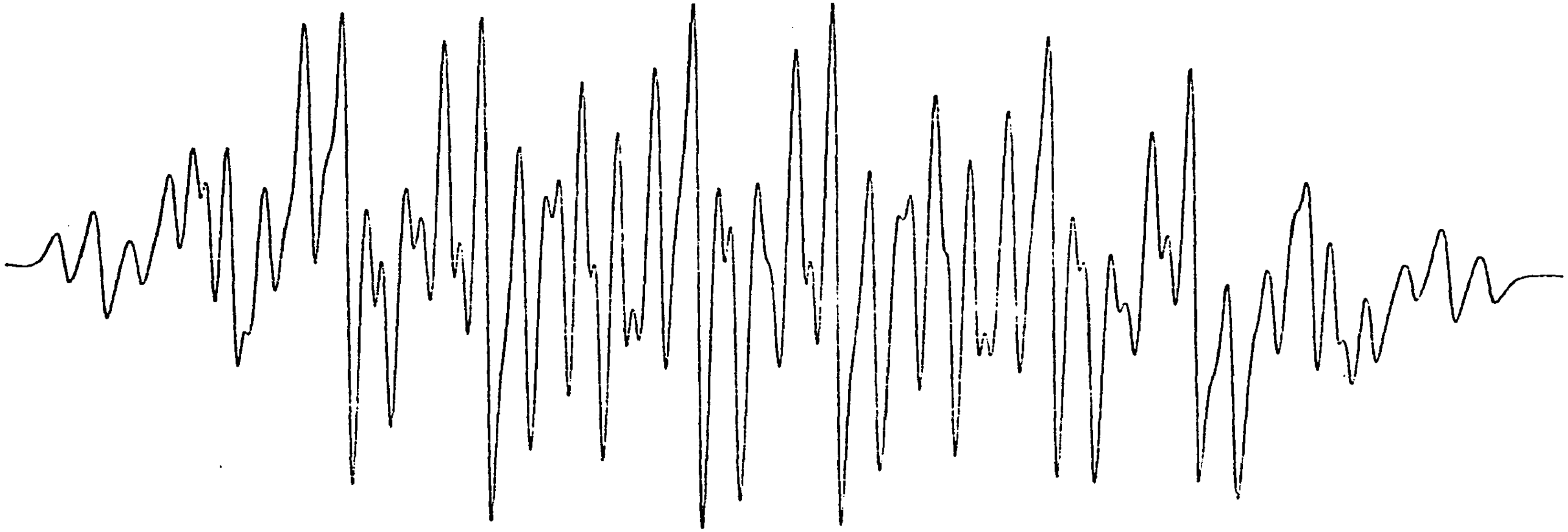
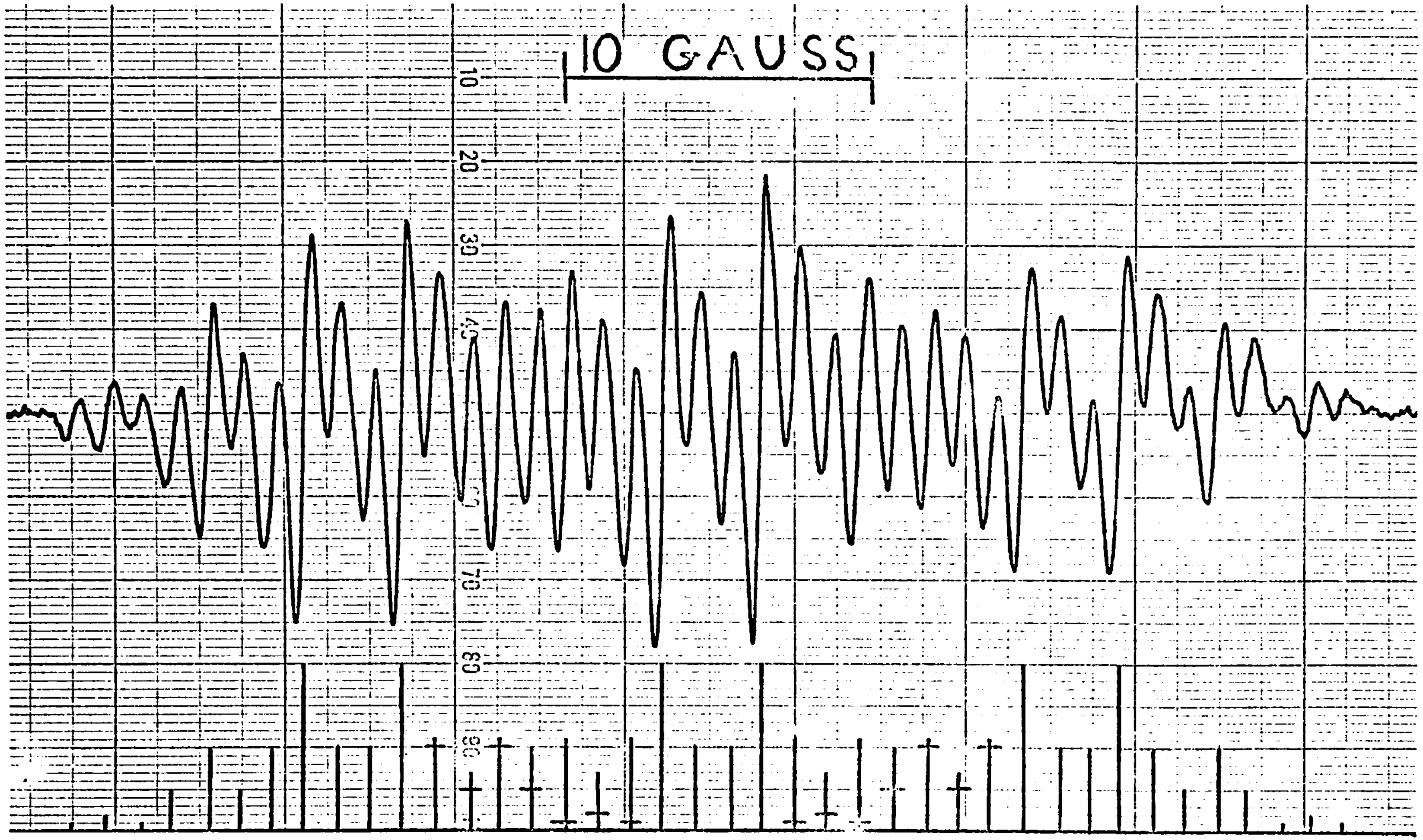


Figure 65. E.S.R. spectrum of p-nitrotoluene radical anion in dimethyl sulfoxide - t-butyl alcohol spontaneously generated in the presence of potassium t-butoxide

spectrum for *p*-nitrotoluene radical anion generated electrolytically in acetonitrile by Maki and Geske (38). On direct comparison it is found that our spectrum had 68 out of 70 of the peaks and shoulders recorded in the published spectrum although numerous peak intensities were different. The great similarity of the spectra concerned allowed us to assign the structure of the *p*-nitrotoluene radical anion to the radical species formed spontaneously in basic solution of *p*-nitrotoluene.

In *t*-butyl alcohol a spectrum of different appearance was obtained (Figure 66). Since the concentrations of *p*-nitrotoluene and potassium *t*-butoxide were 0.05 M and 0.01 M respectively for this experiment higher resolution of the spectra beyond the 40 lines given may have been prevented by the phenomena of line-broadening due to electron-exchange in the presence of the large concentration of *p*-nitrotoluene. The spectrum could be analyzed and splitting constants of $a_N = 12.7$, $a_{\underline{\alpha}\text{-H}}$ $a_{\underline{o}\text{-H}} = 3.4$ and $a_{\underline{m}\text{-H}} = 1.1$ gauss with an error of ± 0.1 gauss were assigned to the *p*-nitrotoluene radical ion in *t*-butyl alcohol containing potassium *t*-butoxide partial overlap and incomplete resolution limiting the number of lines observed to 40. A synthesized spectrum of lines based on the given splitting constants is shown underneath the recorded spectrum for comparison purposes. The short horizontal lines indicate additive overlap of hyperfine components. Maki and Geske (38) found the splitting constants in acetonitrile to be $a_N = 10.79$, $a_{\underline{\alpha}\text{-H}} = 3.98$, $a_{\underline{o}\text{-H}} = 3.39$ and $a_{\underline{m}\text{-H}} = 1.11$ gauss. A comparison of these values indicates a significant solvent effect on the nitrogen splitting constant of *p*-nitrotoluene operating in our solution of *t*-butyl alcohol. About the time of this work a number of publications reporting solvent effects in other solvents

Figure 66. E.S.R. spectrum of p-nitrotoluene radical anion in t-butyl alcohol spontaneously formed by potassium t-butoxide in the absence of air; $a_N = 12.7$, $a_{\underline{\alpha}\text{-H}} = a_{\underline{o}\text{-H}} = 3.4$, $a_{\underline{m}\text{-H}} = 1.1$ gauss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appeared in the literature (41, 139). The origin of the solvent effect is not clear and has not been studied in this work.

Attempts to improve the resolution on the E.S.R. spectrum obtained in t-butyl alcohol was unsuccessful because of the formation of a second strong signal a few minutes after mixing approximately in the middle of the spectrum. Later work indicated that this signal was due to a solid radical, possibly p,p'-dinitrobibenzyl radical anion. Figure 67 (top) gives a typical spectrum obtained in t-butyl alcohol some time after adding potassium t-butoxide to a solution containing p-nitrotoluene. For comparison the spectrum obtained from a much more dilute solution shortly after mixing is given (bottom). It was found that under conditions where unionized p-nitrotoluene was in large excess as in Figure 66 or where all concentrations were very low as in Figure 67 (bottom) the second radical was not observed within reasonable time (approximately 1 hr.) after mixing. In tetrahydrofuran or pyridine a similar spectrum with a strong center peak was recorded and a precipitate was present in the solution, although in dimethyl sulfoxide (Figure 65) all components were in solution and no second radical peak was observable.

The spectrum in Figure 67 (bottom) was recorded from a solution evacuated, degassed and sealed on a high vacuum line on December 16, 1961. On April 12, 1962 the single peak in Figure 68 (top) was obtained from the same solution. The color of the solution which was originally pink had changed to faint yellow-pink and a brownish-yellow precipitate had coated on the glass wall. During the period of 5 months the radical components in the solution had changed to yield species whose hyperfine spectrum could not be resolved. This is indicative from our previous

Figure 67. E.S.R. spectra of spontaneously formed p-nitrotoluene radical anion in t-butyl alcohol indicating second radical species thought to be precipitated, p,p'-dinitrobibenzyl radical anion (top) and for comparison p-nitrotoluene radical anion in a more dilute solution (bottom)

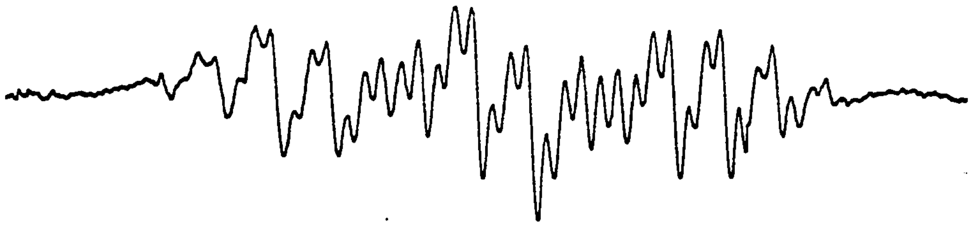
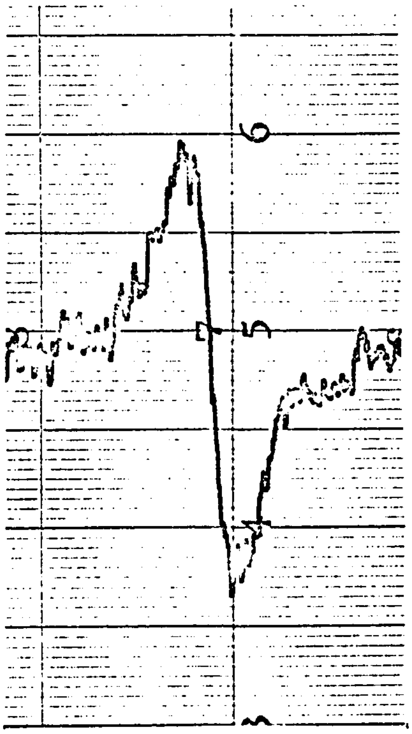


Figure 68. E.S.R. signals from radical species 5 months after mixing solutions of _p_-nitrotoluene and potassium _t_-butoxide in _t_-butyl alcohol (top) and after exposure to air for 2 hrs. (bottom)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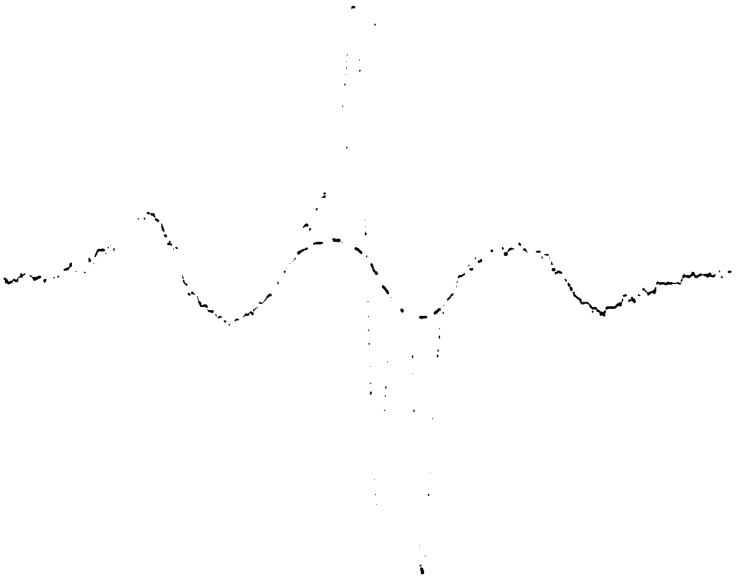


observations that all of the radical species had been converted to the precipitate radical, possibly *p,p'*-dinitrobibenzyl radical anion.

Figure 68 (bottom) shows a spectrum obtained from a solution of *p*-nitrotoluene in *t*-butyl alcohol containing potassium *t*-butoxide which had been exposed to air for 2 hr. A strong radical signal was still evident apparently due to two radical species in the mixture.

A partially resolved spectrum of *p*-nitroethylbenzene radical anion is shown in Figure 69 spontaneously produced by ionization of 0.02 M *p*-nitroethylbenzene in *t*-butyl alcohol with 0.45 M potassium *t*-butoxide 10 min. after mixing. The splitting constants which provide a fairly good fit to the partially resolved spectrum are, $a_N = 13.4_2$, $a_{\alpha\text{-H}} \simeq a_{o\text{-H}} = 3.1_3$ and $a_{m\text{-H}} = 1.1_2 \pm 0.1$ gauss. The synthetic spectrum drawn below the recorded spectrum has been constructed with these parameters. The 3-fold symmetry is evident, the left and middle branches providing the data used in obtaining the constants. At the time of this work for some unknown reason the spectrometer resolved the right branch poorly and showed slightly different field strength in this region. Better spectra should be available at this time.

p-Nitrocumene gave no radicals in *t*-butyl alcohol although in 50% dimethyl sulfoxide - 50% *t*-butyl alcohol *p*-nitrocumene spontaneously gave free radicals (Figure 70) in the presence of potassium *t*-butoxide (1.7×10^{-3} M *p*-nitrocumene, 0.08 M potassium *t*-butoxide). If a similar splitting constant is used for the nitrogen atom as in *p*-nitrotoluene radical anion but a smaller splitting constant for the α-hydrogens than for the *ortho*-hydrogens a splitting pattern can be derived in good agreement with the observed spectrum for the *p*-nitrocumene radical anion.

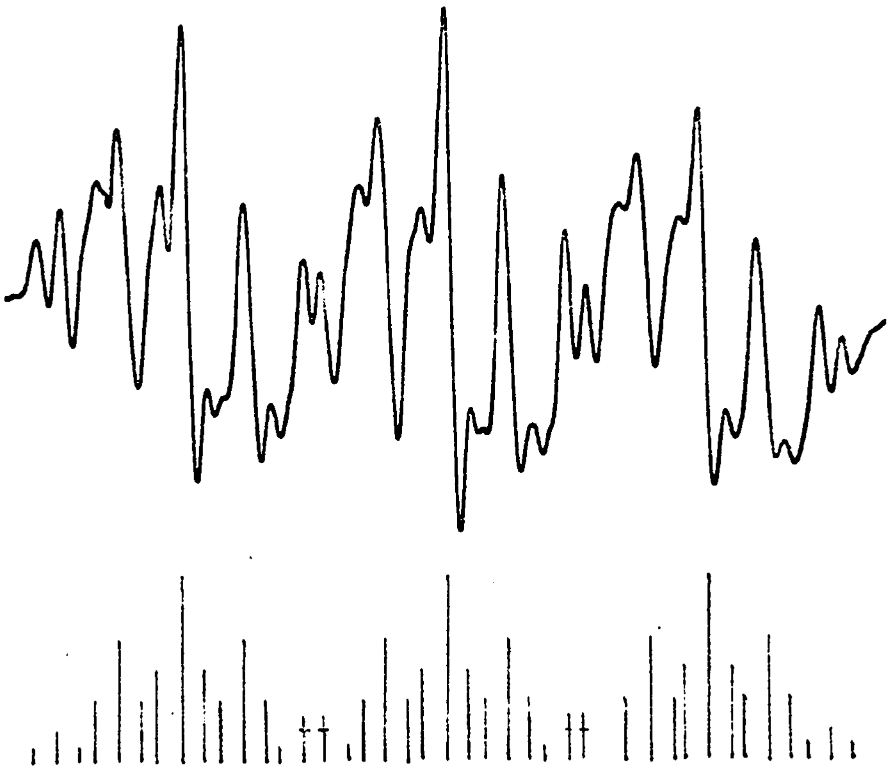
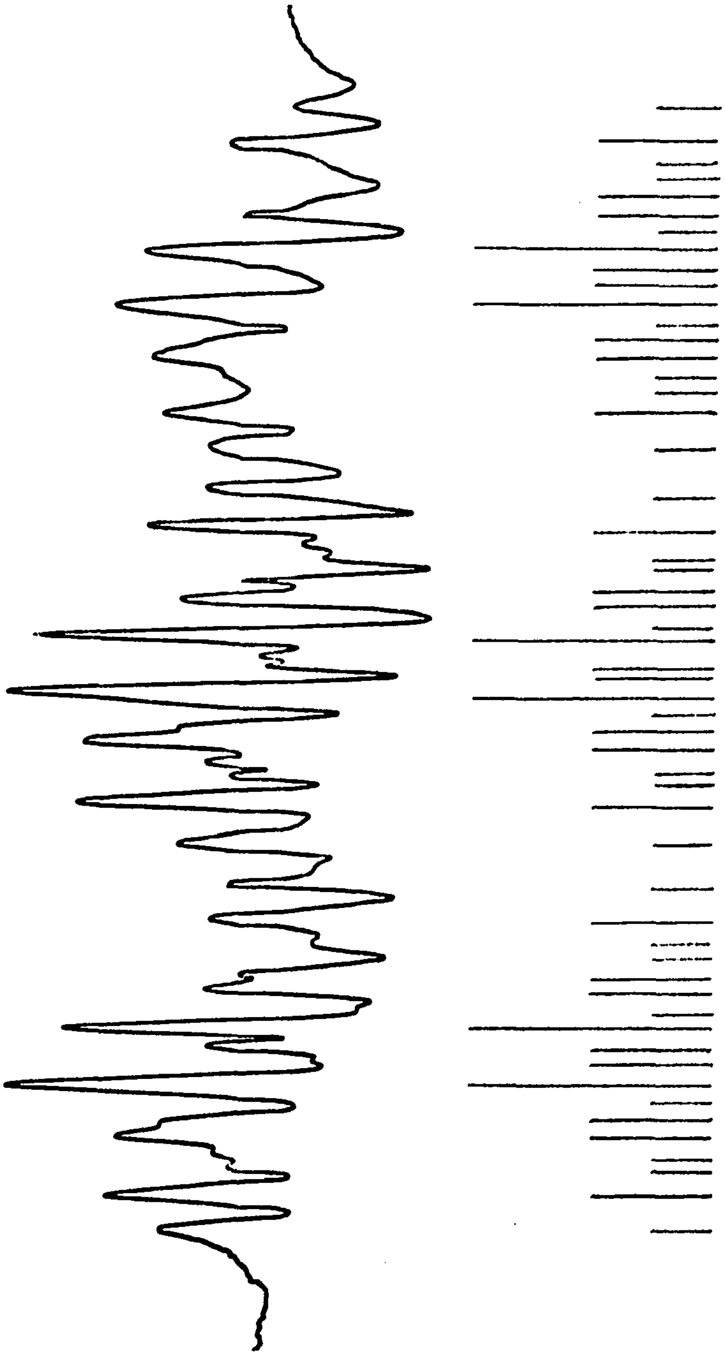


Figure 69. E.S.R. spectrum of p-nitroethylbenzene radical anion in t-butyl alcohol obtained by the action of 0.45 M potassium t-butoxide on 0.02 M p-nitroethylbenzene 10 min. after mixing $a_N = 13.4_2$, $a_{\alpha\text{-H}} \simeq a_{o\text{-H}} = 3.1_3$, $a_{m\text{-H}} = 1.1_2$ gauss ±0.1 gauss

Figure 70. E.S.R. spectrum of p-nitrocumene radical anion in 50% dimethyl sulfoxide - 50% t-butyl alcohol formed by the action of 0.08 M potassium t-butoxide on 1.7 x 10^{-3} M p-nitrocumene; $a_N = 12.1_1$, $a_{\alpha\text{-}H} = 1.7_9$, $a_{o\text{-}H} = 3.3_3$ and $a_{m\text{-}H} = 1.0_7$ gauss ±0.1 gauss



The synthetic spectrum in Figure 70 was constructed from the parameters, $a_N = 12.1_1$, $a_{\underline{\alpha}\text{-}H} = 1.7_9$, $a_{\underline{o}\text{-}H} = 3.3_3$ and $a_{\underline{m}\text{-}H} = 1.0_7 \pm 0.1$ gauss. Geske and McKinney[1] have observed $a_N = 10.62$, $a_{\underline{\alpha}\text{-}H} = 1.78$, $a_{\underline{o}\text{-}H} = 3.27$ and $a_{\underline{m}\text{-}H} = 1.10$ for p-nitrocumene radical anion in acetonitrile. As in the case of the p-nitroethylbenzene radical anion the right branch is more poorly resolved than the left and middle branches.

In the assignment of splitting constants for the three radical anions, p-nitrotoluene (PNT), p-nitroethylbenzene (PNEB) and p-nitrocumene (PNC), the constant for the α-hydrogens in PNT and PNEB were assumed approximately equal within the limits of the partial resolution obtained; however for PNC the splitting constant used for the α-hydrogen was different from the ortho-hydrogens. This choice can be justified by considering the splitting constant of the α-hydrogens of PNT to be slightly larger than those for the ortho-hydrogens, slightly smaller for PNEB and much smaller and now detectable under low resolution for PNC; i.e., the splitting constants follow the sequence

$$\underline{\alpha}\text{-H(PNT)} \gtrapprox \text{all } \underline{o}\text{-H} \gtrapprox \underline{\alpha}\text{-H(PNEB)} > \underline{\alpha}\text{-H(PNC)}$$

If under high resolution this order is still found to be correct it would indicate the following sequence of probability of the shown structures contributing to the resonance hybrid of the respective radical anions:

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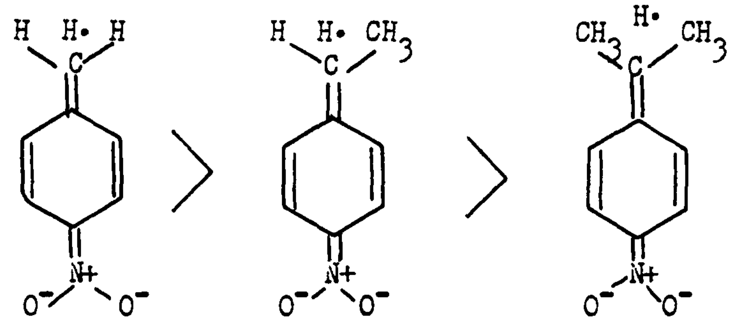
[1] D. H. Geske and T. W. McKinney, Observation of conformational isomers in the electron spin resonance spectrum of the anion free radical of 2,3,5,6-tetraisopropylnitrobenzene. Unpublished paper presented at the 144th Meeting of the American Chemical Society, Los Angeles, California, April, 1963.



All *ortho*-substituted *p*-nitrotoluenes studied gave free radicals spontaneously in base in the absence of air. For some of these splitting constants were obtained from the spectra obtained under low resolution (Table 15). In *t*-butyl alcohol containing potassium *t*-butoxide *o*-bromo-*p*-nitrotoluene gave a blue solution and a reasonably high concentration of radicals (Figure 71, top). The spectrum obtained from *o*-methyl-*p*-nitrotoluene in dimethyl sulfoxide - *t*-butyl alcohol could not be solved easily by inspection (Figure 71, bottom), although in *t*-butyl alcohol (Figure 72) a nitrogen splitting constant of approximately 13 gauss was estimated. *o*-Amino-*p*-nitrotoluene gave a red solution containing some precipitate in *t*-butyl alcohol. The spectrum obtained (Figure 73, top) had a large peak similar to that found for *p*-nitrotoluene approximately in the middle of the spectrum possibly also due to a precipitated free radical. The potassium salt of *o*-sulfonate-*p*-nitrotoluene was extremely insoluble in *t*-butyl alcohol and a very weak unresolved absorption peak was obtained from a pale blue solution. However in 50% dimethyl sulfoxide - 50% *t*-butyl alcohol potassium *t*-butoxide produced the free radical spectrum shown in Figure 73 (bottom). Again apparently a solid radical

Table 15. Splitting constants for nitroaromatic radical anions

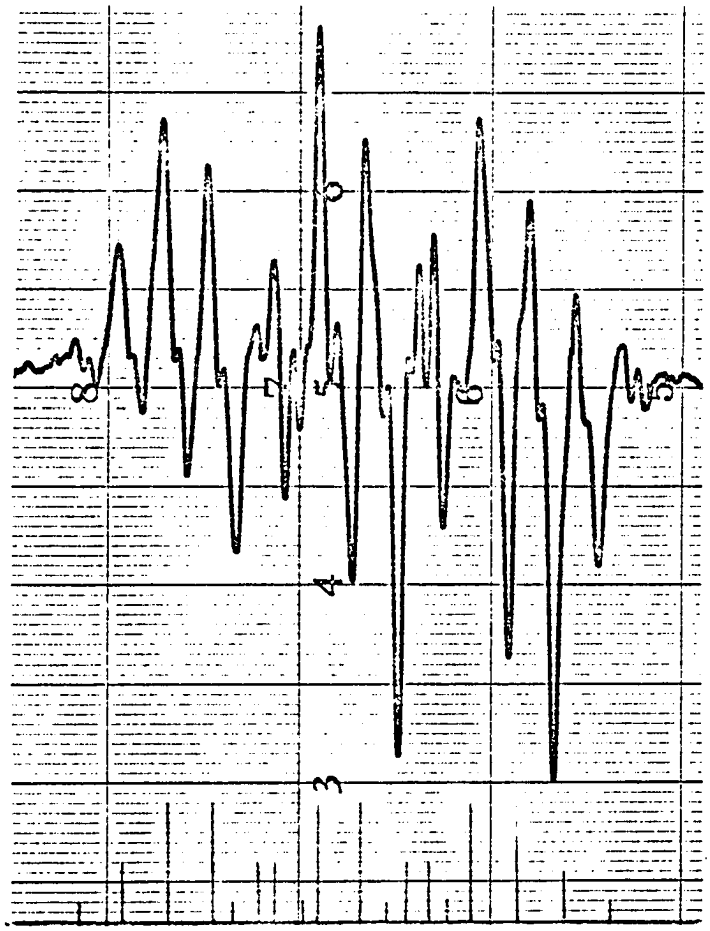
Radical anion	Figure	a_N	$a_{\alpha\text{-H}}$	$a_{o\text{-H}}$	$a_{m\text{-H}}$	Solvent[a]
p-nitrotoluene[b]		10.79	3.98	3.39	1.11	CH_3CN
p-nitrotoluene	66	12.7	3.4	3.4	1.1	*t*-BuOH
p-nitroethylbenzene	69	13.4_2	3.1_3	3.1_3	1.1_2	*t*-BuOH
p-nitrocumene	70	12.1_1	1.7_9	3.3_3	1.0_7	50/50
t-butoxy-*p*-nitrobenzoate (?)	75	9.3_4		3.0_8	0.7_8	*t*-BuOH
o-bromo-*p*-nitrotoluene	71	12.8	3.6_6			*t*-BuOH
o-methyl-*p*-nitrotoluene	72	13.0				*t*-BuOH
o-amino-*p*-nitrotoluene	73	12.8_2	3.4_4			*t*-BuOH
o-nitro-*p*-nitrotoluene	74	11.8_5	3.4_7			*t*-BuOH
o-nitrotoluene	76	13.2				*t*-BuOH
o-nitroethylbenzene	77	13.3				*t*-BuOH
nitromesitylene	77	18.7				DMSO/BuOH
2-nitrofluorene	81	12.1_0		3.2_7		*t*-BuOH

[a] CH_3CN = acetonitrile; *t*-BuOH = *t*-butyl alcohol; 50/50 = 50% dimethyl sulfoxide - 50% *t*-butyl alcohol; DMSO/*t*-BuOH = dimethyl sulfoxide - *t*-butyl alcohol

[b] Maki and Geske (38)

was present in the solution which gave the strong narrow peak in the center of the spectrum. 2,4-Dinitrotoluene gave a reasonable concentration of radicals in *t*-butyl alcohol in deficient base; however the signal had almost entirely disappeared by 0.5 hr. (Figure 74, 0.02 M dinitrotoluene, 0.01 M potassium *t*-butoxide). In excess base (0.16 M potassium *t*-butoxide) a very weak signal was obtained which could not be resolved. 2,4,6-Trinitrotoluene gave a very weak unresolved peak in excess base but no signal in

Figure 71. E.S.R. spectra of o-bromo-p-nitrotoluene radical anion (top) spontaneously formed in t-butyl alcohol after ionization by potassium t-butoxide in the absence of air (a_N = 12.8 gauss) and o-methyl-p-nitrotoluene radical anion (bottom) in dimethyl sulfoxide - t-butyl alcohol containing potassium t-butoxide in the presence of a trace of air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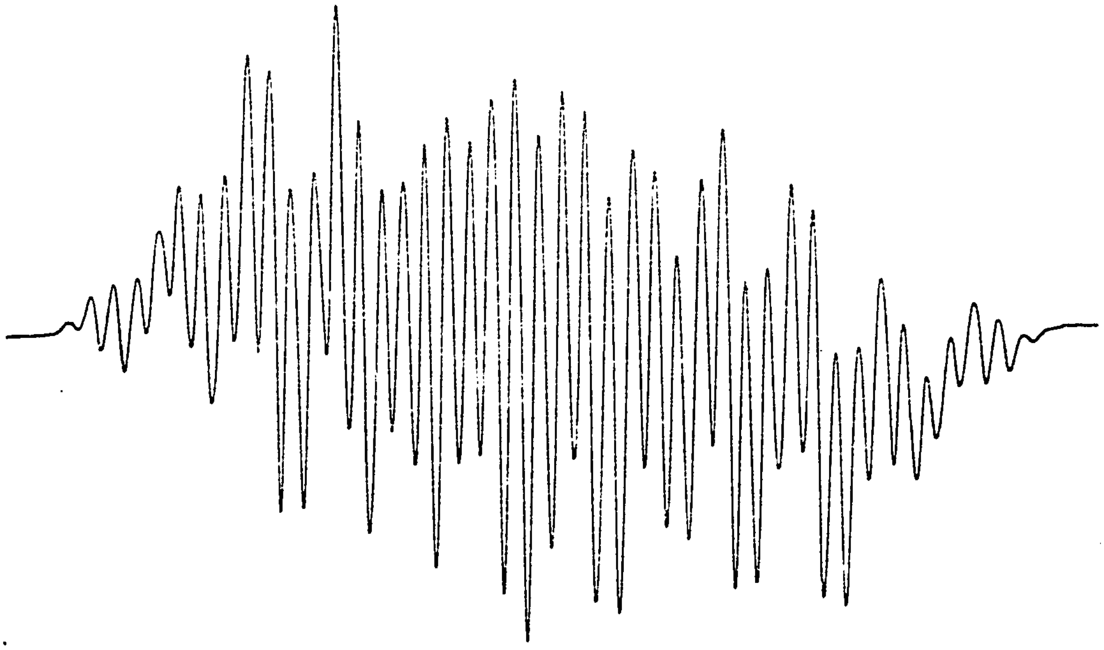

Figure 72. E.S.R. spectrum of o-methyl-p-nitrotoluene radical anion in t-butyl alcohol formed in the absence of air by potassium t-butoxide (a_N = 13.0 gauss)

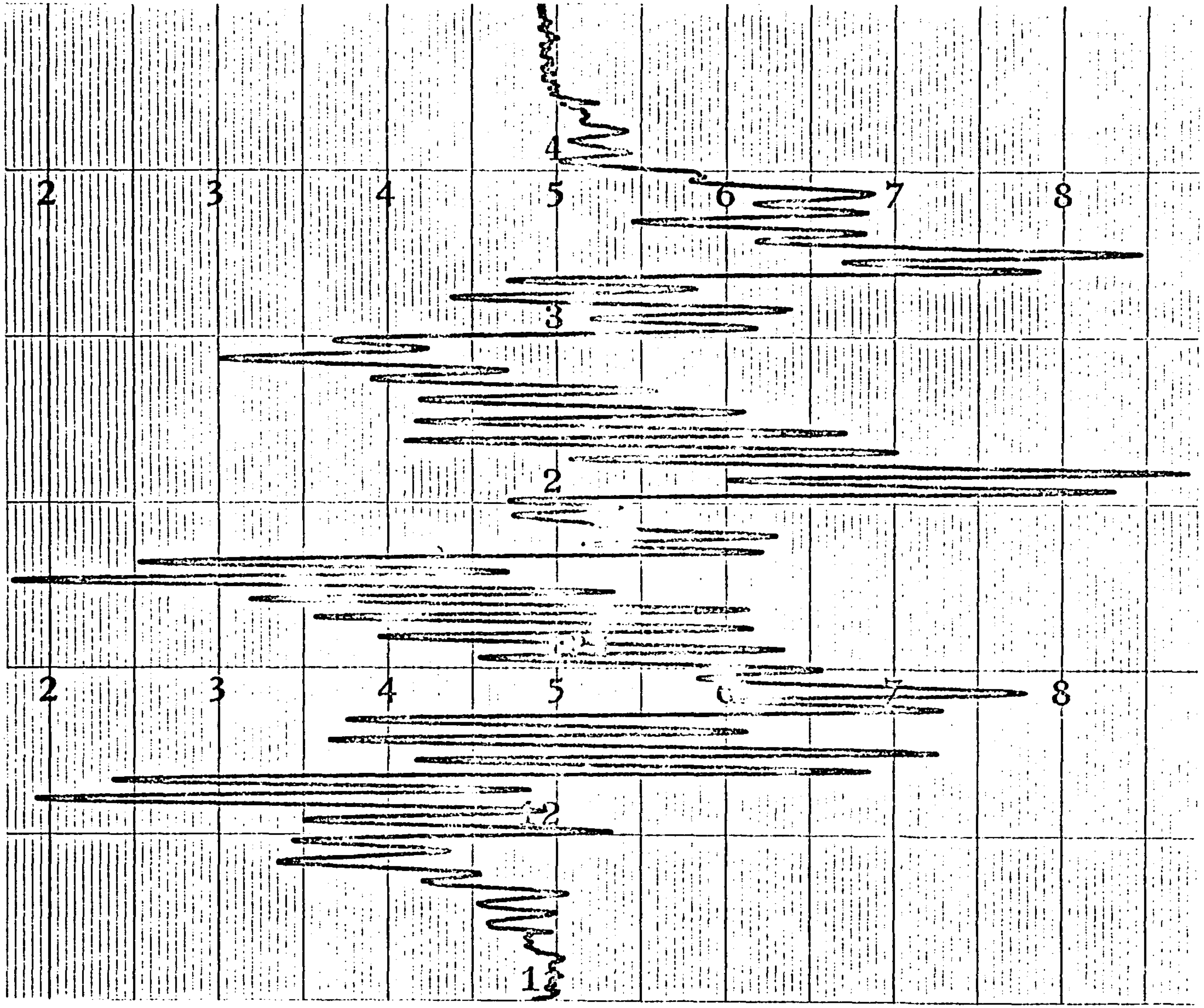
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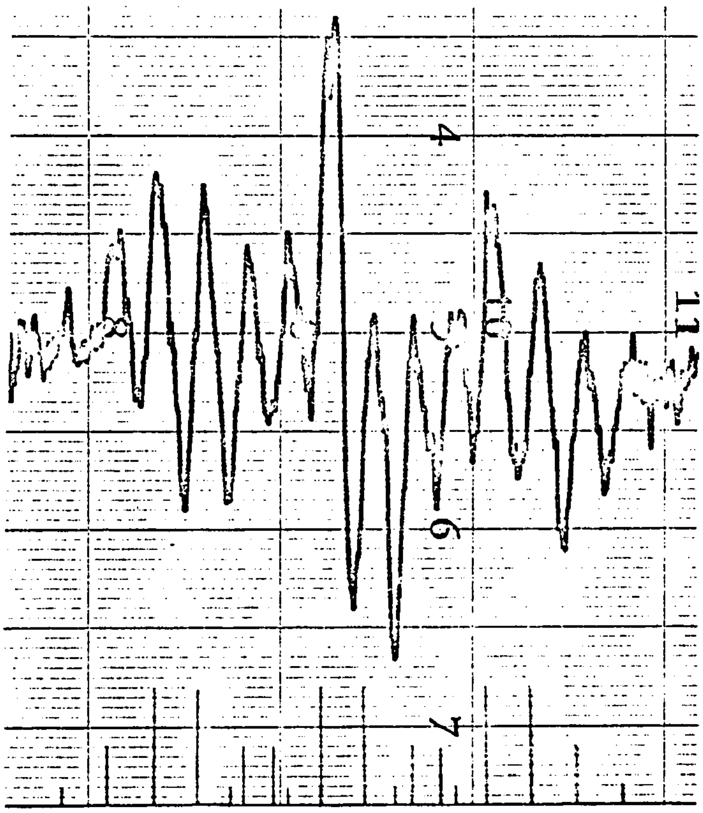
Figure 73. E.S.R. spectrum of o-amino-p-nitrotoluene radical ion (top) in t-butyl alcohol formed spontaneously with potassium t-butoxide ($a_N = 12.8_2$ gauss) and the radical species from potassium o-sulfonate-p-nitrotoluene in 50% dimethyl sulfoxide - 50% t-butyl alcohol containing potassium t-butoxide (bottom)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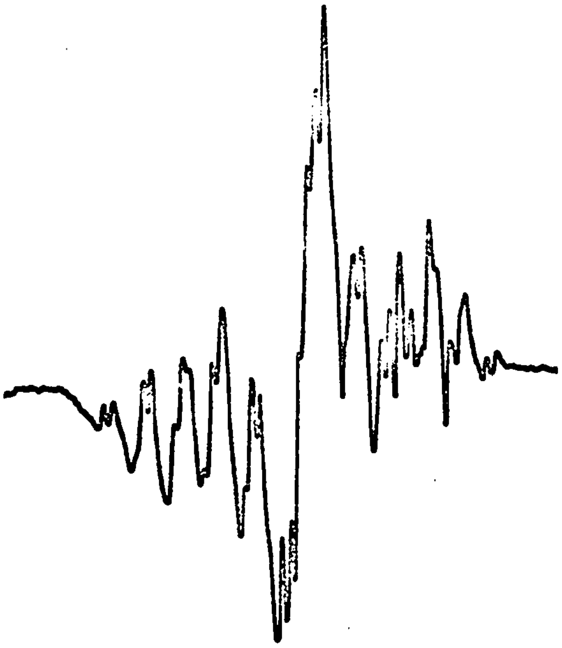
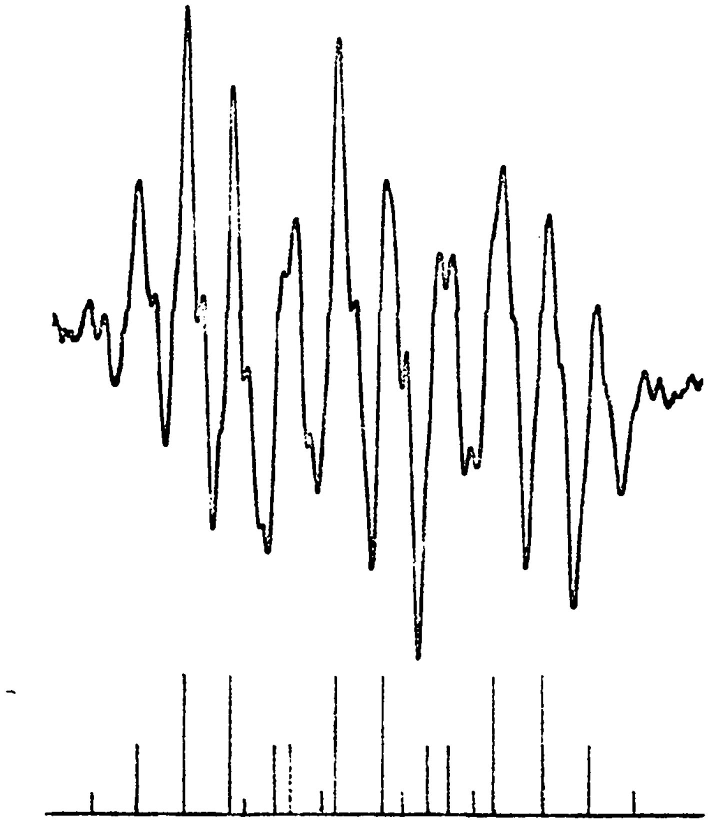
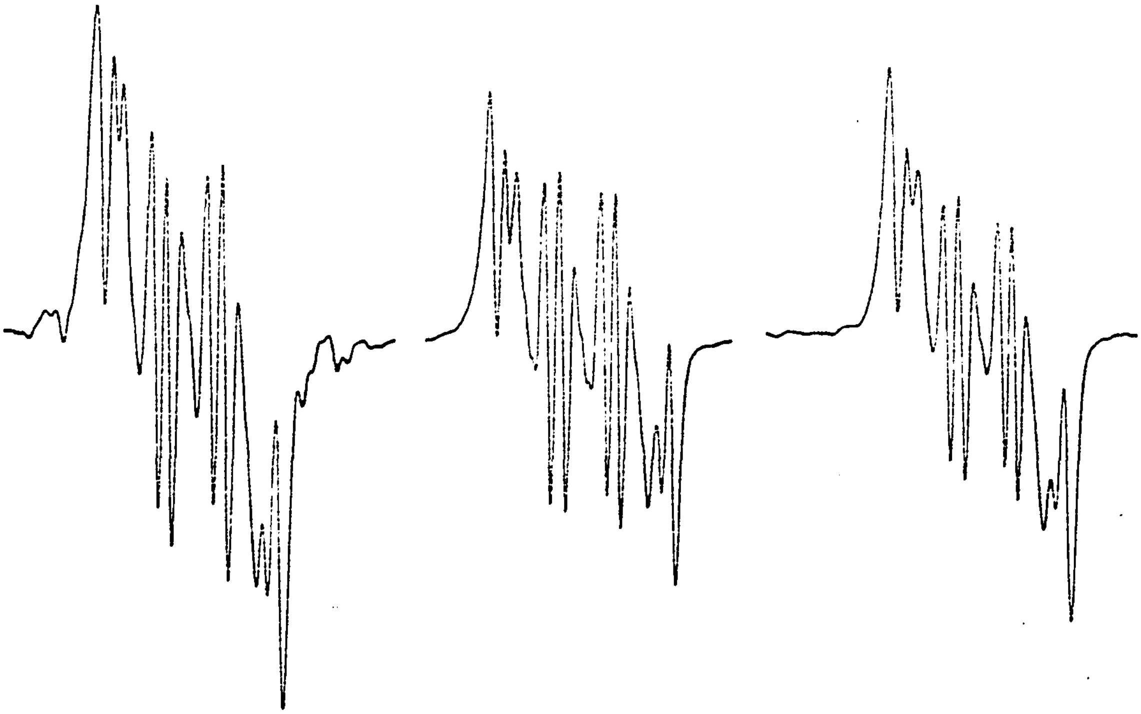


Figure 74. E.S.R. spectrum (top) of 2,4-dinitrotoluene radical anion in t-butyl alcohol spontaneously generated in deficient base by potassium t-butoxide (a_N = 11.8$_5$ gauss)

E.S.R. spectra (bottom) in dimethyl sulfoxide - t-butyl alcohol containing potassium t-butoxide of p-nitrobenzyl alcohol in the absence of air (left), and p-nitrobenzyl alcohol (middle) and p-nitrobenzaldehyde (right) in the presence of a trace of air



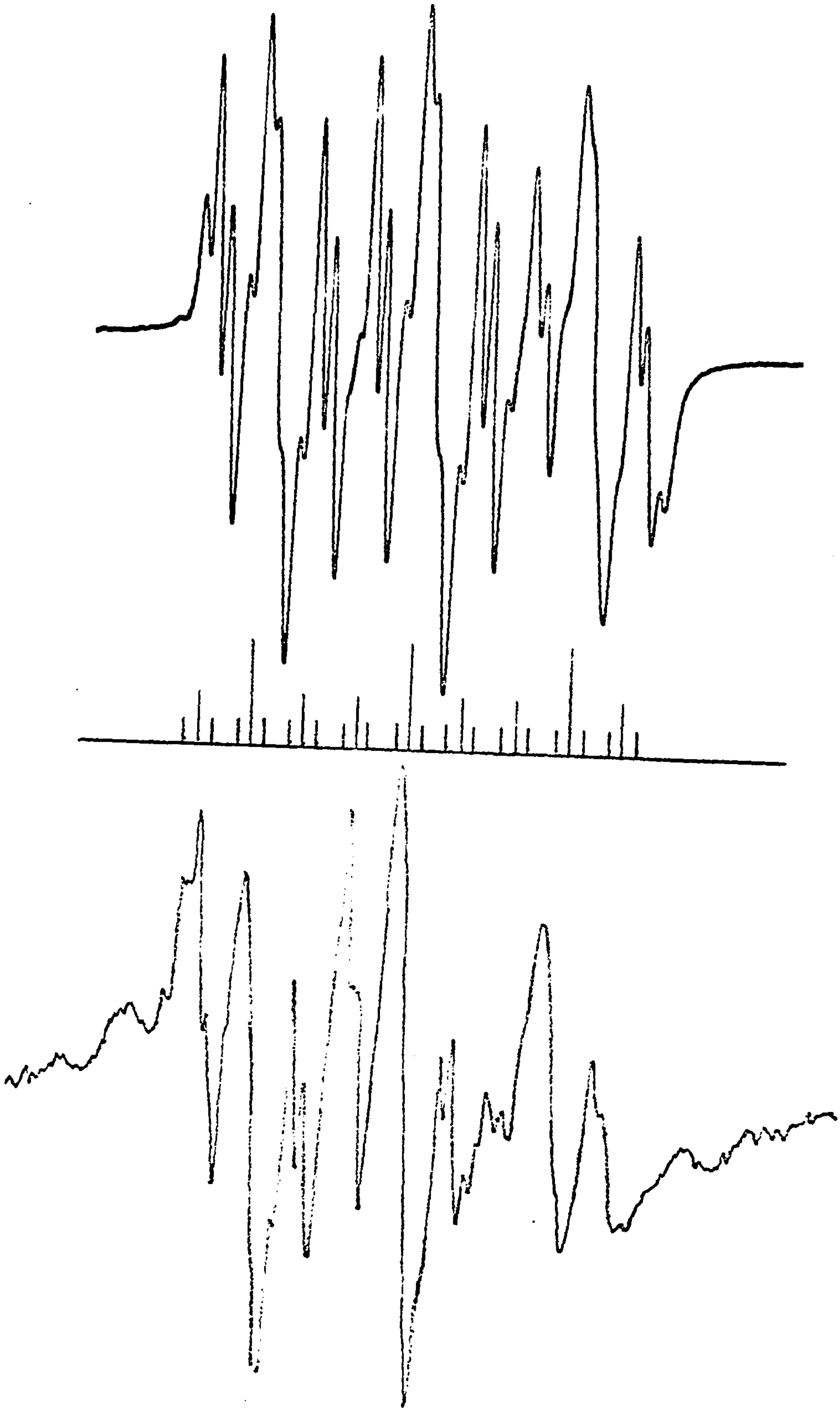


deficient base.

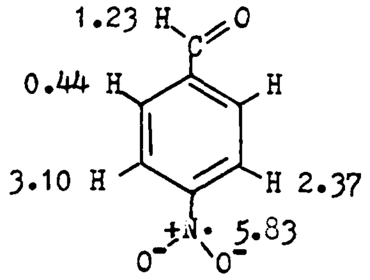
The spectra of the *ortho*-substituted *p*-nitrotoluenes from which the nitrogen and hydrogen splitting constants were obtained were solved by analogy to the described spectrum of *p*-nitrotoluene in *t*-butyl alcohol. The splitting constants for the *α*-hydrogens were assumed approximately equal to the hydrogens ortho to the nitro group. If these hydrogens were exactly equivalent 5 peaks with intensity 1:5:10:10:5:1 would be expected; if the 5 hydrogens were approximately equivalent, with 2 and 3 hydrogens identical but differing slightly in splitting constants so that they could not be resolved, one might expect 6 peaks again but with intensities 1:3:6:6:3:1 since the overlap was not exact enough to be additive. The constructed spectra for the *ortho*-substituted *p*-nitrotoluenes have been drawn to the latter scale. The spectrum of *p*-nitroethylbenzene radical anion however has the constructed lines in an order of intensity 1:4:6:4:1 for 4 exactly equivalent hydrogens (*α*- and *o*-).

Both *p*-nitrobenzyl alcohol and *p*-nitrobenzaldehyde formed free radicals spontaneously in basic solutions. In dimethyl sulfoxide - *t*-butyl alcohol containing potassium *t*-butoxide in the presence of a trace of air the spectra obtained from *p*-nitrobenzaldehyde and *p*-nitrobenzyl alcohol were virtually identical (Figure 74, bottom); in the absence of air almost the same spectra was obtained from *p*-nitrobenzyl alcohol except for a few additional peaks on both edges. In *t*-butyl alcohol a fairly well resolved spectrum was obtained from *p*-nitrobenzaldehyde (Figure 75, top) which could be fitted to three splitting constants due to its 3-fold symmetry: 9.3_4, 3.0_8 and 0.7_8 gauss. Since the spectrum could be considered a set of 9 triplets, the largest splitting constant was assigned to the nitrogen of the

Figure 75. E.S.R. spectra of radical species spontaneously formed in t-butyl alcohol by 0.02 M p-nitrobenzaldehyde (top) and 0.02 M p-nitrobenzyl alcohol (bottom) in the presence of potassium t-butoxide

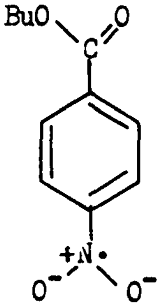


nitro group, $a_N = 9.34$ gauss; for two equivalent protons probably ortho to the nitrogen, $a_{\underline{o}\text{-}H} = 3.08$ gauss, and for two more equivalent protons, $a_H = 0.78$ gauss. Maki and Geske reported the following splitting constants for p-nitrobenzaldehyde radical anion in acetonitrile (38):



XXXIII

We had observed a solvent effect for p-nitrotoluene of approximately 2 gauss greater for the nitrogen splitting constant in t-butyl alcohol than in acetonitrile. On the assumption that the t-butyl alcohol solvent effect would increase the nitrogen splitting constant in our spectrum by approximately the same amount the value should be about 7.8 gauss if the radical species were p-nitrobenzaldehyde radical anion. The difference of 1.5 gauss suggested that p-nitrobenzaldehyde radical anion was not the radical observed, nor was the splitting pattern easily reconciled with that expected from p-nitrobenzaldehyde radical anion. Of the para-substituted nitrobenzene radical anions reported by Maki and Geske (38) the splitting constants for methyl p-nitrobenzoate best agree with those obtained from our spectra, $a_N = 7.73$ ($7.73 + 2$ (solvent effect) $= 9.7$) and $a_{\underline{o}\text{-}H} = 3.11$ gauss. The conclusion has been made that the radical species spontaneously formed in t-butyl alcohol from potassium t-butoxide and p-nitrobenzaldehyde is t-butyl nitrobenzoate radical anion.

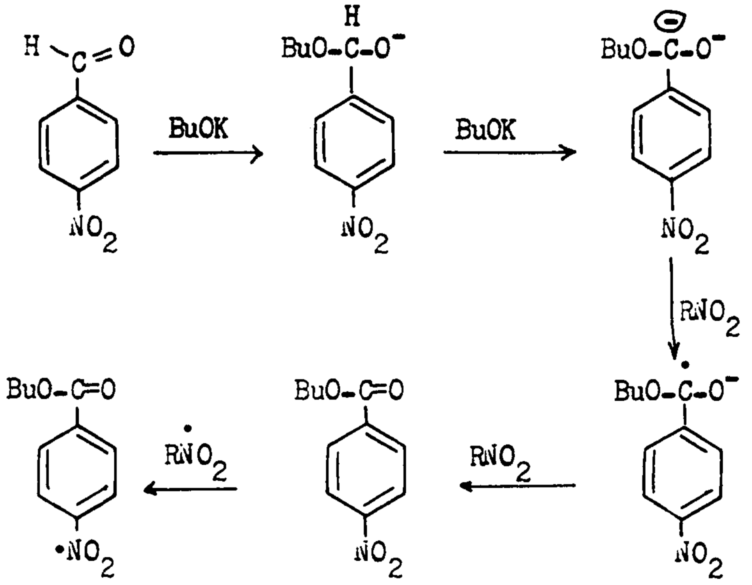


XXXIV

Maki and Geske (38) observed hindered rotation of the aldehyde group in p-nitrobenzaldehyde radical anion which caused the splitting constants to differ for the protons ortho to the nitro group. In methyl p-nitrobenzoate the broad peaks obtained possibly due to a higher frequency of rotation of the carbomethoxy group did not allow them to separate two different hydrogen splitting constants although their presence was suggested. The parameters chosen to construct the comparing spectrum in Figure 75 provide a reasonable fit but do not reproduce the observed spectrum exactly since a number of small peaks are unaccounted for. It is possible that if our spectrum is that of t-butyl p-nitrobenzoate radical anion the rotational frequency of the carbo-t-butoxy group is low enough (due to large steric hindrance to rotation) to cause a significant difference in the ortho-hydrogen splitting constants of the radical anion as was the case in p-nitrobenzaldehyde radical anion reported.

The presence of t-butyl p-nitrobenzoate radical anion in a solution of potassium t-butoxide in t-butyl alcohol can be accounted for by the following reaction:

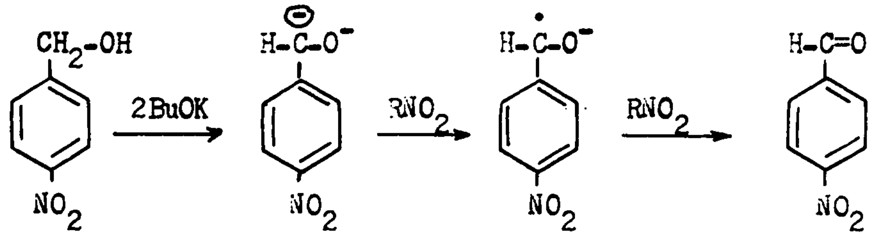
(166)



The same spectra was obtained in excess or deficient base (0.05 M or 0.02 M potassium *t*-butoxide with 0.02 M *p*-nitrobenzaldehyde). The different number of absorption peaks for this reaction in dimethyl sulfoxide suggests adduct formation involving the methylsulfinyl carbanion.

The spectra obtained from *p*-nitrobenzyl alcohol were never well resolved and at best in the absence of air indicated the presence of two radical species in solution both in dimethyl sulfoxide (Figure 74, bottom left) and in *t*-butyl alcohol (Figure 75, bottom). In both cases the great similarity in appearances of the absorption peaks suggested that *p*-nitrobenzaldehyde was formed spontaneously from *p*-nitrobenzyl alcohol in the basic solution.

(167)



An interesting effect of steric interaction between an *ortho*-alkyl group and the nitro substituent in a nitroaromatic radical anion was observed in the compounds *o*-nitrotoluene, *o*-nitroethylbenzene and nitromesitylene. The hindrance to rotation of the nitro group has the effect of reducing co-planarity of the substituent with the benzene ring causing a larger localization of the unpaired spin density on the nitrogen atom. This effect is reflected in the larger nitrogen splitting constant of these compounds (Table 15). During the time of this work Geske and Ragle (132) reported the same effect for a number of sterically hindered *ortho*-substituted nitrobenzenes. The spectra for *o*-nitrotoluene in *t*-butyl alcohol were not well resolved and only a nitrogen splitting constant was estimated (Figure 76, Table 15). The solution of the spectra for *o*-nitroethylbenzene and nitromesitylene was not attempted although the nitrogen splitting constant was easily obtained from the 3-fold symmetry of the splitting pattern (Figure 77, Table 15).

Both *p*,*p*'-dinitrobibenzyl and *bis*-2,3-(*p*-nitrophenyl)-butane gave radicals spontaneously in base. Figure 78 shows the spectra of the bibenzyl containing 14 lines observed either in the presence of air in dimethyl sulfoxide - *t*-butyl alcohol or in the absence of air in *t*-butyl alcohol. A better resolved spectrum in *t*-butyl alcohol at lower concentrations of bibenzyl is given in Figure 79. The spectra could not be solved by inspection although the relatively narrow total line width of approximately 25 gauss was suggestive of

$$NO_2\text{-}C_6H_4\text{-}\overset{\cdot}{C}H\text{-}\overset{\ominus}{C}H\text{-}C_6H_4\text{-}NO_2 \quad \text{rather than} \quad R\text{-}C_6H_4\text{-}\overset{\cdot}{N}O_2^-$$

for the structure of the radical. More work will be required both in

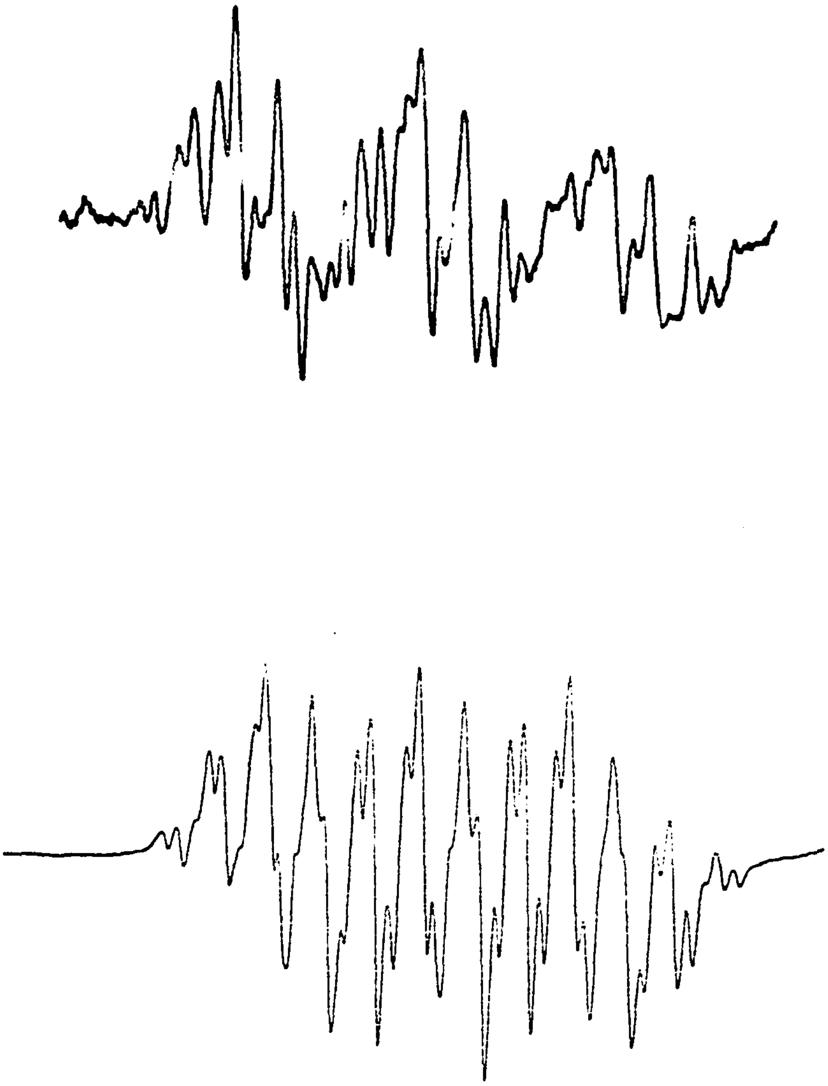
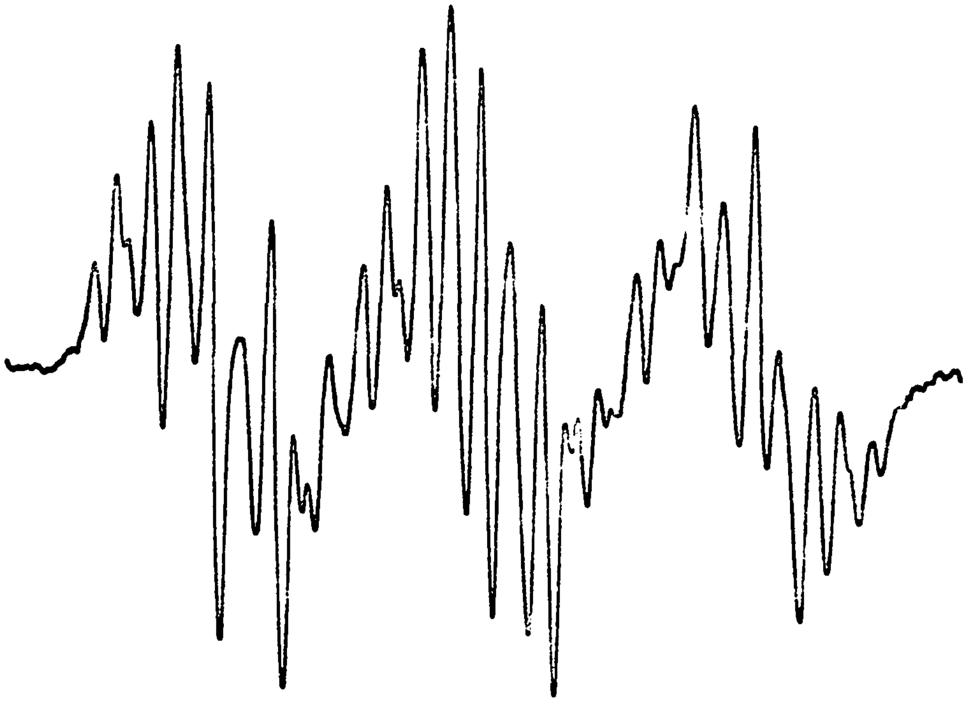


Figure 76. E.S.R. spectra of radical species from *o*-nitrotoluene spontaneously generated by potassium *t*-butoxide in *t*-butyl alcohol in the absence of air (top, a_N = 13.2 gauss) and in dimethyl sulfoxide - *t*-butyl alcohol in the presence of a trace of air (bottom, 1 cm. = 5.78 gauss)

Figure 77. E.S.R. spectra of radical species spontaneously formed in *t*-butyl alcohol from *o*-nitroethylbenzene (top, $a_N = 13.3$ gauss) and nitromesitylene in dimethyl sulfoxide - *t*-butyl alcohol (bottom, $a_N = 18.7$ gauss) in the presence of potassium *t*-butoxide



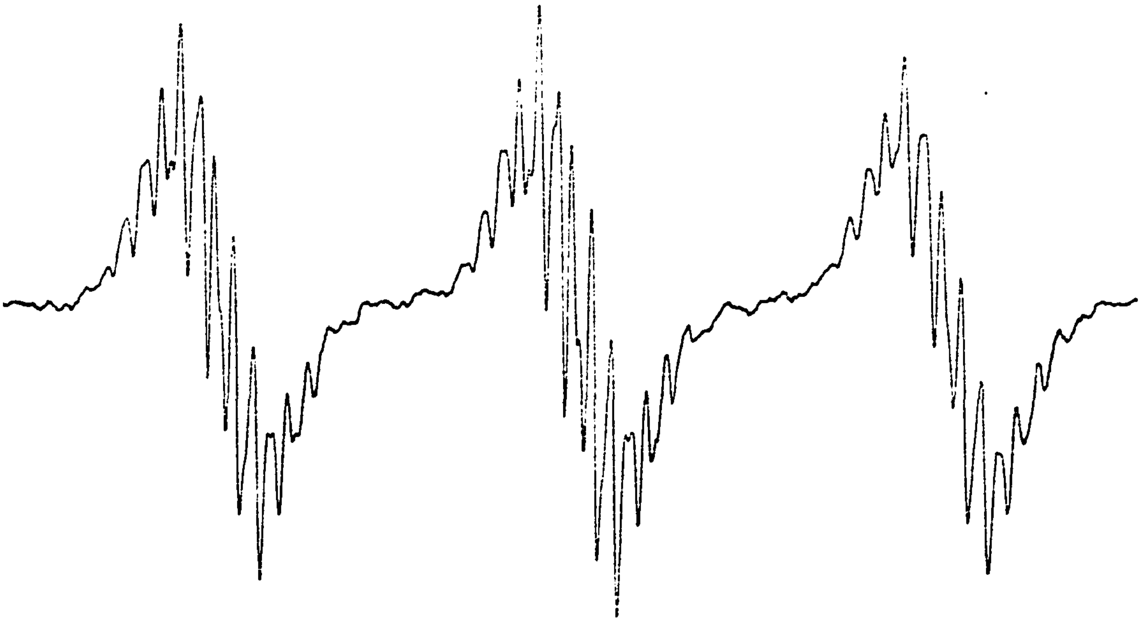
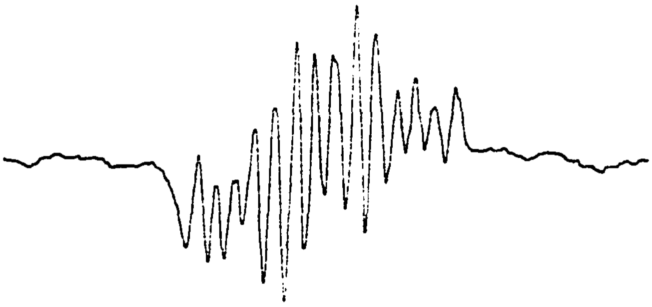
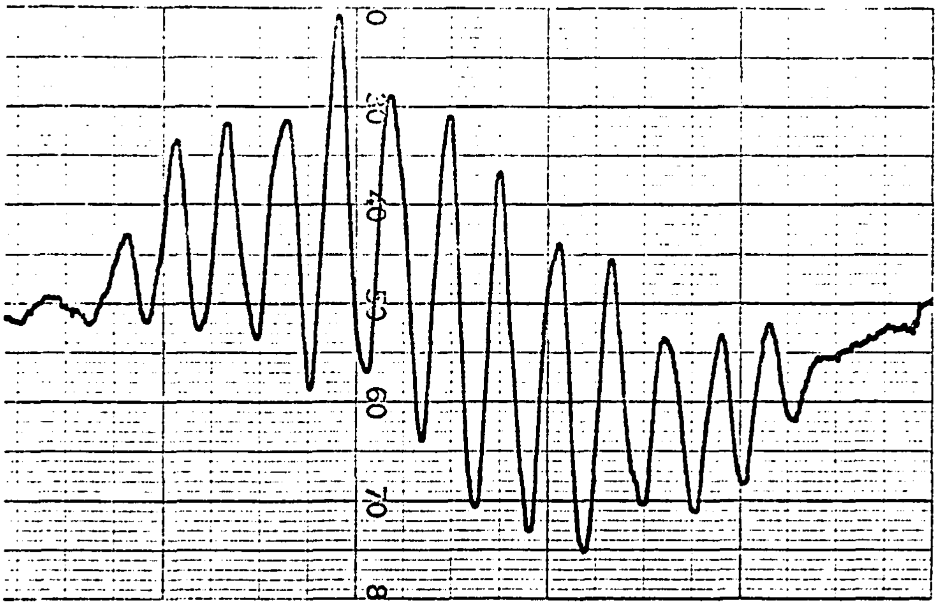


Figure 78. E.S.R. spectra of radical species formed from p,p'-dinitrobibenzyl and potassium t-butoxide in dimethyl sulfoxide - t-butyl alcohol with a trace of air (top) and in t-butyl alcohol in the absence of air (bottom, 1 cm. = 2.38 gauss)




0
30
40
50
60
70
80

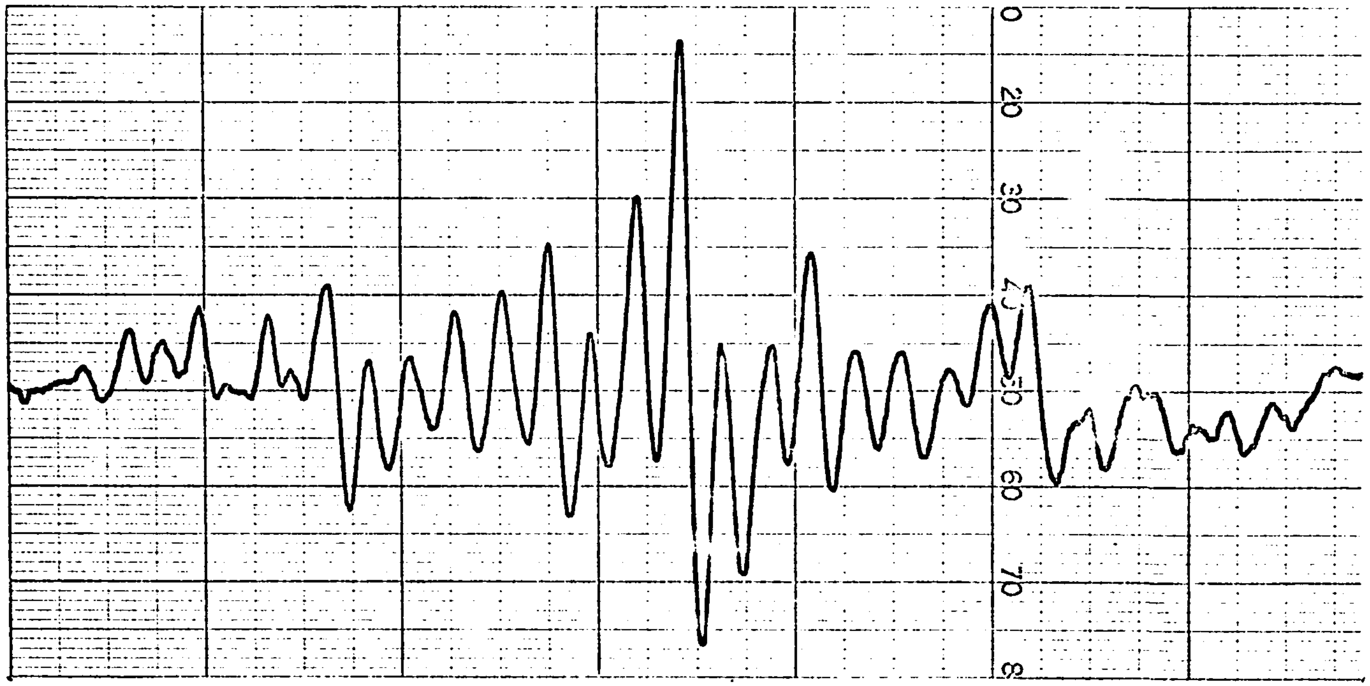


Figure 79. E.S.R. spectrum of spontaneously generated radical species in *t*-butyl alcohol in the absence of air by the action of potassium *t*-butoxide on *p*,*p*'-dinitrobibenzyl (1 cm. = 1.56 gauss)

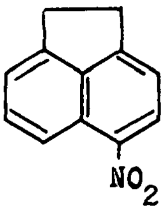
improving resolution and parameter fitting to solve the spectrum. Possibly a trans form of the radical must be taken into account. The spectra of the radical species from bis-2,3-(p-nitrophenyl)-butane were similar whether the reaction was run in the presence or absence of air (Figure 80) indicating as in the case of p,p'-dinitrobibenzyl that the same radical was formed under either conditions. The total line width of approximately 35 gauss did not rule out either of the following possible structures

$$NO_2\text{-}C_6H_4\text{-}\overset{\bullet}{C}\text{-}\overset{\ominus}{C}\text{-}C_6H_4\text{-}NO_2 \quad \text{or} \quad R\text{-}C_6H_4\text{-}\overset{\bullet}{N}O_2^-$$

and since the spectrum could not be solved by inspection no conclusions could be made about the radical species.

The spectrum of the free radical produced in t-butyl alcohol from 2-nitrofluorene and potassium t-butoxide could be assigned to the 2-nitrofluorene radical anion by inspection (Figure 81, top left). Three triplets gave the following splitting constants under low resolution: $a_N = 12.1_0$, $a_{1,3\text{-}H} = 3.2_7 \pm 0.1$ gauss.

5-Nitroacenaphthene,



reacted rapidly in base to give radical species, not very stable in the presence of trace amounts of air, of total line width approximately 28 gauss in dimethyl sulfoxide - t-butyl alcohol (Figure 80, top right).

Figure 80. E.S.R. spectra of radical species formed spontaneously from bis-2,3-(p-nitrophenyl)-butane by potassium t-butoxide in dimethyl sulfoxide - t-butyl alcohol in the presence of a trace of air (top left) and in the absence of air (top right, low resolution, 1 cm. = 8.18 gauss; bottom, high resolution, 1 cm. = 2.38 gauss)

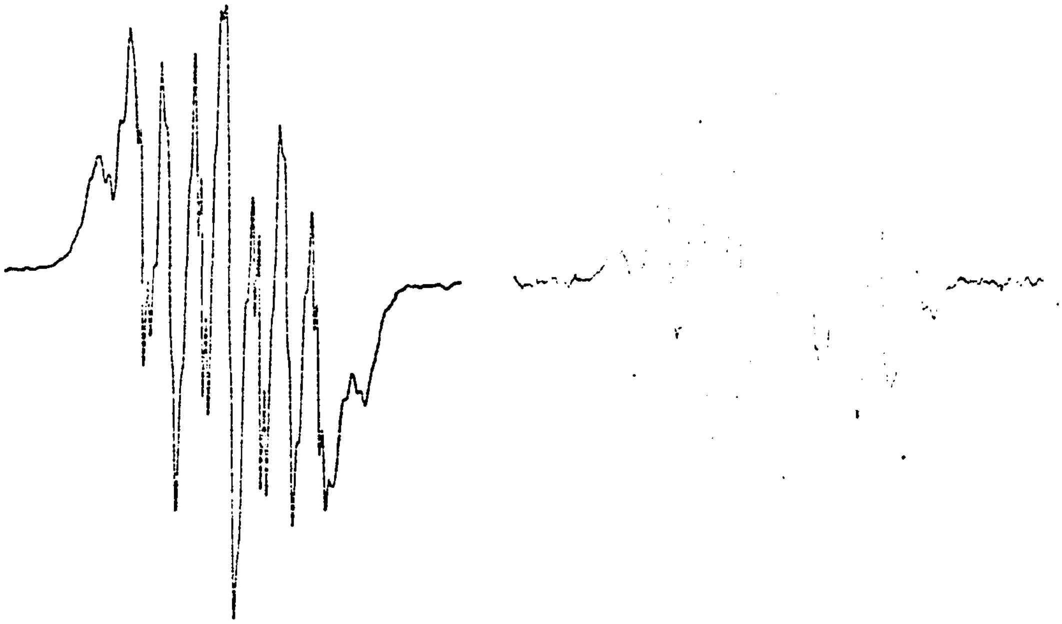
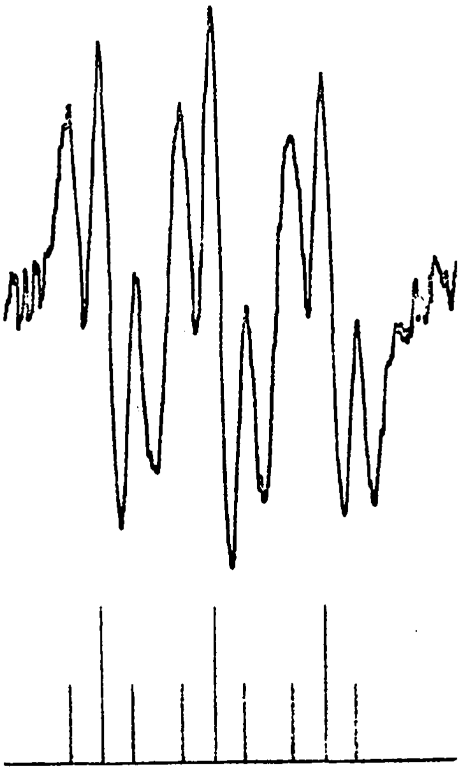
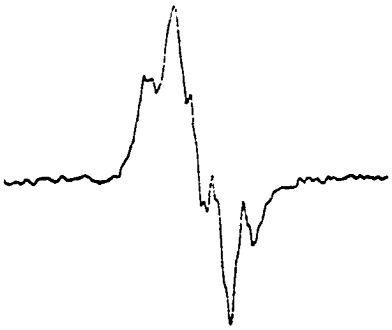
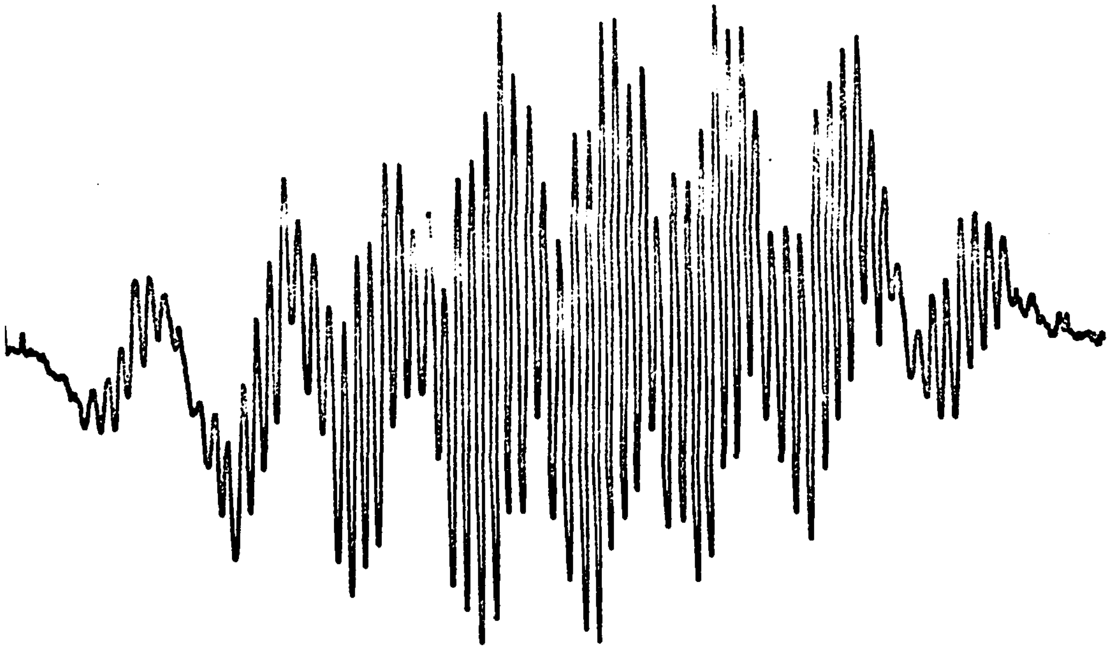


Figure 81. E.S.R. spectra of 2-nitrofluorene radical anion in t-butyl alcohol (top left, $a_N = 12.1_0$, $a_{1,3-H} = 3.2_7$ gauss) and of 5-nitroacenaphthene in dimethyl sulfoxide - t-butyl alcohol in the presence of a trace of air (top right) and in t-butyl alcohol in the absence of air (bottom) all formed spontaneously by the action of potassium t-butoxide on the substrate







However in the absence of air in t-butyl alcohol containing potassium t-butoxide a very complex spectrum with a total line width of approximately 53 gauss was observed (Figure 80, bottom). The solution of these spectra was not attempted.

The mechanism of spontaneous free radical formation for alkyl nitroaromatics in general is consistent with an electron transfer reaction from the carbanion to the unionized nitroaromatic.

$$(168) \qquad R^{\ominus} + NO_2R \longrightarrow \underset{\downarrow\, ?}{R\cdot} + \underset{\text{detected by E.S.R.}}{\dot{N}O_2\text{-}R^{-}}$$

In the case of a very acidic carbanion the concentration of radicals should be larger in deficient base than in excess base as was found to be the case for 2,4-dinitrotoluene. For very stable carbanions no electron transfer should be expected in deficient or excess base. Accordingly very low concentrations of radicals or none were found for 2,4,6-trinitrotoluene, p-nitrophenylacetonitrile, bis-(2,4-dinitrophenyl)-methane and tris-(p-nitrophenyl)-methane[1].

b. p-Nitrotoluene kinetics The initial rate of spontaneous formation of p-nitrotoluene radical anion from p-nitrotoluene and

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[1] The latter example is in contradiction with our earlier suggestion that electron transfer accounted for the faster rates of oxidation in deficient base; however until the radical species can be formed by an independent method and shown stable under the reaction conditions the autocatalytic effect on oxidation can still be explained by electron transfer.

$$(169) \qquad (NO_2C_6H_4)_2CH\text{-}C_6H_4NO_2^{\overline{\cdot}} \xrightarrow{?} NO_2C_6H_4\cdot + \overset{\ominus}{C}H(NO_2C_6H_4)$$

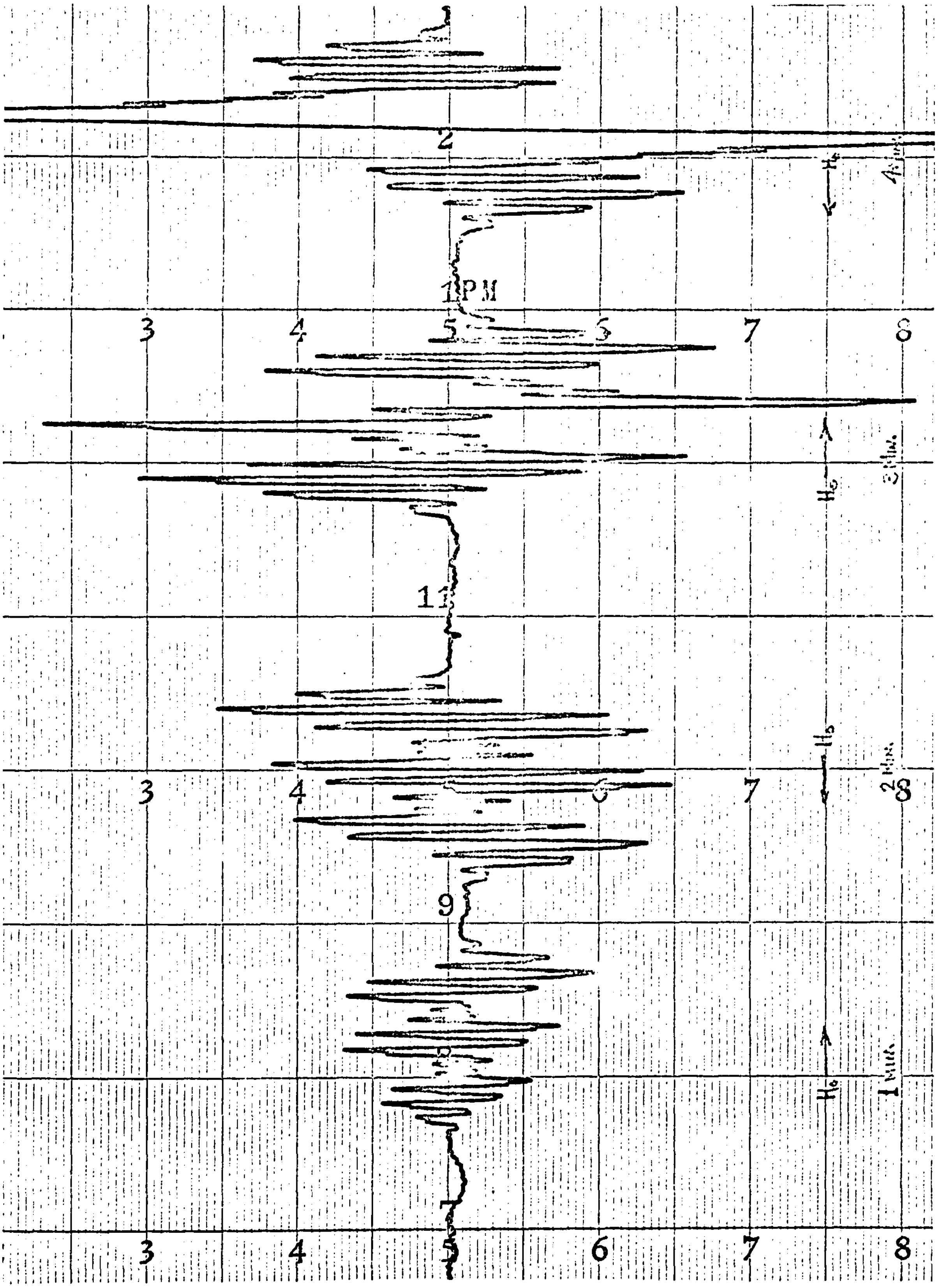
potassium t-butoxide was studied as a function of solvent, added nitrobenzene and starting concentration of potassium t-butoxide or p-nitrotoluene. A flow system was used which allowed two solutions, one containing p-nitrotoluene and the other potassium t-butoxide both dissolved in t-butyl alcohol, to mix in a T-tube and flow through a flat E.S.R. cell in the cavity of the spectrometer wave-guide (see Experimental). The reaction was too slow in t-butyl alcohol for radicals to form during free flow of the mixed solutions but if the flow was stopped the spectrum of the p-nitrotoluene radical anion could be recorded 15-60 sec. later, depending on the sensitivity settings of the spectrometer. The intensity of the observed peaks increased rapidly with time (Figure 82).

The appearance of the red color in solution described earlier under spontaneous dimerization was not exactly coincident with the first observation of a signal since on high sensitivity settings the first part of a 14-peak p-nitrotoluene radical spectrum could be obtained shortly before the red color appeared. However the appearance of the intense narrow peak in the center of the spectrum approximately 3.5 min. after mixing (Figure 82) was in all trials coincident with the first indication of turbidity and formation of a precipitate in the solution. The conclusion was made that the precipitate contained a radical species since it is known that radicals existing as a solid have narrower line widths than the same radicals in solution[1] (22). The stoichiometry of the reaction as

---

[1] The line width at half height for diphenylpicrylhydrazyl is approximately 2.7 gauss with no hyperfine components in the solid state; in benzene the well resolved 5-peak spectrum has an approximate line width of 60 gauss.

Figure 82. E.S.R. spectra of p-nitrotoluene radical anion spontaneously formed in a flow system in t-butyl alcohol showing the increase in intensity of peaks as a function of time while scanning through resonance; the precipitate peak is shown in the third and fourth spectra


1
2
H₀
4 Min.
1 P M
3
4
5
6
7
8
H₀
3 Min.
11
H₀
2 Min.
3
4
6
7
8
9
H₀
1 Min.
7
3
4
5
6
7
8

discussed earlier suggested that the structure of this radical was p,p'-dinitrobibenzyl radical anion. When the p-nitrotoluene radical peak height was followed as a function of time it was found that after the precipitate and the central peak appeared the peak height of the p-nitrotoluene radical remained essentially constant while the precipitate peak increased rapidly for periods up to 1 hr. All rate studies were performed on the initially formed free radical species, p-nitrotoluene radical anion, before the appearance of the precipitated radical.

The initial rates of p-nitrotoluene radical formation were obtained in arbitrary units as a function of the initial concentrations of potassium t-butoxide and p-nitrotoluene. It was found that scanning up field and down field through the first four peaks of the p-nitrotoluene radical anion spectrum produced peak heights which described fairly straight lines and extrapolated back to a common origin (Figure 83). The initial slopes of radical formation as a function of time were obtained by setting the spectrometer on the third peak of the spectrum or by scanning up field and down field through the same peak. Examples of both are shown in Figures 84 and 85. The values obtained with 2.5×10^{-2} M and 2.5×10^{-3} M p-nitrotoluene in t-butyl alcohol as potassium t-butoxide was varied from 5×10^{-3} M to 0.6 M are given in Table 16 and plotted in Figures 86 and 87. A good linear relationship considering the inherent inaccuracies in our determinations was obtained when the initial rates were plotted as a function of initial base strength. Similarly the initial slopes were obtained as a function of p-nitrotoluene concentration in the presence of 0.2 M potassium t-butoxide (Table 17, Figure 88). Not as many determinations were available and the fit to a

Figure 83. E.S.R. spectra of p-nitrotoluene radical anion scanning up field and down field through the first branch of the nitrogen triplet containing four main peaks; the lines joining the peak heights of corresponding peaks originate at approximately the same point

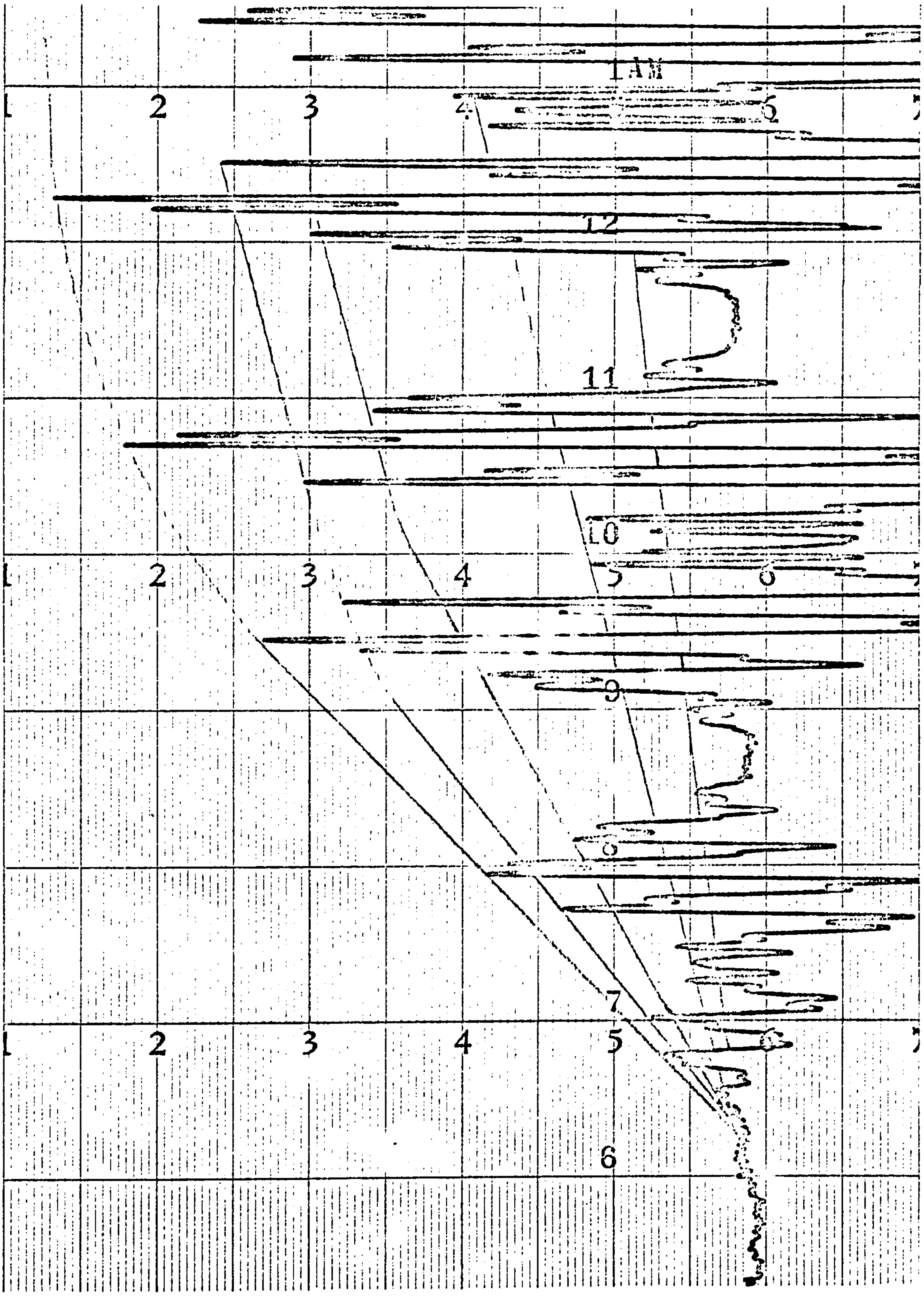

1AM
1
2
3
4
5
6
12
11
10
9
8
7
6

Figure 84. The increase in p-nitrotoluene radical concentration as a function of time, E.S.R. spectrometer set on the third peak (see Figure 82). In excess p-nitrotoluene over potassium t-butoxide as in this case free radicals are observed immediately after flow is stopped

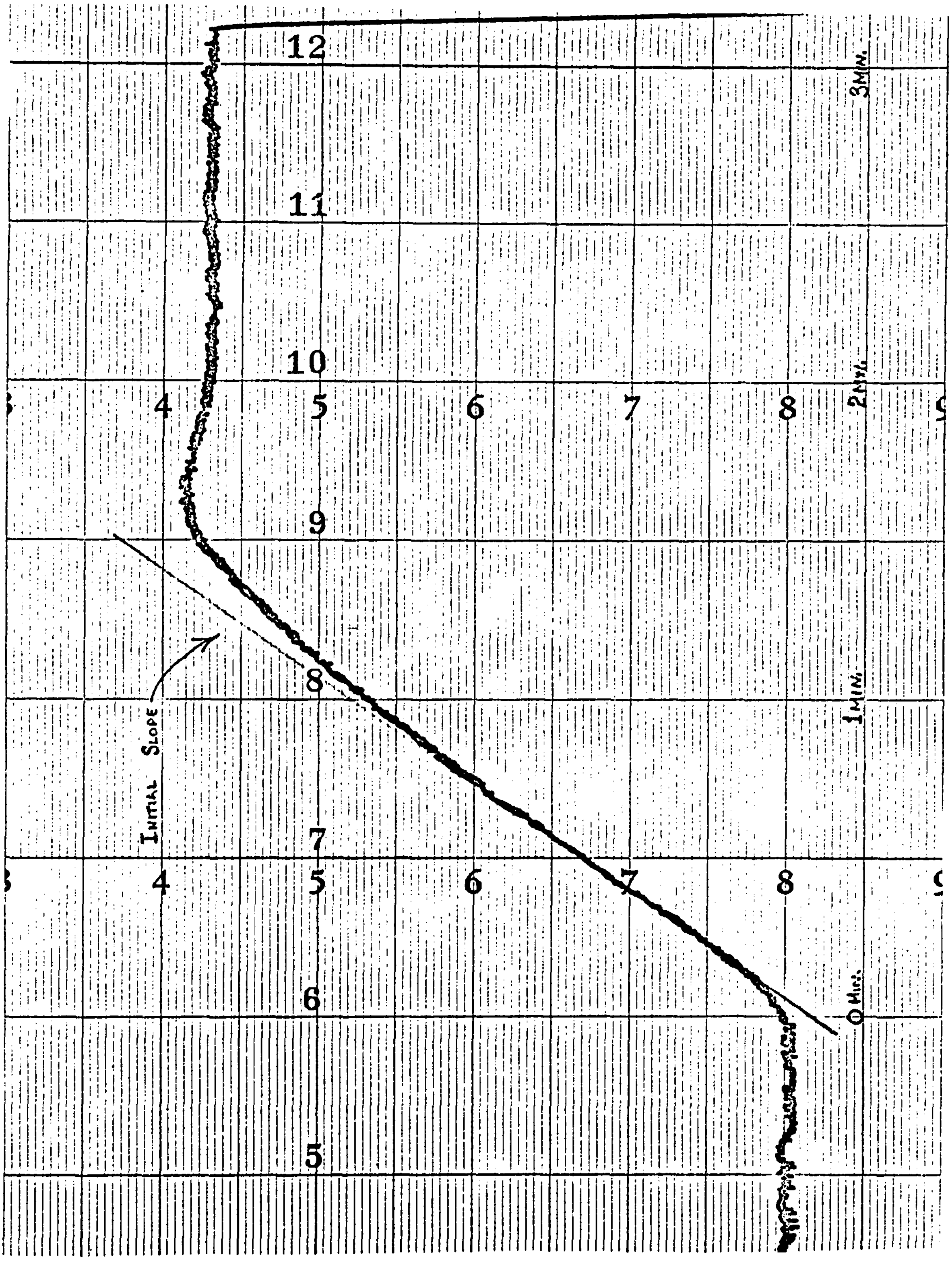

12
11
10
9
8
7
6
5
4
5
6
7
8
4
5
6
7
8
3MIN.
2MIN.
1MIN.
0 MIN.
INITIAL SLOPE

Figure 85. A plot similar to Figure 84 scanning up field and down field through the third peak of a partially resolved spectra of p-nitrotoluene radical anion (see Figure 82); initial slope obtained is the straight line drawn through the tops of the peaks

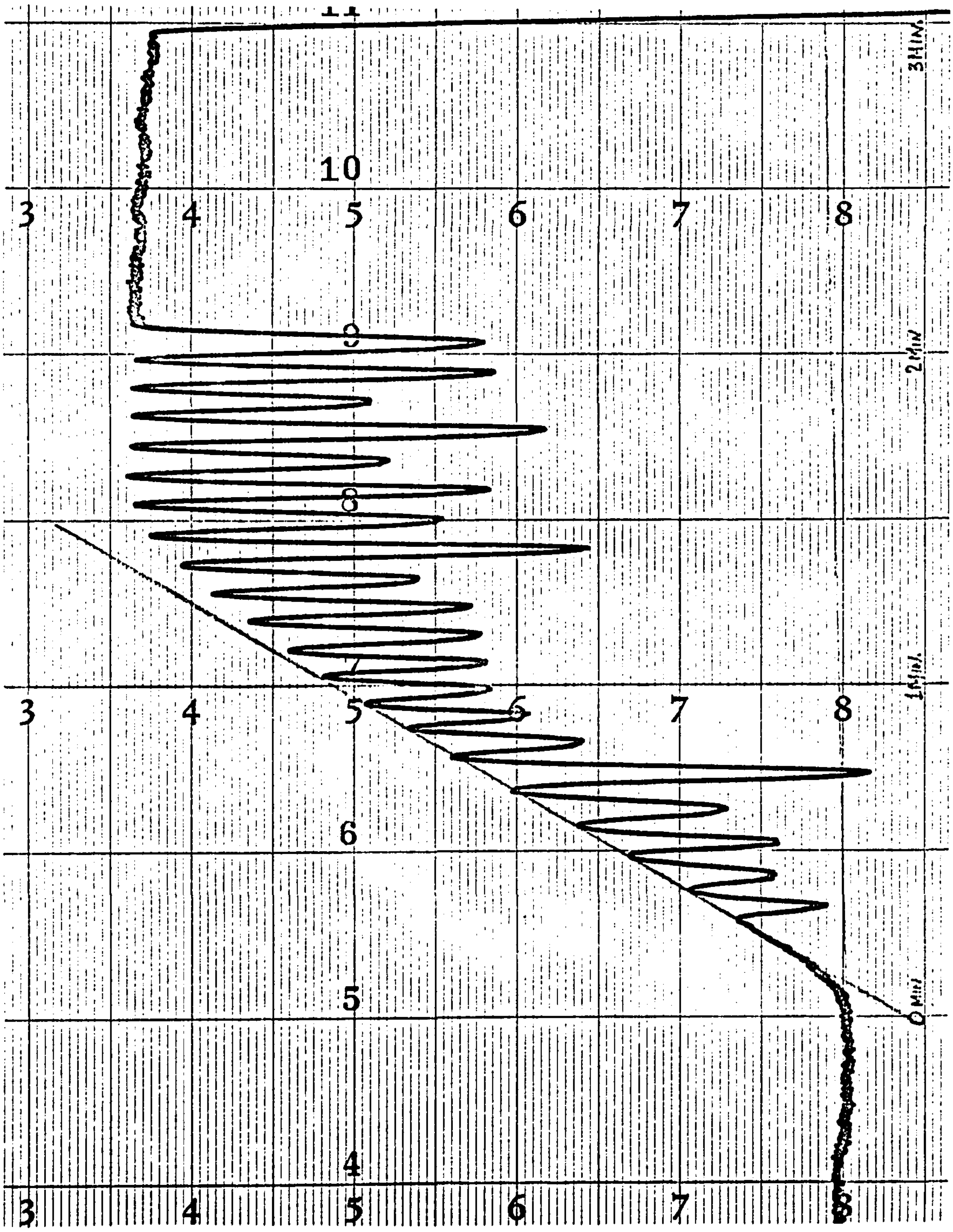

11
3HIN.
10
3
4
5
6
7
8
9
2MIN
8
7
1MIN.
3
4
5
6
7
8
6
5
0MIN
4
3
4
5
6
7
8

Table 16. Initial rate of p-nitrotoluene radical anion formation in t-butyl alcohol at 38-40° as a function of potassium t-butoxide

t-BuOK (M)	0.025 M p-nitrotoluene dR·/dt[b] S	n	$S_{cor.}$	Signal level[c]	Correction factor	0.0025 M p-nitrotoluene[a] t-BuOK (M)	dR·/dt S	n
0.005	0.075	3	0.042	63	0.552[d]	0.080	0.516	4
.010	.185	3	.102	63	.552	.100	.628	4
.015	.271	5	.150	63	.552	.125	.821	5
.020	.369	4	.204	63	.552	.150	.973	5
.025	.516	6	.285	63	.552	.175	1.283	5
.025	.285	4	.285	20	1.0	.225	1.50	5
.035	.430	4	.430	20	1	.225	1.66	4
.045	.638	3	.638	20	1	.300	1.96	1
.055	.884	4	.884	20	1	.380	2.34	3
.065	.945	3	.945	20	1	.450	1.99	4
.075	1.40	4	1.40	20	1	.600	2.30	1
.100	1.44	9	1.88	16	1.25			
.125	1.18	2	1.89	12.5	1.60			
.150	1.18	2	2.00	10[e]	1.80[e]			
.210	1.91	2	3.44	10	1.80			
.250	2.12	1	3.81	10	1.80			
.600	3.18	1	6.73	8	2.12			

[a] Signal level = 125

[b] dR·/dt = initial or steepest slope; S = average of n trials with same solution; $S_{cor.}$ = slope corrected to reference setting (signal 20, Scan 2,2)

[c] Spectrometer signal level dial setting

[d] 0.552 = 0.285/0.516, Two trials with 0.025 M t-BuOK, signal 63 and 20

[e] Scan 2,1 also for subsequent trials; correction factor compensated

Figure 86. Plot of the initial rate of formation of p-nitrotoluene radical anion in t-butyl alcohol as a function of potassium t-butoxide (0.025 M p-nitrotoluene, radical concentration in arbitrary units)

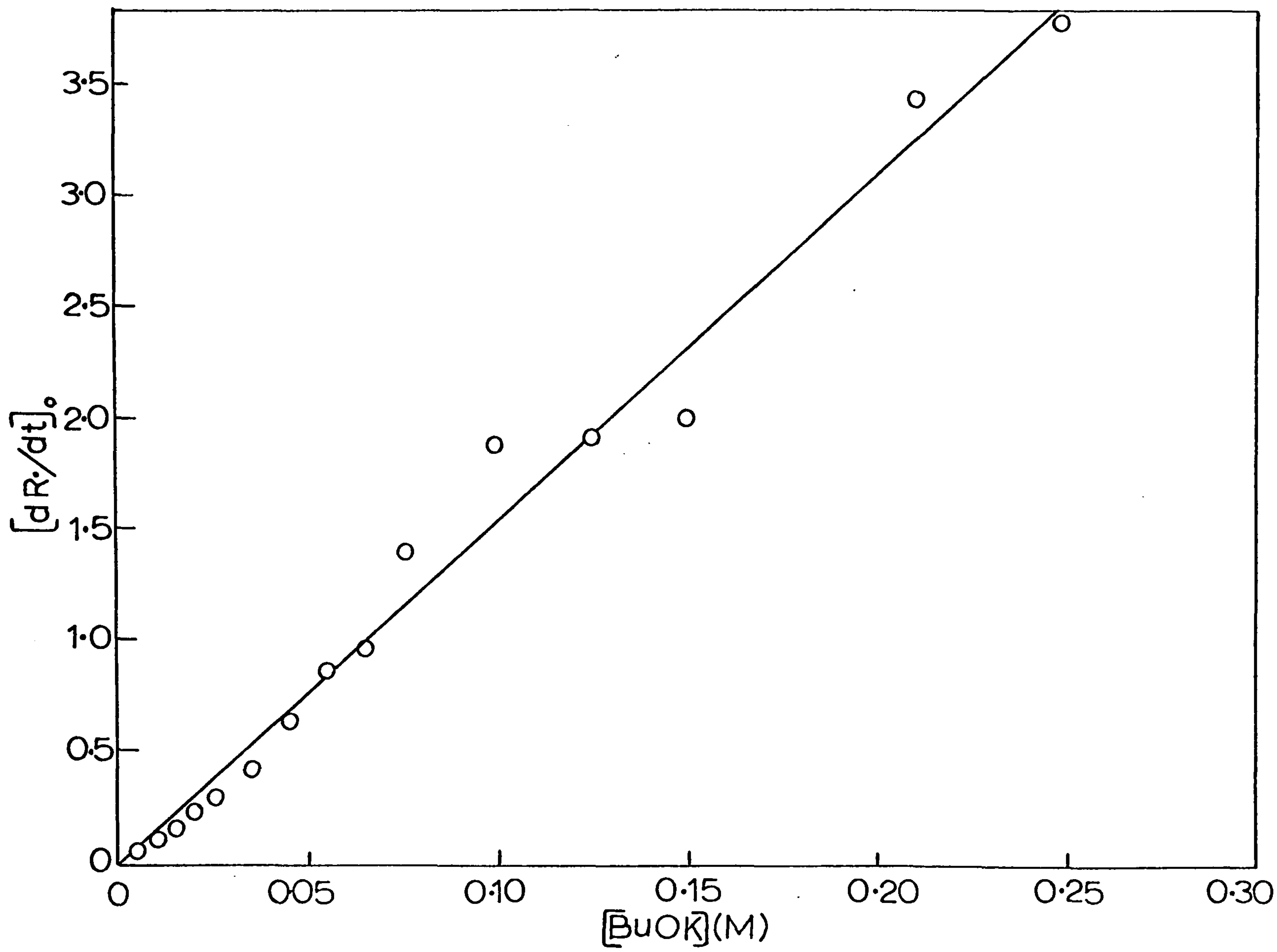

3·5
3·0
2·5
2·0
1·5
1·0
0·5
0
[dR·/dt]₀
0
0·05
0·10
0·15
0·20
0·25
0·30
[BuOK](M)

Figure 87. Plot of the initial rate of formation of p-nitrotoluene radical anion in t-butyl alcohol as a function of potassium t-butoxide (0.0025 M potassium t-butoxide, radical concentration in arbitrary units)

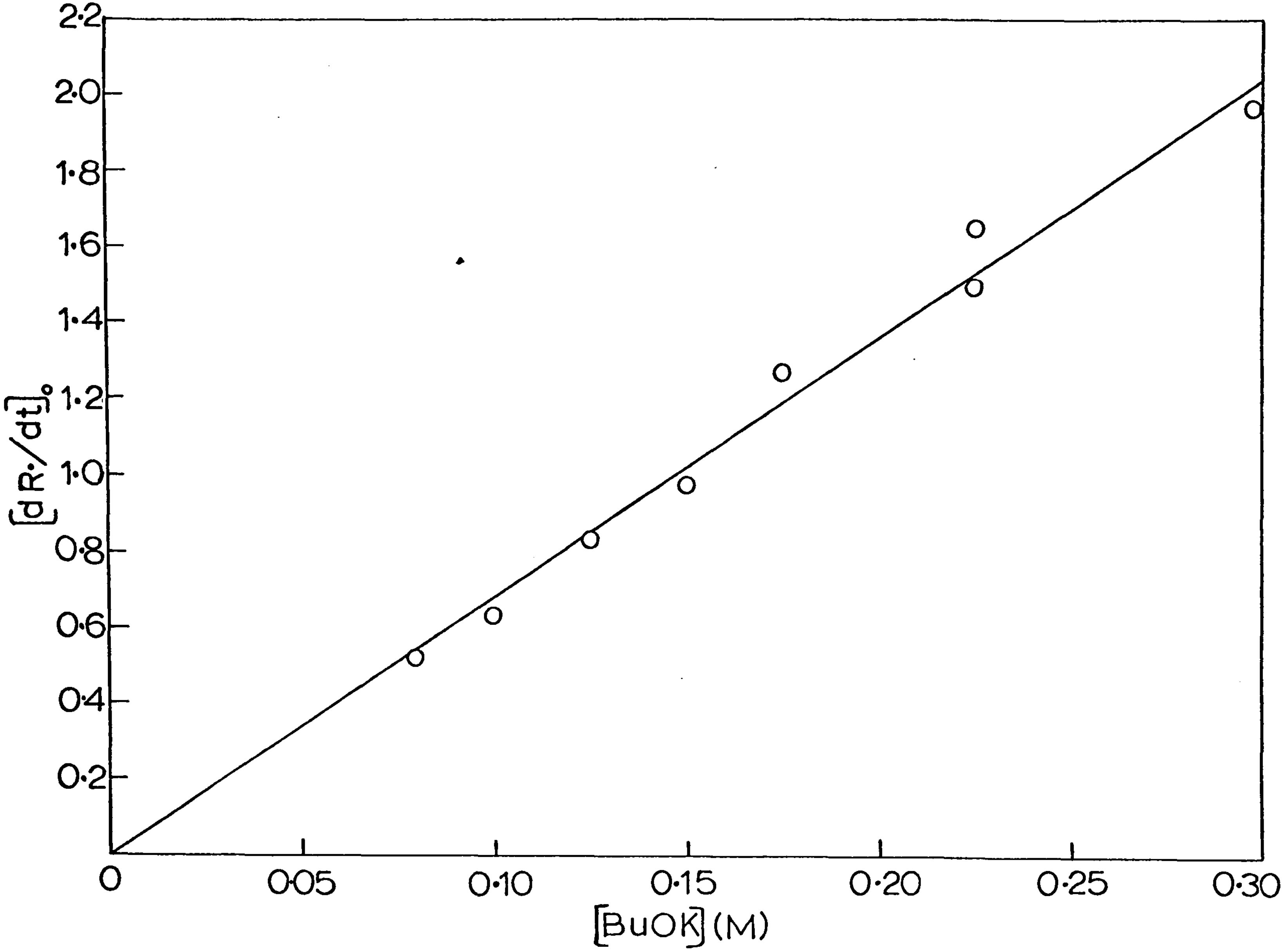

$[dR\cdot/dt]_0$
2·2
2·0
1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0
0·05
0·10
0·15
0·20
0·25
0·30
[BuOK] (M)

Table 17. Initial rate of p-nitrotoluene radical anion formation in t-butyl alcohol at 44° as a function of p-nitrotoluene in 0.2 M potassium t-butoxide

PNT[a] (M)	PNT^2 M^2 x 10^6	dR•/dt[b] S	n
0.0025	6.25	0.40	2
.0050	25	1.16	2
.0075	56.2	1.88	2
.0100	100	2.56	2
.0125	156	3.94	3

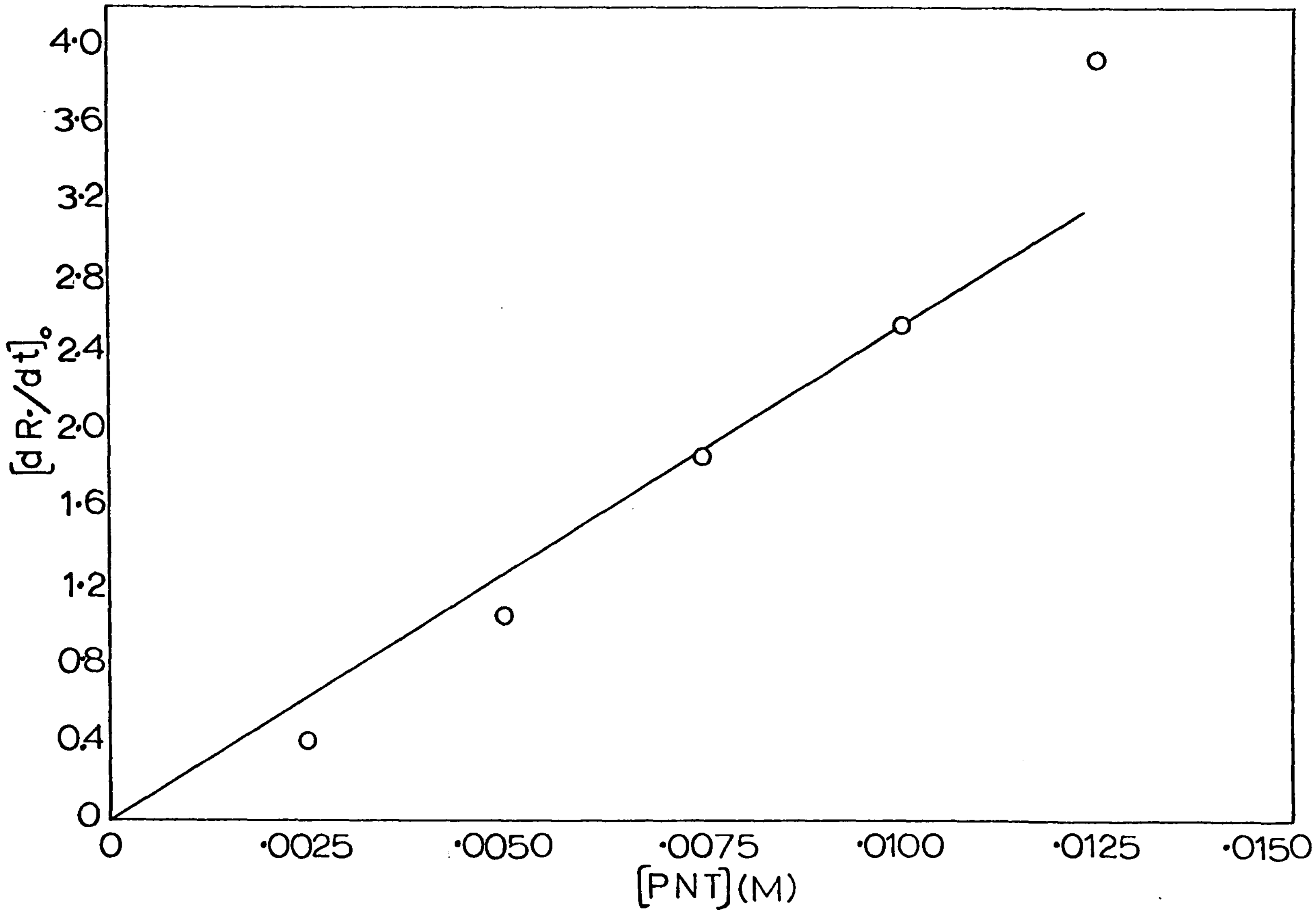
[a] PNT = p-nitrotoluene

[b] dR•/dt = initial or steepest slope in arbitrary units; S = average of n number of trials with the same solution

straight line for all the points was not very good. A plot as a function of p-nitrotoluene to the second power is linear after the initial point but does not go through the origin. There were experimental difficulties in the precise determination of the initial slopes at the very low and high concentrations of p-nitrotoluene. The plot of the initial slopes as a function of the initial concentration of p-nitrotoluene to the first power can be considered linear at least to 0.01 M p-nitrotoluene concentration in the presence of 0.2 M potassium t-butoxide.

In 50% dimethyl sulfoxide - 50% t-butyl alcohol the spontaneous formation of p-nitrotoluene radical anion was rapid enough so that a signal could be recorded during flow through the cavity and the increase of

Figure 88. Plot of the initial rate of formation of p-nitrotoluene radical anion in t-butyl alcohol as a function of p-nitrotoluene (0.2 M potassium t-butoxide, radical concentration in arbitrary units)


4·0
3·6
3·2
2·8
2·4
2·0
1·6
1·2
0·8
0·4
0
$[dR\cdot/dt]_o$
0
·0025
·0050
·0075
·0100
·0125
·0150
[PNT] (M)

radical concentration after the flow was stopped was very rapid (Figure 89).

In the presence of excess nitrobenzene the curve for the nitrobenzene radical formation was initially very similar to that for the *p*-nitrotoluene radical formation in the absence of nitrobenzene although the curves diverged with time, the nitrobenzene radical anion concentration finally ending at approximately twice the concentration of the radical observed for *p*-nitrotoluene (Figure 90).

A mechanism can be postulated in agreement with the known facts about the spontaneous formation of free radicals in basic solutions of *p*-nitrotoluene. Evidence has been presented in favor of an electron transfer reaction for carbanions and nitroaromatics.

$$R^{\ominus} + A \longrightarrow R\cdot + A\cdot^{-}$$

where $R^{\ominus}$ = carbanion

A = acceptor, *e.g.*, nitrobenzene

This reaction cannot be predominant in the spontaneous radical formation of *p*-nitrotoluene because nitrobenzene does not greatly increase the rate of radical formation as it should if simple electron transfer produced a *p*-nitrobenzyl radical and *p*-nitrotoluene radical anion.

$$(170) \qquad PNT^{\ominus} + \begin{matrix} PNT \\ NB \end{matrix} \longrightarrow \underset{B\text{-}B}{PNT\cdot} + \begin{matrix} PNT\overset{-}{\cdot} \\ NB\overset{-}{\cdot} \end{matrix}$$

Moreover in the base-catalyzed oxidation of *p*-nitrotoluene the high yield of *p*,*p*'-dinitrobibenzyl cannot come from dimerization of *p*-nitrobenzyl radicals since in oxygen these should all be trapped and lead eventually

Figure 89. The increase in p-nitrotoluene radical anion concentration as a function of time in 50% dimethyl sulfoxide - 50% t-butyl alcohol containing 4×10^{-3} M p-nitrotoluene and 8×10^{-2} M potassium t-butoxide

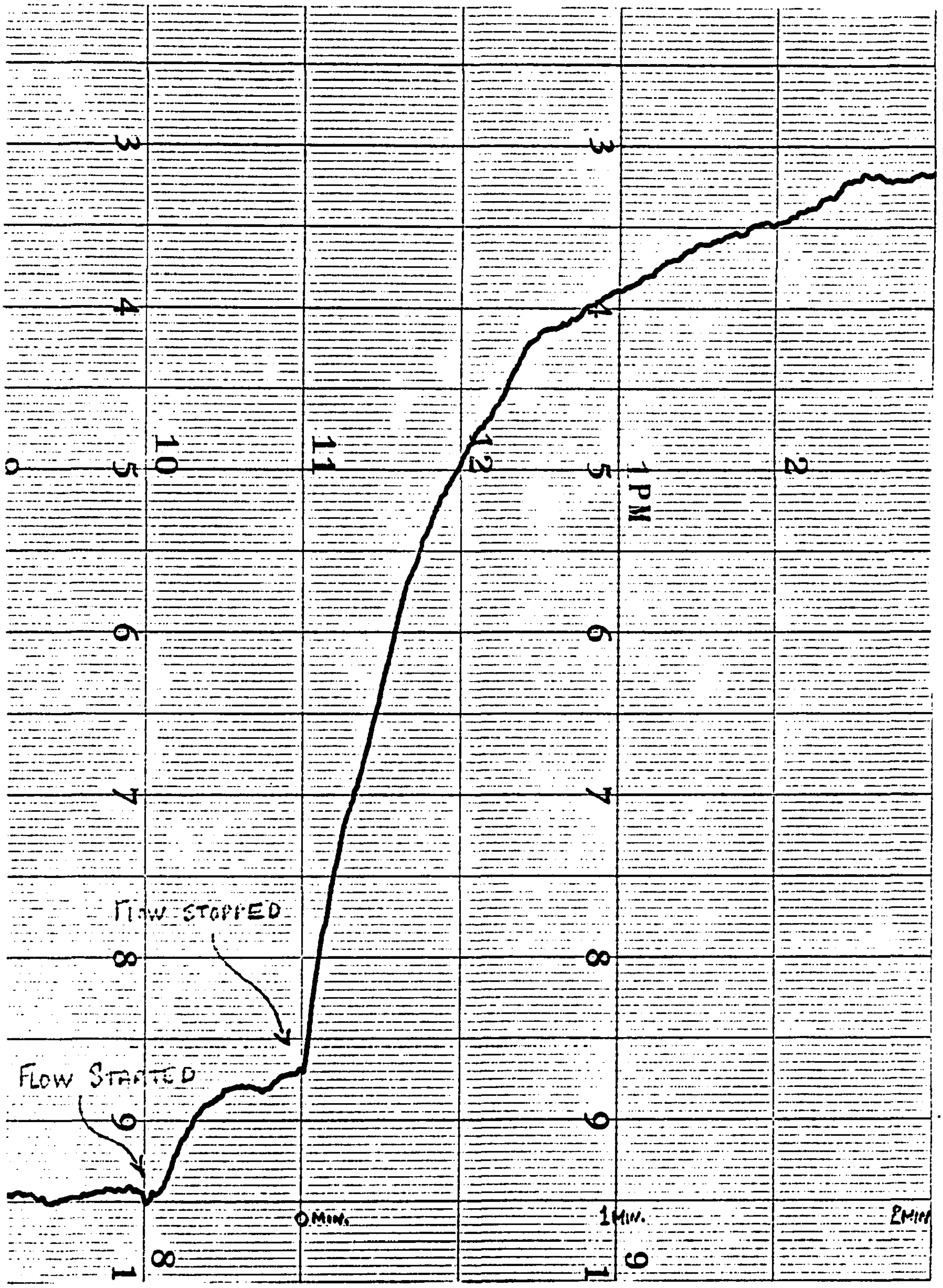
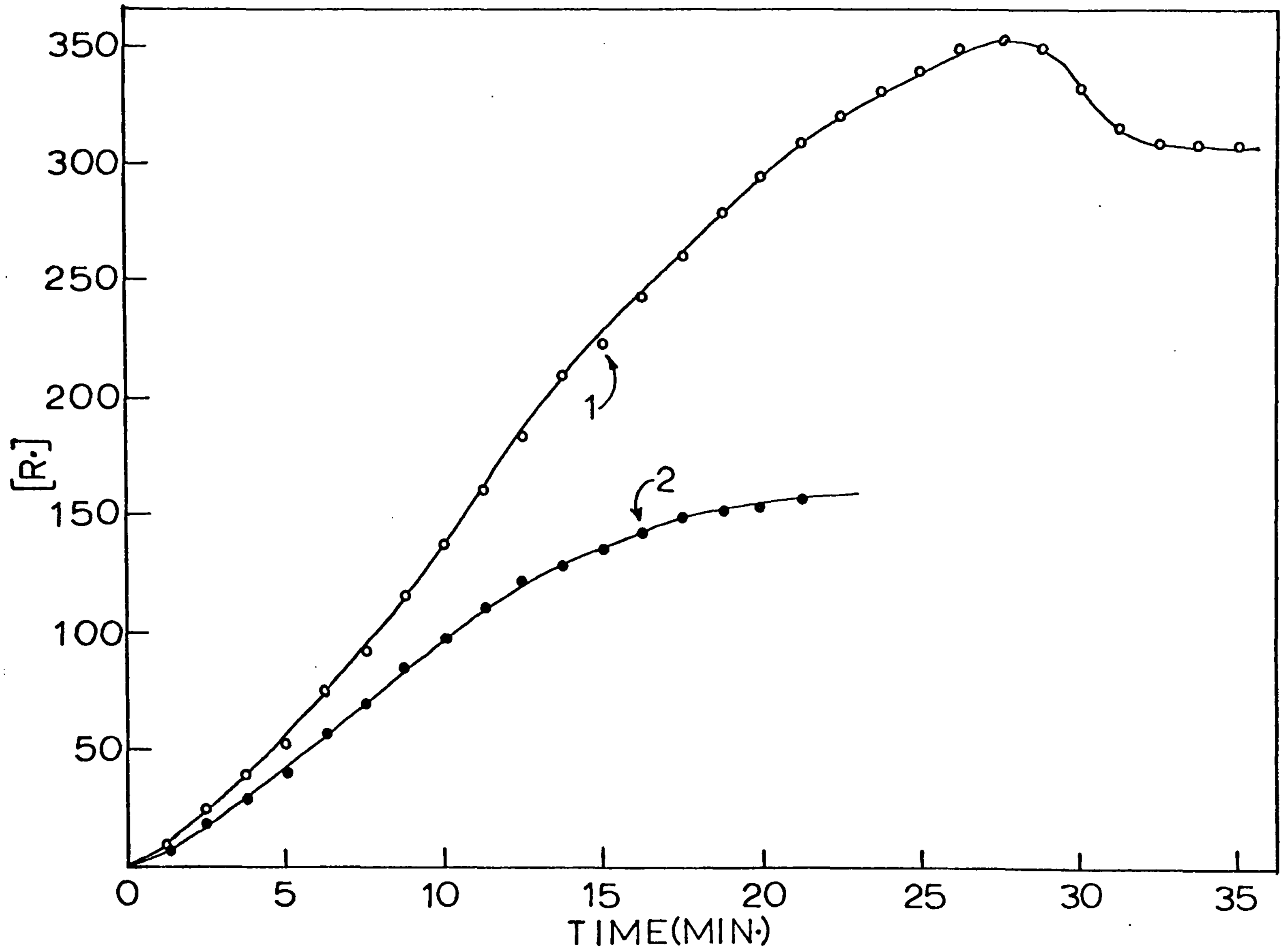

3
4
5
6
7
8
9
1
10
11
12
1 PM
2
Flow stopped
Flow Started
0 MIN.
1 MIN.
2 MIN

Figure 90. Plot of nitrobenzene radical anion formation as a function of time formed by electron exchange from p-nitrotoluene radical anion generated spontaneously from p-nitrotoluene in the presence of potassium t-butoxide in t-butyl alcohol (Curve 1, ~0.3 M nitrobenzene) and the same reaction in the absence of nitrobenzene (Curve 2, p-nitrotoluene radical anion) 0.05 M p-nitrotoluene, 0.025 M potassium t-butoxide in both experiments; concentration of radical anions in arbitrary units


[R·]
350
300
250
200
150
100
50
0
5
10
15
20
25
30
35
TIME(MIN·)
1
2

to p-nitrobenzoic acid.

The mechanism suggested in a previous section involved a charge-transfer complex intermediate with radical formation the result of electron transfer from the complex before or after the removal of a proton from the complex by excess base. If a steady state assumption is made for p-nitrobenzyl carbanion, the complex, and p,p'-dinitrobibenzyl radical anion during the initial time of the reaction, a rate expression can be derived which predicts that the rate of radical production will be first order in the initial concentrations of base and p-nitrotoluene. If a small amount of direct electron transfer from the p-nitrobenzyl carbanion to p-nitrotoluene occurs it can be accommodated without changing the overall expression.

The mechanism suggested for the spontaneous formation of free radicals from p-nitrotoluene in t-butyl alcohol is given on Page 253. From the experiment with nitrobenzene it must be concluded that the slow step preceeds k_4 since nitrobenzene which has a similar reduction potential to p-nitrotoluene should be expected to serve just as well as p-nitrotoluene in Step 4 and hence increase the rate of spontaneous radical formation. The electron transfer from a negative charge-transfer complex has no analogy and has not been reported.

The rate of radical production was studied as near to initial conditions as possible. The proportions of various species present more nearly at equilibrium have been described and it was concluded that after 15-20 min. reaction time under the given concentrations the fast dimerization reaction was essentially over. At this time it was suggested no free p-nitrobenzyl anion or p-nitrotoluene were present in solution but

Step

1 $$\mathrm{PNT} + \mathrm{B}^- \xrightarrow{k_1} \mathrm{PNT}^{\ominus} + \mathrm{BH}$$

2 $$\mathrm{PNT}^{\ominus} + \mathrm{PNT} \xrightarrow{k_2} \mathrm{PNT}\cdot + \mathrm{PNT}^{\cdot -}$$

3 $$\mathrm{PNT}^{\ominus} + \mathrm{PNT} \xrightarrow{k_3} (\mathrm{PNT} \rightarrow \mathrm{PNT})^- \qquad k_3 > k_2$$

charge transfer complex

4 $$(\mathrm{PNT} \rightarrow \mathrm{PNT})^- + \mathrm{PNT} + \mathrm{B}^- \xrightarrow{k_4} \mathrm{B\text{-}B}^{\cdot -} + \mathrm{PNT}^{\cdot -} + \mathrm{BH}$$

5 $$\mathrm{B\text{-}B}^{\cdot -} + \mathrm{PNT} \xrightarrow{k_5} \mathrm{B\text{-}B} + \mathrm{PNT}^{\cdot -}$$

$$d(\mathrm{PNT}^{\cdot -})/dt = k_4 \left[\text{complex}\right]\left[\mathrm{PNT}\right]\left[\mathrm{B}^-\right] + k_5 \left[\mathrm{B\text{-}B}^{\cdot -}\right]\left[\mathrm{PNT}\right]$$

Steady state assumptions for $\left[\mathrm{PNT}^-\right]$, $\left[\text{complex}\right]$ and $\left[\mathrm{B\text{-}B}^{\cdot -}\right]$

$$\left[\mathrm{PNT}^-\right] = k_1 \left[\mathrm{B}^-\right] / k_2 + k_3$$

$$\left[\text{complex}\right] = k_1 k_2 / k_4 (k_2 + k_3)$$

$$\left[\mathrm{B\text{-}B}^{\cdot -}\right] = k_1 k_2 \left[\mathrm{B}^-\right] / k_5 (k_2 + k_3)$$

$$\frac{d(\mathrm{PNT}^{\cdot -})}{dt} = \frac{(k_1 k_5 + 2k_1 k_2)\left[\mathrm{PNT}\right]\left[\mathrm{B}^-\right]}{k_2 + k_3} = K \left[\mathrm{PNT}\right]\left[\mathrm{B}^-\right]$$

that the components were the charge-transfer complex, p,p'-dinitrobibenzyl radical anion and p-nitrotoluene radical anion.

$$\text{Total PNT} = (\mathrm{PNT} \rightarrow \mathrm{PNT})^- + \mathrm{B\text{-}B}^{\cdot -} + \mathrm{PNT}^{\cdot -}$$

Our observations on the flow system indicate that initially all the p,p'-dinitrobibenzyl radical anions undergo electron exchange with unionized p-nitrotoluene to yield only p-nitrotoluene radical anions.

(171) $\text{B-B}^{\overset{-}{\cdot}} + \text{PNT} \longrightarrow \text{B-B} + \text{PNT}^{\overset{-}{\cdot}}$

In the experiments in the presence of excess potassium t-butoxide the concentration of unionized p-nitrotoluene decreases as the reaction proceeds to the point where the p,p'-dinitrobibenzyl radical anion precipitates as a solid radical because of the low concentration of a suitable electron acceptor in solution. At the same time the dissolved bibenzyl formed at the very beginning of the reaction undergoes electron exchange from the p-nitrotoluene radical to produce p,p'-dinitrobibenzyl radical which also precipitates. This explanation agrees with the observation that in excess p-nitrotoluene no intense central peak was observed.

c. 1,4-Dianions The well known stability of ketyl radical anions suggested that pinacols might spontaneously dissociate in strongly basic solutions to produce ketyl radical anions:

(172)

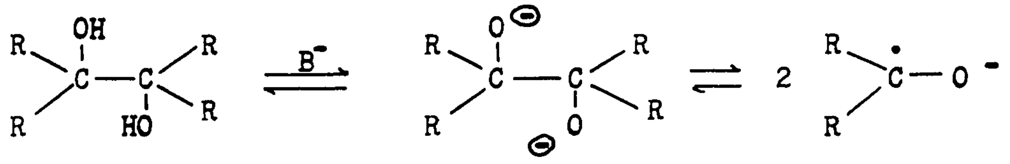
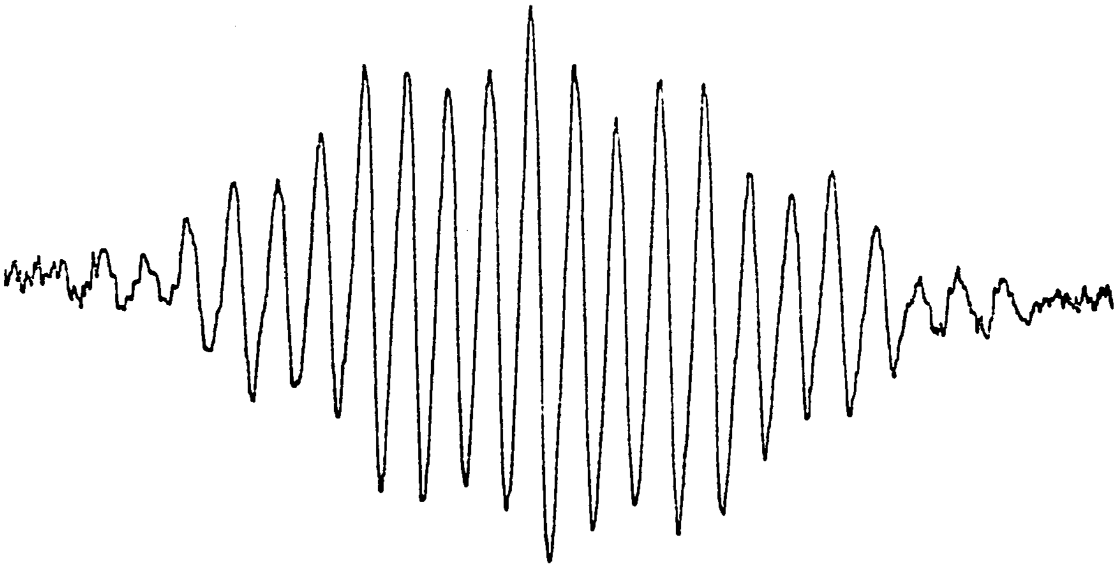
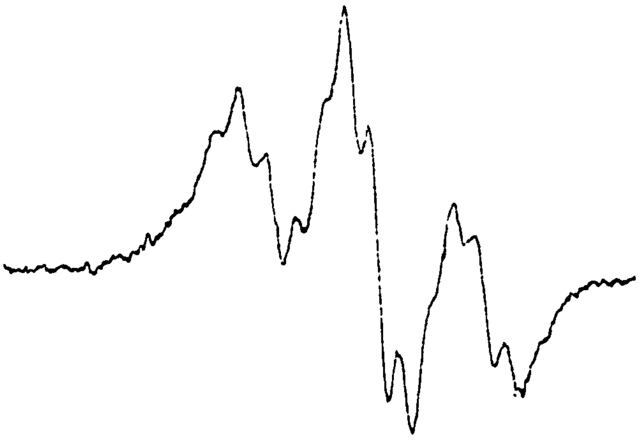


Figure 91 shows a well resolved spectrum of 23 lines for the benzophenone ketyl radical anion obtained in 20% dimethyl sulfoxide - 80% t-butyl alcohol from the ionization of benzopinacol by potassium t-butoxide (total line width 21.14 gauss). Free radical signals could also be obtained readily in ethanol containing sodium ethoxide (see Electron transfer from carbanions) and pyridine containing lithium t-butoxide.

Figure 91. E.S.R. spectrum of benzophenone ketyl radical anion (top) generated spontaneously from benzopinacol (0.02 M) in 20% dimethyl sulfoxide - 80% *t*-butoxide in the absence of air (1 cm. = 1.56 gauss) and of radical species generated from *α*,*α'*-diphenyladipamide (bottom) in dimethyl sulfoxide - *t*-butyl alcohol containing potassium *t*-butoxide

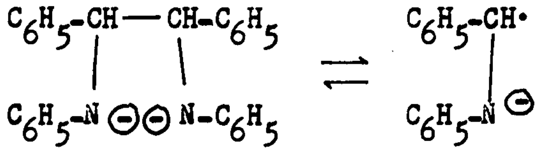




The fluorenone ketyl radical anion could also be readily obtained from the pinacol in solutions of t-butyl alcohol containing potassium t-butoxide or Triton B and in benzene containing Triton B or pyridine containing lithium t-butoxide (see Ketyls, Appendix) but not in mixtures of dimethyl sulfoxide containing potassium t-butoxide. This seems in contradiction to the observation that the fluorenone ketyl was formed in these solutions from fluorenol as described earlier. Possibly too much air was present for the dilute solutions of pinacol used for the E.S.R. experiments.

In an attempt to extend the reactions from 1,4-di-oxygen-anions to 1,4-di-nitrogen-anions 1,2,N,N'-tetraphenylethylenediamine was synthesized and studied in a strongly basic solution. It was hoped homolytic dissociation would occur for this dianion as well.

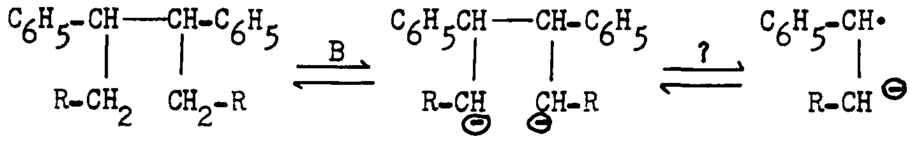
(173)



$$\begin{array}{c} C_6H_5\text{-}CH - CH\text{-}C_6H_5 \\ | \qquad\qquad | \\ C_6H_5\text{-}N^{\ominus}\;{}^{\ominus}N\text{-}C_6H_5 \end{array} \rightleftharpoons \begin{array}{c} C_6H_5\text{-}CH\cdot \\ | \\ C_6H_5\text{-}N^{\ominus} \end{array}$$

Although radicals were formed slowly which could be reconciled with the shown structure it was found (described earlier) that the presence of trace amounts of oxygen had caused this radical species to be formed and the conclusion had to be made that in 80% dimethyl sulfoxide - 20% t-butyl alcohol as well as in pure dimethyl sulfoxide containing potassium t-butoxide the right conditions had not been found for the dissociation reaction to occur if they do indeed exist.

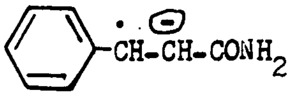
It was of interest to try a similar reaction on a 1,4-dicarbanion. Two examples were tried in this series:

(174) 

$$C_6H_5\text{-}\underset{R\text{-}CH_2}{\underset{|}{CH}}\text{—}\underset{CH_2\text{-}R}{\underset{|}{CH}}\text{-}C_6H_5 \overset{B}{\rightleftharpoons} C_6H_5\underset{R\text{-}\underset{\ominus}{CH}}{\underset{|}{CH}}\text{—}\underset{\underset{\ominus}{CH}\text{-}R}{\underset{|}{CH}}\text{-}C_6H_5 \overset{?}{\rightleftharpoons} C_6H_5\text{-}\underset{R\text{-}CH^{\ominus}}{\underset{|}{CH}}\cdot$$

where R = $COOCH_3$, $CONH_2$

For the ester a very weak unresolved signal was obtained in 80% dimethyl sulfoxide - 20% t-butyl alcohol with potassium t-butoxide. Apparently cyclization in base is a fast reaction for this compound and it was a poor choice for this experiment. A better spectrum was obtained from the amide (Figure 91, bottom) in 80% dimethyl sulfoxide - 20% t-butyl alcohol containing potassium t-butoxide. Three main peaks separated by 3.4 gauss were resolved, as well as 12 hyperfine components separated by approximately 0.65 gauss. The spectrum was not inconsistent with that expected for



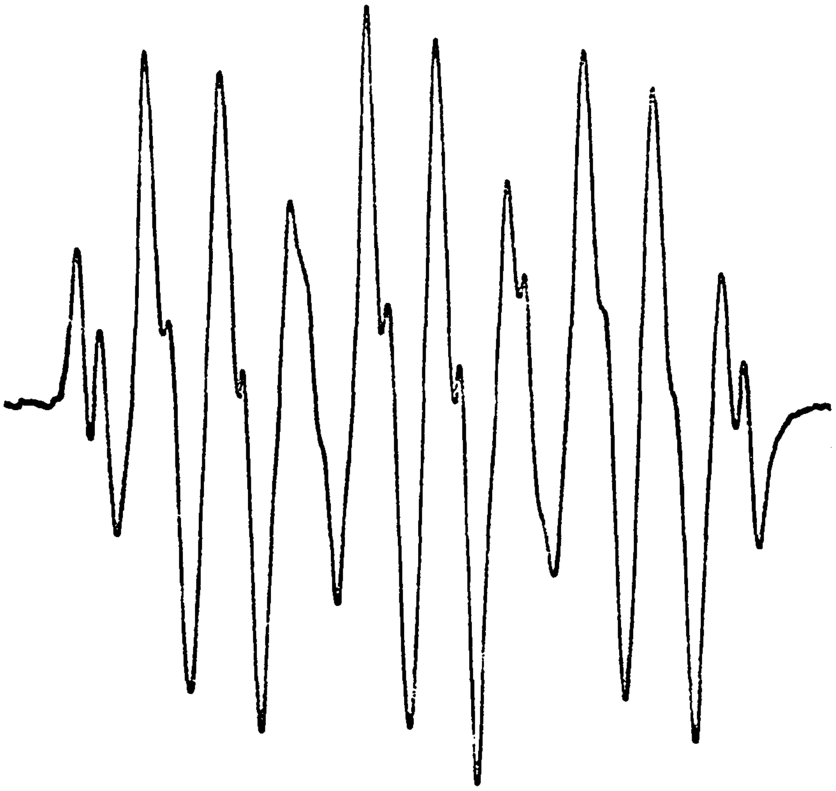
XXXV

Although the solutions were degassed with nitrogen, air was not excluded rigorously and the radicals observed may also have been the products of carbanion oxidation.

4. Electron transfer involving solvent

It was found that certain polynitroaromatic compounds gave large concentrations of free radicals in basic solution; for example, m-dinitrobenzene spontaneously produced the free radical species which had the E.S.R. spectrum shown in Figure 92 in t-butyl alcohol containing potassium t-butoxide. The spectrum had 10 major peaks and a total line width of 35.2 gauss (Table 18). The line width observed in t-butyl alcohol is

Figure 92. E.S.R. spectra of m-dinitrobenzene radical anion spontaneously formed in t-butyl alcohol in the absence of air by the action of t-butoxide on 0.02 M m-dinitrobenzene (top, 1 cm. = 3.89 gauss) and in ethanol by electron transfer from nitroethyl carbanion (bottom, 1 cm. = 5.78 gauss)



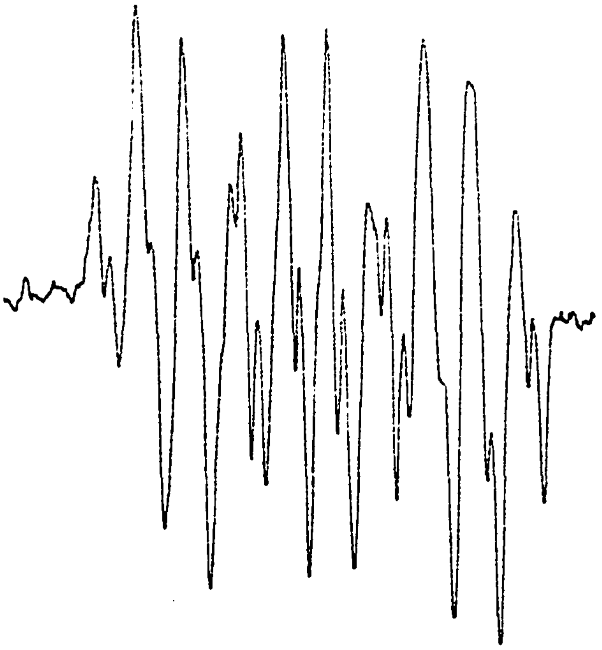


Table 18. Data on free radicals generated from dinitrobenzene derivatives

Substrate[a] (M)	*t*-BuOK[b] (M)	Solvent[c]	Major peaks	Total line width (gauss)	Figure
m-DNB		CH_3CN		31.28[d]	
m-DNB (0.02)	0.01	*t*-BuOH	10	35.20	92
m-DNB (.005)	.05	20/80	10	32.37	
m-DNB (.01)	.005	80/20	8 (22)	29.95[e]	93
m-DNB (.01)	.1	80/20	8 (23 +)	31.57	93
m-DNBB (.01)	.1	80/20	8 (22 +)	29.95	
m-DNCB (.01)	.1	80/20	8? (23 +)	30.34	
m-DNBB (.01)	.005	80/20	0		
m-DNCB (.01)	.005	80/20	0		
p-DNB		CH_3CN		11.44[f]	
p-DNB (.01)	.005	80/20	9	11.67	94
p-DNB (.01)	.1	80/20	27	33.65	94
o-DNB		CH_3CN	11	16.98[g]	
o-DNB (.01)	.005	80/20	11	15.56	
o-DNB (.01)	.1	80/20	11	17.12	95
o-DNB (.005)	.05	20/80	26	19.66[h]	95

[a] DNB = dinitrobenzene, DNBB = dinitrobromobenzene, DNCB = dinitrochlorobenzene

[b] *t*-BuOK = potassium *t*-butoxide

[c] CH_3CN = acetonitrile; *t*-BuOH = *t*-butyl alcohol; 20/80 and 80/20 = % dimethyl sulfoxide in *t*-butyl alcohol

[d] $a_N = 4.68$, $a_{4,6\text{-}H} = 4.19$, $a_{2\text{-}H} = 3.11$ and $a_{5\text{-}H} = 1.08$ gauss (39)

[e] $a_N = a_{4,6\text{-}H} = 4.2_8$, $a_{2\text{-}H} = 3.1_0$ and $a_{5\text{-}H} = 1.05$ gauss

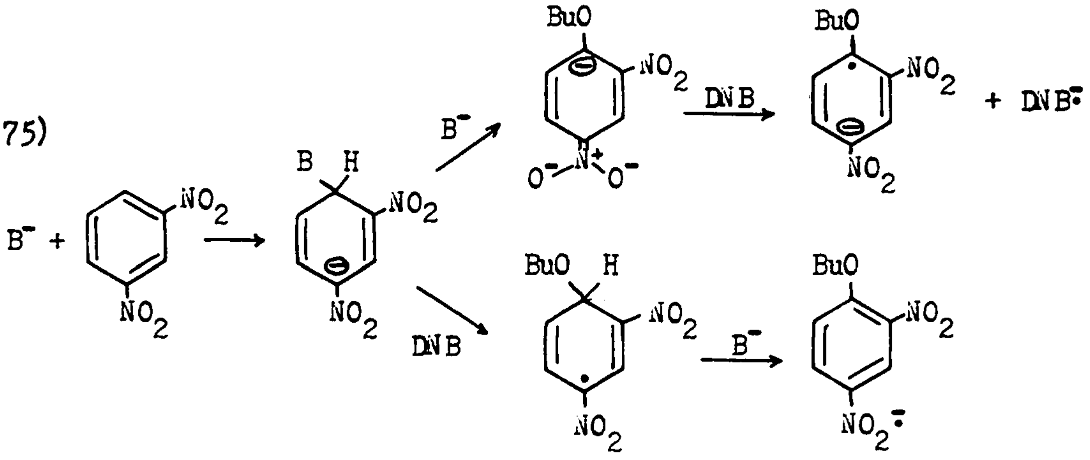
[f] $a_N = 1.74$ and $a_H = 1.12$ gauss (39)

[g] $a_N = 3.22$, $a_{4\text{-}H} = 1.63$ and $a_{3\text{-}H} = 0.42$ gauss (39)

[h] $a_N = 3.9_2$, $a_H = 1.5_0 = 2a'_H$, $a'_H = 0.75$ gauss

probably about 4 gauss greater than expected in acetonitrile since it has been found that in t-butyl alcohol nitroaromatic radical anions have a nitrogen splitting constant approximately 2 gauss greater than reported in acetonitrile (Table 15). After correcting for this solvent effect the observed radical has a total line width of 31 gauss (35.2 - 4), very indicative of the m-dinitrobenzene radical anion which was reported by Maki and Geske (39) to have a line width of 31.28 gauss. However the splitting constants have not been evaluated. Since one mechanism of formation involves an addition of base followed by electron exchange[1] more than one radical species could be expected.

(175)



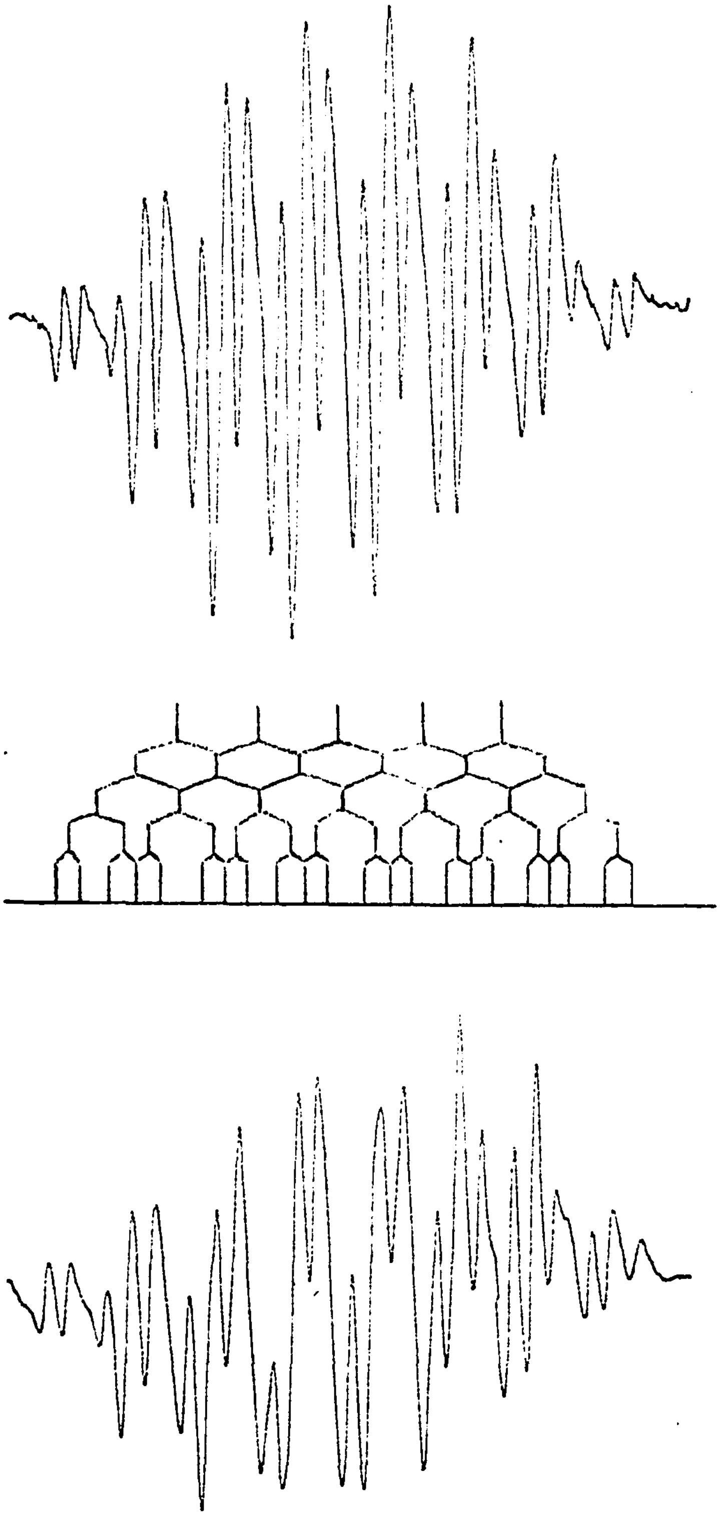
In 80% dimethyl sulfoxide - 20% t-butyl alcohol a spectrum of different appearance was obtained (Figure 93) with a total line width and splitting constants (Table 18) very similar to that reported by Maki and

---

[1] Electron transfer from potassium t-butoxide or t-butyl alcohol is unfeasible.

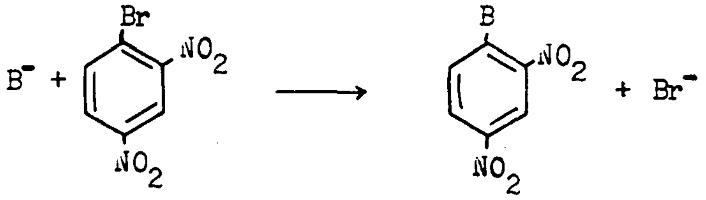
$$t\text{-BuOK} + C_6H_4(NO_2)_2 \not\longrightarrow t\text{-BuO}\cdot + C_6H_4(NO_2)_2{}^{\cdot -}$$

Figure 93. E.S.R. spectra of m-dinitrobenzene radical anion obtained from 0.01 M m-dinitrobenzene in 80% dimethyl sulfoxide - 20% t-butyl alcohol containing 0.005 M potassium t-butoxide (top, $a_N = a_{4,6-H} = 4.2_8$ for two equivalent nitrogens and hydrogens, $a_{2-H} = 3.1_0$ and $a_{5-H} = 1.0_5 \pm 0.1$ gauss) and 0.1 M potassium t-butoxide (bottom, 1 cm. = 3.89 gauss); the energy level diagram refers to the top spectrum and was constructed with the parameters given above



Geske (39) for m-dinitrobenzene radical anion in acetonitrile[1]. The spectra were very similar in deficient or excess base although in the latter case resolution was not as good and one more peak was present than in the spectrum from deficient base (Figure 93). In the hope that in the case of 2,4-dinitrobromobenzene or 2,4-dinitrochlorobenzene under the same conditions a different spectrum might be obtained if the preferred reaction was addition to the ring,

(176)



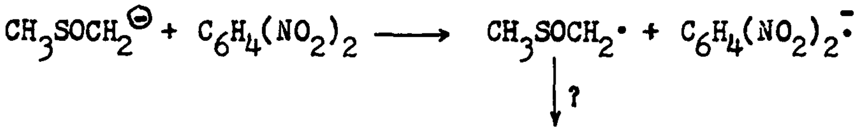
these two compounds were tried under conditions of deficient and excess base (Table 18). In deficient potassium t-butoxide a weak signal was obtained which died very quickly and could not be resolved for both the bromo and chloro derivatives. In excess base a strong stable signal appeared which could be resolved into a series of peaks which were very similar to those observed for m-dinitrobenzene itself, the spectrum obtained from 2,4-dinitrobromobenzene comparing best with that from m-dinitrobenzene in deficient base and from 2,4-dinitrochlorobenzene comparing best with that from m-dinitrobenzene in excess base. Although the radical species still could have been generated from addition

---

[1] Very little difference has been found in solvent interactions with radical anions between acetonitrile and 80% dimethyl sulfoxide - 20% t-butyl alcohol.

reactions followed by electron transfer the described observations did not support this mechanism. A simple electron transfer mechanism was best in accord with the information obtained.

(177)



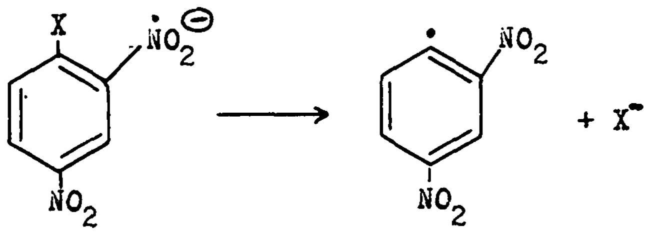
$$CH_3SOCH_2^{\ominus} + C_6H_4(NO_2)_2 \longrightarrow \underset{\downarrow ?}{CH_3SOCH_2\cdot} + C_6H_4(NO_2)_2^{\overline{\cdot}}$$

That the radical species from the dinitrohalobenzenes were not stable is consistent with what is known for another series of radicals anions, the substituted benzonitriles (60):

$$\overset{\ominus\,\cdot}{N}=C-C_6H_4-X \longrightarrow N\equiv C-C_6H_4\cdot + X^-$$

Dinitrohalobenzene radical anions might decompose by the same reaction,

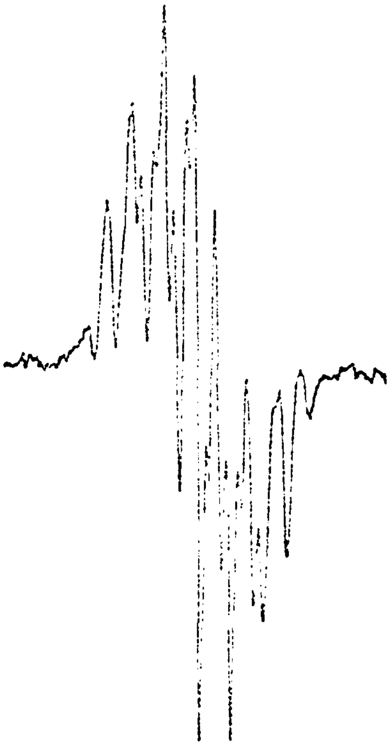
(178)

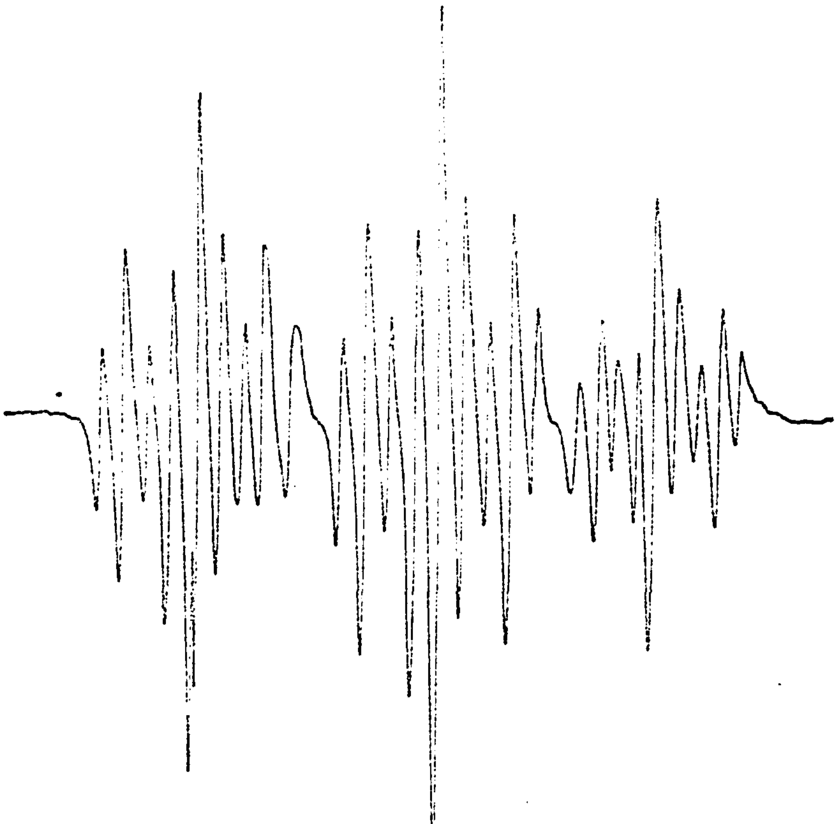


producing dinitrophenyl radicals which after abstraction of hydrogens from the solvent would yield m-dinitrobenzene which in excess base would give the characteristic spectrum.

The change in appearance of the E.S.R. spectrum for radicals from p-dinitrobenzene in deficient or excess potassium t-butoxide was more dramatic. Figure 94 shows the large increase in line width in excess base in 80% dimethyl sulfoxide - 20% t-butyl alcohol as compared to that in deficient base. In deficient base the line width of the radical observed

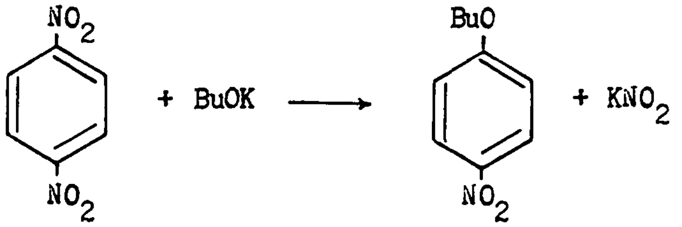
Figure 94. E.S.R. spectra of p-dinitrobenzene radical anion (top) and p-t-butoxynitrobenzene radical anion (bottom) in 80% dimethyl sulfoxide - 20% t-butyl alcohol generated in the presence of deficient and excess potassium t-butoxide respectively in the absence of air (0.01 M p-dinitrobenzene, 0.005 M and 0.2 M potassium t-butoxide; 1 cm. = 3.89 gauss)



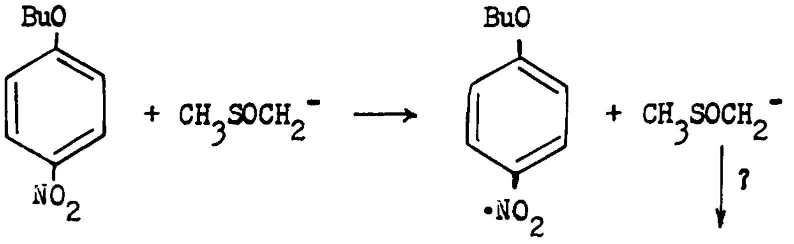


correlated well with that reported for p-dinitrobenzene radical anion (Table 18). In excess base the obvious 3-fold symmetry of the spectrum gave splitting constants 11.7_9, 3.5_0 and 1.1_9 gauss. These constants are remarkably similar to those reported for p-methoxynitrobenzene by Maki and Geske (38). For this compound in acetonitrile $a_N = 11.57$, $a_{\underline{o}\text{-H}} = 3.43$, $a_{\underline{m}\text{-H}} = 1.11$ and $a_{OCH_3} = 0.30$ gauss. The structure of the radical species in excess potassium t-butoxide generated from p-dinitrobenzene in 80% dimethyl sulfoxide - 20% t-butyl alcohol has been assigned to p-t-butoxynitrobenzene radical anion with $a_N = 11.7_9$, $a_{\underline{o}\text{-H}} = 3.5_0$ and $a_{\underline{m}\text{-H}} = 1.1_9$ ±0.1 gauss.

(179)

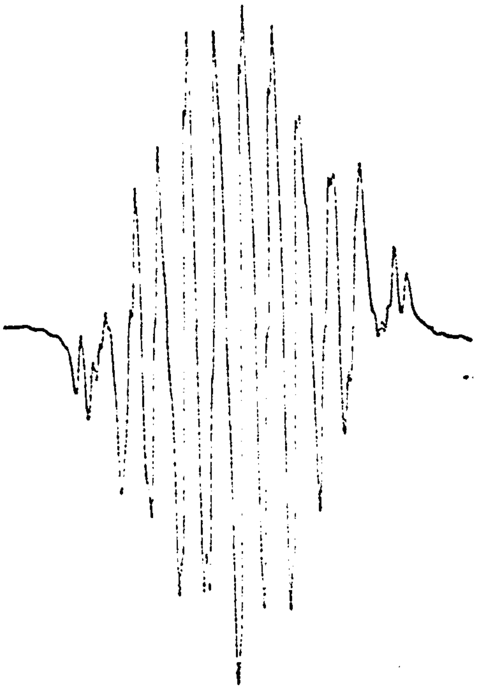


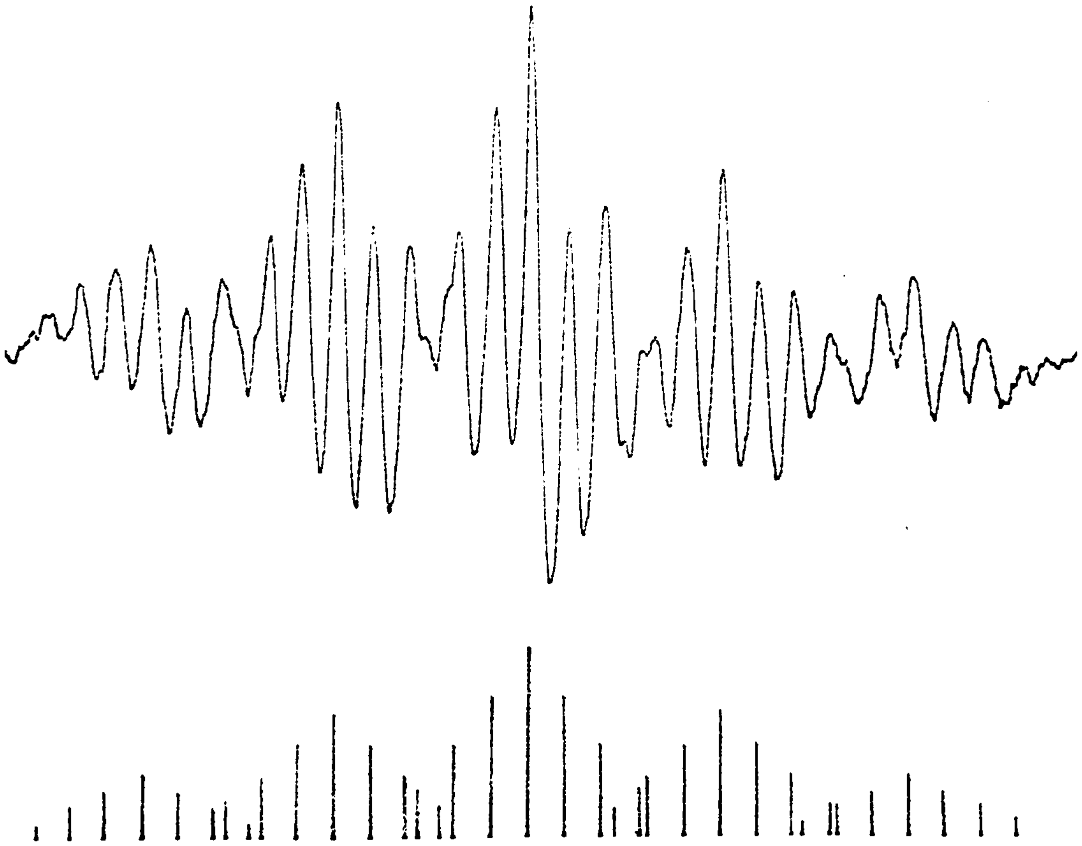
(180)



o-Dinitrobenzene gave spectra in deficient or excess base in 80% dimethyl sulfoxide - 20% t-butyl alcohol which were very similar to that reported for the o-dinitrobenzene radical anion in acetonitrile (see Table 18, Figure 95). However in 20% dimethyl sulfoxide - 80% t-butyl alcohol a different spectrum was obtained with an obvious 5-fold symmetry. The assumption was made that the radical was o-dinitrobenzene radical ion

Figure 95. E.S.R. spectra of o-dinitrobenzene radical anion from 0.01 M o-dinitrobenzene in 80% dimethyl sulfoxide - 20% t-butyl alcohol containing 0.1 M potassium t-butoxide (top, 1 cm. = 3.89 gauss) and from 0.005 M o-dinitrobenzene in 20% dimethyl sulfoxide - 80% t-butyl alcohol containing 0.05 M potassium t-butoxide (bottom, $a_N = 3.9_2$, $a_H = 1.5_0$, $a'_H = 0.7_5 \pm 0.1$ gauss) in the absence of air

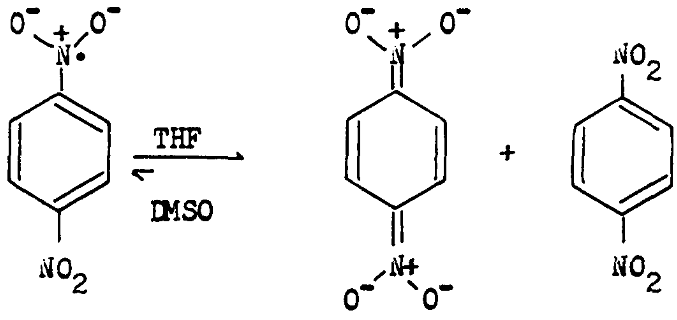




with the following splitting constants, $a_N = 3.9_2$ (for 2 equivalent nitrogen atoms), $a_H = 1.50 = 2a'_H$, $a'_H = 0.75 \pm 0.1$ gauss. These parameters were used to construct a synthetic spectrum which compared well with the recorded spectrum (Figure 95).

Since the p-dinitrobenzene radical anion was found to be unstable at room temperature in dimethoxyethane (41) the spectra reported were obtained at -70° C. Presumably disproportionation is a preferred reaction in this solvent at room temperature.

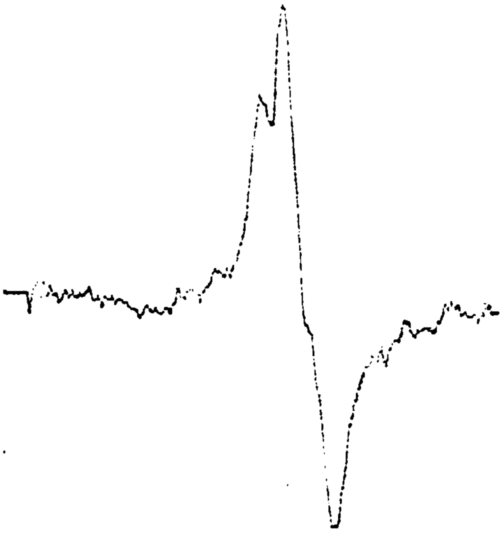
(181)

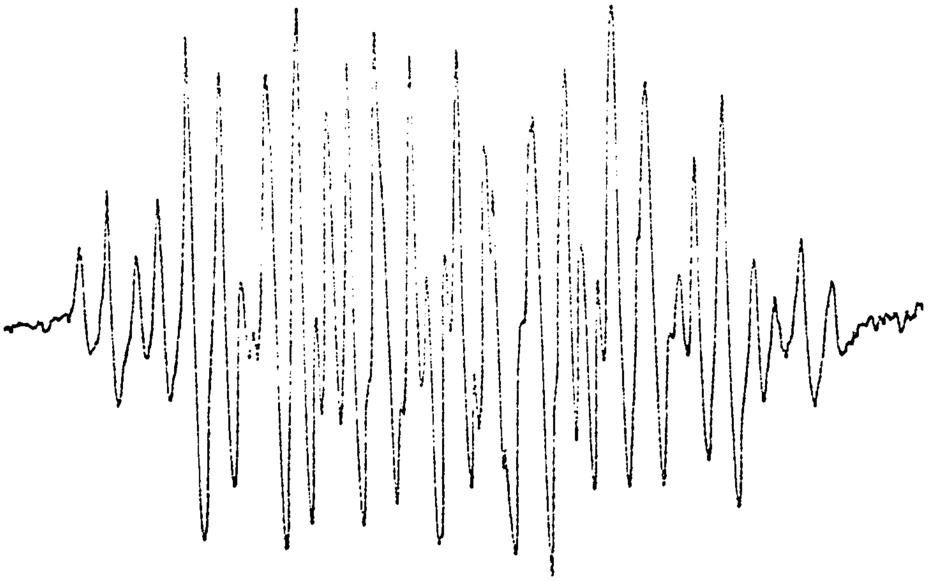


It is of interest that these radical ions can be observed in dimethyl sulfoxide apparently because the equilibrium is displaced more to the left in this solvent. The formation of o- or p-dinitrobenzene radical anions in 80% dimethyl sulfoxide - 20% t-butyl alcohol can best be attributed to rapid electron transfer from the methylsulfinyl carbanion present in these solutions except for p-dinitrobenzene in excess base where p-t-butoxy-nitrobenzene is thought to be produced rapidly via nucleophilic displacement of a p-nitro group.

A very weak unresolved signal was observed for sym-trinitrobenzene (0.01 M) in 80% dimethyl sulfoxide - 20% t-butyl alcohol in the presence of 0.1 M potassium t-butoxide (Figure 96, top).

Figure 96. E.S.R. spectra obtained from 0.01 M *sym*-trinitrobenzene by the action of 0.1 M potassium *t*-butoxide (top) and from 0.01 M 4-nitropyridine-N-oxide with 0.005 M potassium *t*-butoxide (bottom, 1 cm. = 3.89 gauss) in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol in the absence of air





4-Nitropyridine-N-oxide produced radicals in the presence of potassium t-butoxide in 80% dimethyl sulfoxide - 20% t-butyl alcohol yielding an E.S.R. spectrum of more than 25 well resolved lines with a total line width of 39.1 gauss (Figure 96, bottom). In absolute ethonol containing sodium ethoxide a different appearing spectrum of approximately 45 equidistant well resolved lines with a total line width of 23.65 gauss was obtained (Figure 97). The spectra were not analyzed although the spectrum obtained in ethanol was like one anticipated from full resolution of the 4-nitropyridine-N-oxide radical anion (5 (2 equivalent nitrogen atoms) x 3 x 3 (2 pairs of equivalent hydrogens) = 45). The most likely splitting constants might be expected to involve two different nitrogen atoms[1].

Nitrosobenzene also reacted with a basic solvent to give free radicals. In 20% dimethyl sulfoxide - 80% t-butyl alcohol the spectrum of 32 fairly well resolved lines given in Figure 98 was obtained from 0.005 M nitrosobenzene and 0.05 M potassium t-butoxide. Comparison with the nitrobenzene radical anion spectrum proved that the same number of peaks were obtained for both radicals under fairly good resolution but the sequence of intensities was different. The radicals could arise from electron transfer from the methylsulfinyl anion,

$$(182)\qquad CH_3SOCH_2^{\ominus} + C_6H_5N{=}O \longrightarrow CH_3SOCH_2\cdot + C_6H_5\dot{N}{-}\overset{-}{O}$$

but in view of Geels' work[2] showing that nitrosobenzene radical anion is not stable in ethanol containing sodium ethoxide produced from the

---

[1] The pyridine-N-oxide grouping in radical anions has not been reported.

[2] Russell and Geels, op. cit., p. 19.

Figure 97. E.S.R. spectra of radical species formed in a solution of 4-nitropyridine-N-oxide in ethanol containing sodium ethoxide in the absence of air

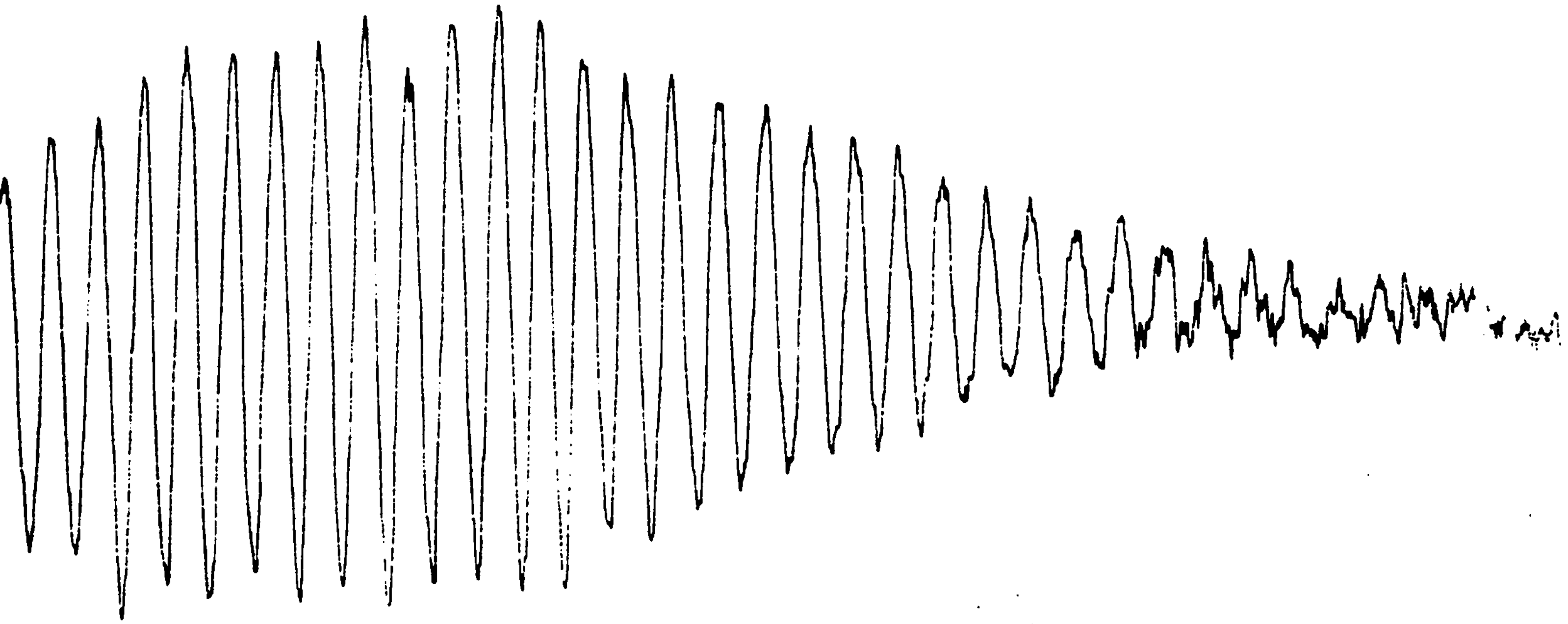
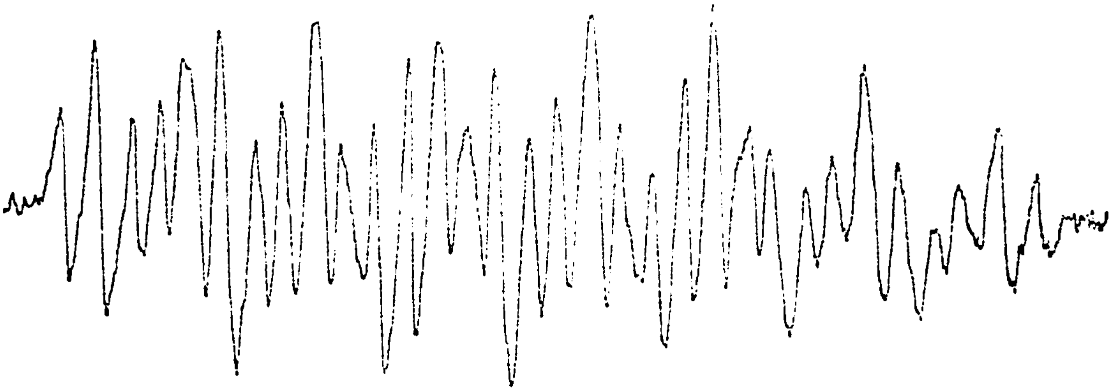
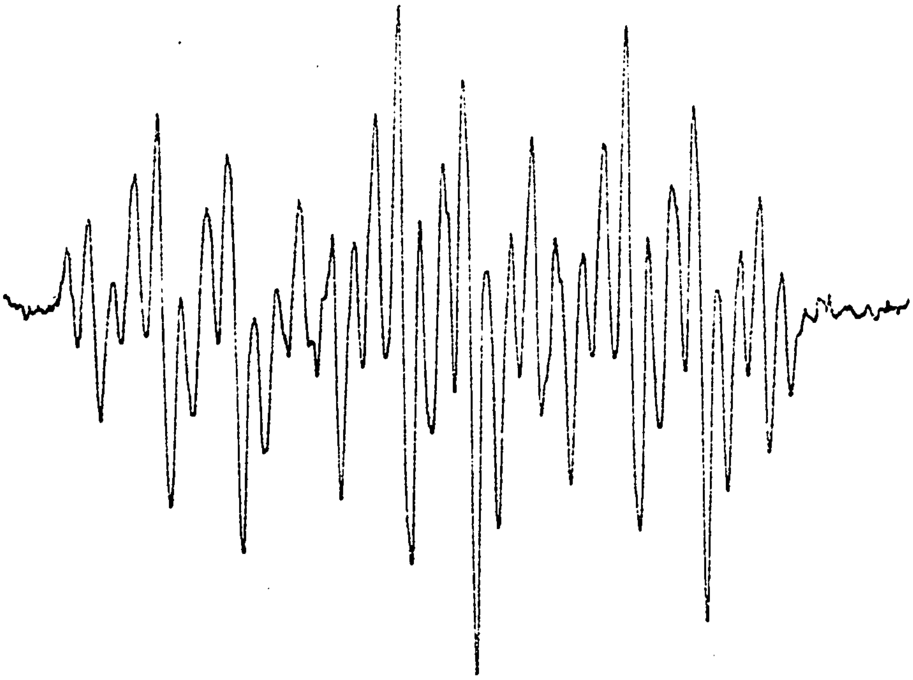


Figure 98. E.S.R. spectrum of radical species obtained from the action of potassium t-butoxide on nitrosobenzene in 20% dimethyl sulfoxide - 80% t-butyl alcohol (top) and a typical 32 line spectrum of nitrobenzene radical anion displayed for comparison purposes

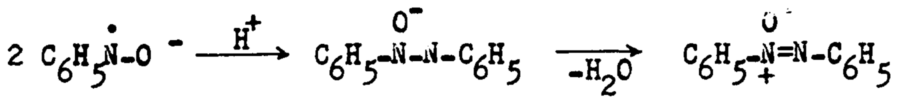




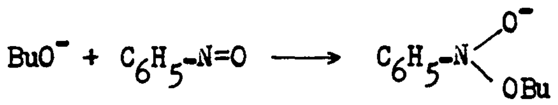
symmetrical electron exchange experiment with phenylhydroxylamine and nitrosobenzene,

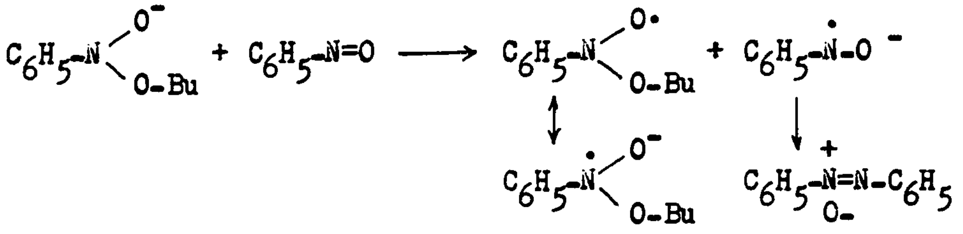
(183) $C_6H_5N{=}O + C_6H_5\text{-}\overset{\ominus}{N}\text{-}\overset{\ominus}{O} \rightleftharpoons C_6H_5\dot{N}\text{-}O^-$

presumably because dimerization followed by elimination of water forms azoxybenzene,

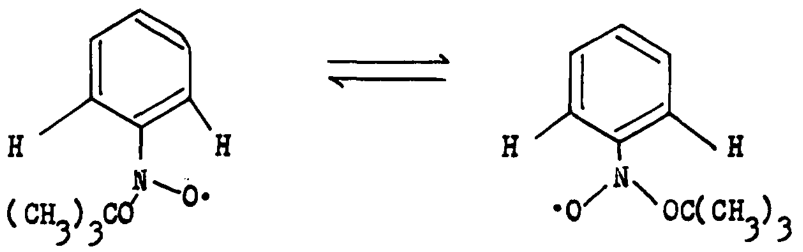
(184) 
$2\ C_6H_5\dot{N}\text{-}O^- \xrightarrow{H^+} C_6H_5\text{-}\overset{O^-}{N}\text{-}N\text{-}C_6H_5 \xrightarrow[-H_2O]{} C_6H_5\text{-}\underset{+}{\overset{O^-}{N}}{=}N\text{-}C_6H_5$

the electron transfer mechanism seems unlikely. The second possibility involves base addition followed by electron transfer.

(185) 

(186) 

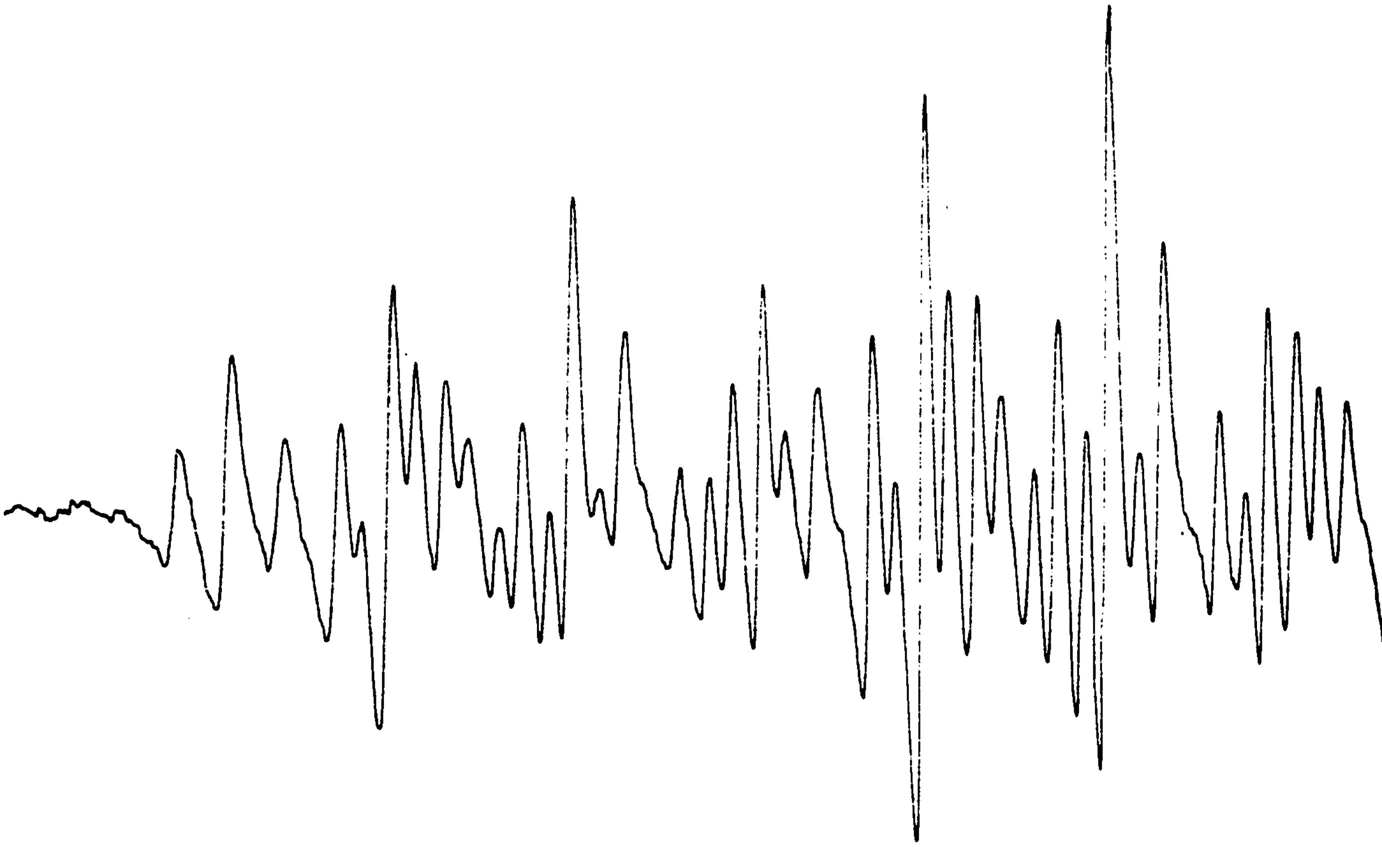
The spectrum of the N-oxide radical might be expected to be similar to that of nitrobenzene radical anion (presumably this would also be true for nitrosobenzene radical anion). A difference in the ortho proton splitting constants might be observed for this radical:

(187) 

A perfectly resolved spectrum of 54 lines for the nitrobenzene radical anion could be obtained in basic solutions of 20% dimethyl sulfoxide - 80% t-butyl alcohol containing nitrobenzene. After approximately 1 hr. the solution containing 0.005 M nitrobenzene with 0.05 M potassium t-butoxide had become pink and the spectrum shown in Figure 99 was recorded. The splitting constants which reproduced the spectrum were $a_N = 10.90$, $a_{p\text{-}H} = 3.70$, $a_{o\text{-}H} = 3.28$ and $a_{m\text{-}H} = 1.06$ gauss; Geske and Maki's in acetonitrile (37) were $a_N = 10.32$, $a_{p\text{-}H} = 3.97$, $a_{o\text{-}H} = 3.39$ and $a_{m\text{-}H} = 1.09$ gauss. In 80% dimethyl sulfoxide - 20% t-butyl alcohol similar spectra could be obtained (Figure 100, top) from nitrobenzene generated by electron transfer from the methylsulfinyl carbanion in potassium t-butoxide. The splitting constants in this solvent were $a_N = 10.21$, $a_{p\text{-}H} = 3.84$, $a_{o\text{-}H} = 3.34$, and $a_{m\text{-}H} = 1.07$ gauss obtained from a solution containing deficient potassium t-butoxide. In excess base resolution was slightly diminished, however the nitrogen splitting constants were essentially the same as in deficient base. Only small differences in nitrogen splitting constants were observed in the solvent mixtures containing dimethyl sulfoxide as compared to those reported in acetonitrile.

In hexamethylphosphoramide a new spectra was obtained indicating two radical species. Possibly the radical of larger total line width was that of the nitrobenzene radical anion. Figure 100 (bottom) shows a comparison of the radical species in 80% hexamethylphosphoramide - 20% t-butyl alcohol and in dimethyl sulfoxide. The total line width was found to be 32 gauss as compared to 34 gauss in dimethyl sulfoxide with the second radical species approximately 13.6 gauss. More surprising was the

Figure 99. Perfectly resolved E.S.R. spectrum of nitrobenzene radical anion in 20% dimethyl sulfoxide - 80% *t*-butyl alcohol



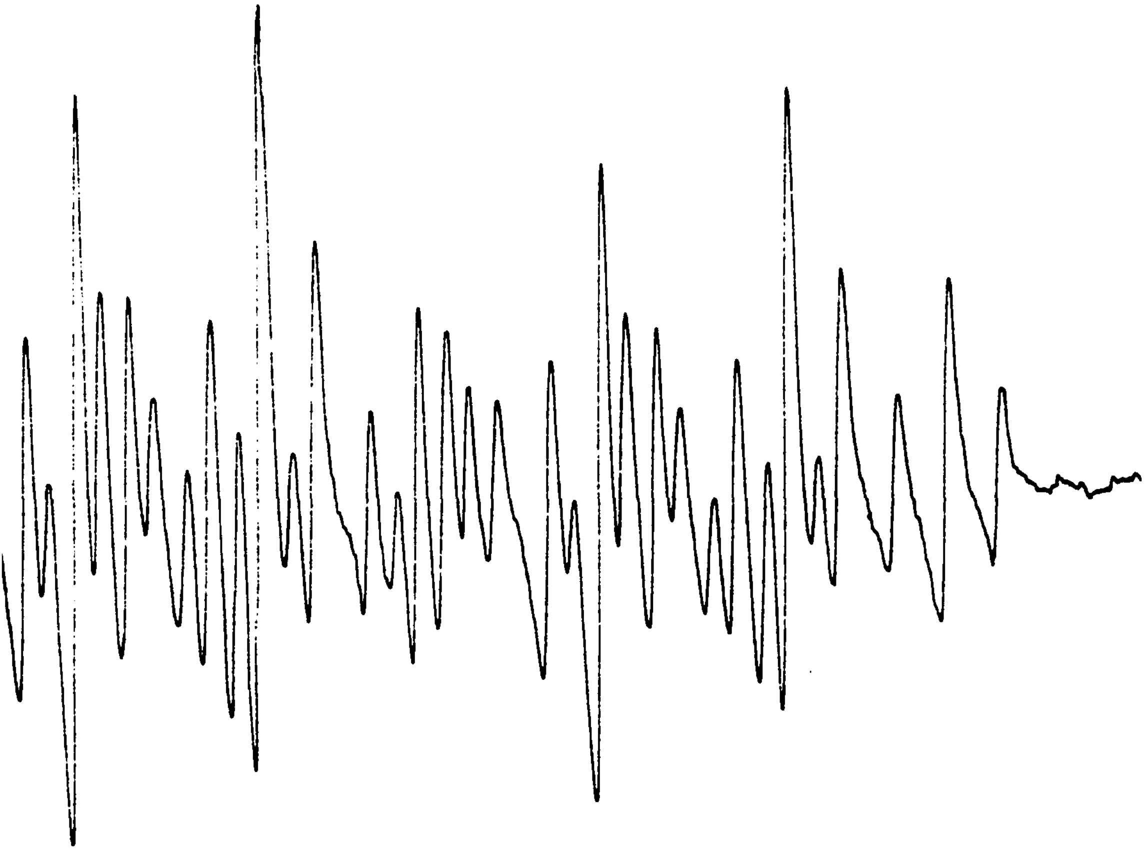
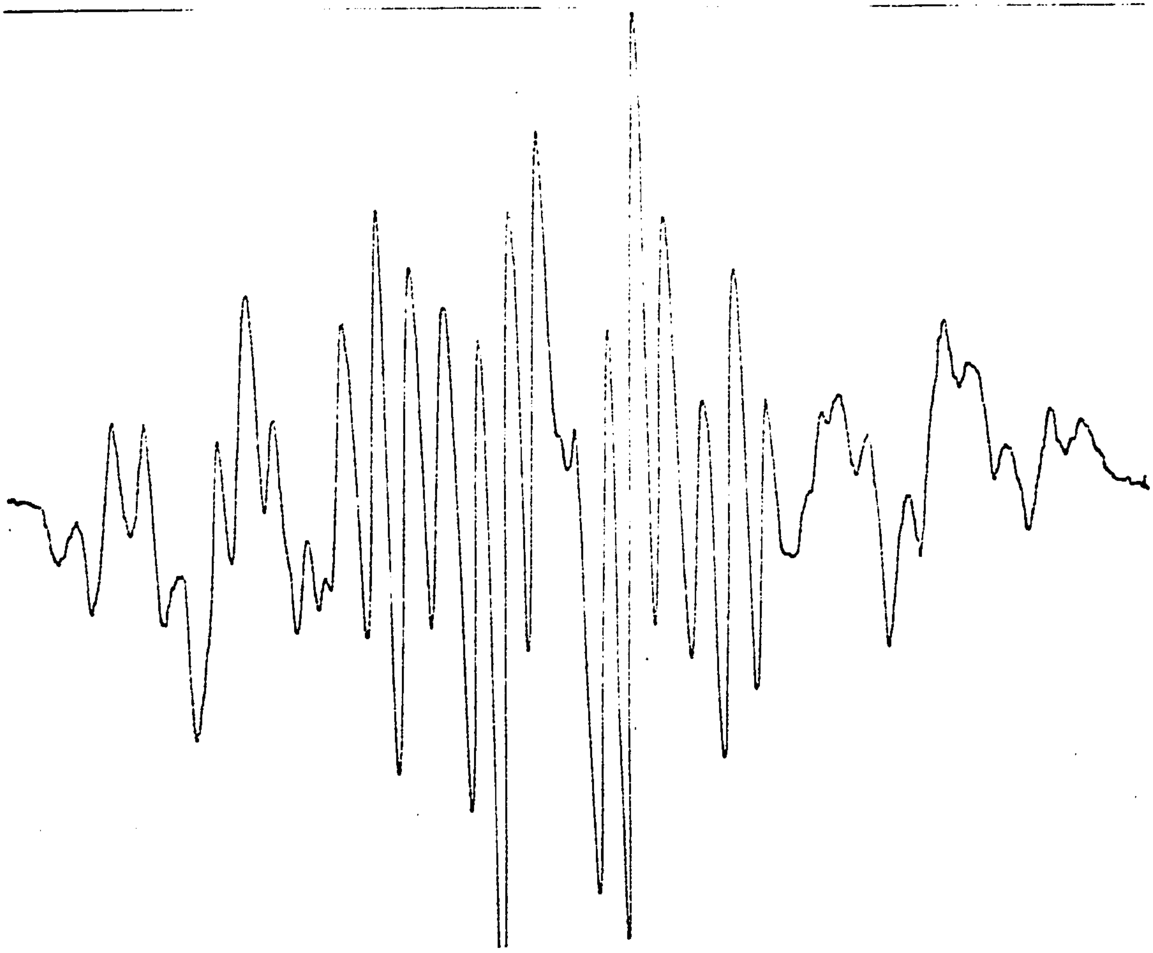


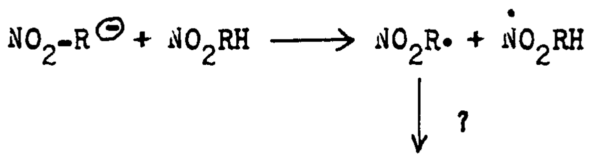
Figure 100. E.S.R. spectra obtained from nitrobenzene in basic solutions; 0.01 M nitrobenzene in 80% dimethyl sulfoxide - 20% _t_-butyl alcohol containing 0.005 M potassium _t_-butoxide (top) and 0.025 M nitrobenzene in 80% hexamethylphosphoramide - 20% _t_-butyl alcohol containing 0.05 M potassium _t_-butoxide (bottom) in the absence of air (1 cm. = 3.89 gauss)



observation that radicals were present in hexamethylphosphoramide containing nitrobenzene and no base in the presence or absence of air!

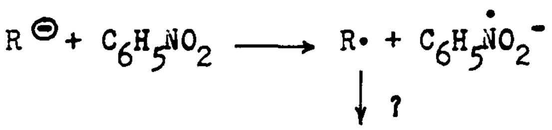
5. Electron transfer from carbanions

The most general mecanism suggested for the spontaneous formation of free radicals from p-nitrotoluene derivatives in basic solutions involved electron transfer from the carbanion to unionized nitroaromatic.



$$NO_2\text{-}R^{\ominus} + NO_2RH \longrightarrow \underset{\downarrow\ ?}{NO_2R\cdot} + \dot{N}O_2RH^{-}$$

The catalytic effect of nitrobenzene on the base-catalyzed oxidation of fluorene indicated that other carbanions not stabilized by a nitro group could electron transfer to nitrobenzene to generate free radicals.



$$R^{\ominus} + C_6H_5NO_2 \longrightarrow \underset{\downarrow\ ?}{R\cdot} + C_6H_5\dot{N}O_2^{-}$$

It was of interest to investigate the generality of the electron transfer reaction of carbanions to nitrobenzene. A suitable solvent system had to be used which would ionize the substrate appreciably but at the same time not furnish an abundance of radicals by electron transfer from the solvent components. For this purpose 80% dimethyl sulfoxide - 20% t-butyl alcohol containing potassium t-butoxide was found unsuitable because extensive electron transfer occurred with the solvent. A mixture of 20% dimethyl sulfoxide - 80% t-butyl alcohol containing 0.05 M potassium t-butoxide could be used; after 5 min. less than 0.1% electron transfer based on the nitrobenzene concentration had occurred in the presence of 0.005 M nitrobenzene. The concentrations of substrate, potassium t-butoxide and nitrobenzene used for this study were 0.025 M, 0.050 M and 0.005 M respectively, chosen to produce the largest extent of electron transfer possible from a given carbanion with the smallest radical formation from solvent alone. The concentration of nitrobenzene radical anion was estimated by comparison of the maximum peak heights of the radical with diphenylpicrylhydrazyl previously recorded in the same solvent at known concentrations.

In these experiments solutions of the substrate and nitrobenzene were degassed with prepurified nitrogen and mixed with degassed solutions of base and transferred into the E.S.R. cell (see Experimental). Two or three minutes were required to introduce the cell into the cavity, turn on the spectrometer and begin scanning through the nitrobenzene radical spectrum. After this time in most cases the radical concentration increased slowly until approximately 10 min. after mixing and then remained constant for considerable periods of time indicating good stability of the nitrobenzene radical ion under these conditions. The extent of electron transfer from a variety of carbanions, oxygen anions, sulfur anions and nitranions is given in Table 19 determined by the method described. The data reflect the ease of ionization of the substrate as well as the ease of electron transfer from the carbanion to nitrobenzene in 20% dimethyl sulfoxide - 80% t-butyl alcohol. The frequent occurrence of colored solutions containing the carbanion and nitrobenzene not attributable to the color of the carbanion or radical anion suggested charge-transfer complex formation where the carbanion served the function of the donor and nitrobenzene the acceptor. Moreover since free radicals were observed

Table 19. Extent of electron transfer from carbanions to nitrobenzene in 20% dimethyl sulfoxide - 80% *t*-butyl alcohol; 0.025 M substrate, 0.050 M potassium *t*-butoxide, 0.005 M nitrobenzene

Substrate	Per cent transfer[a] after			Color change in solution
	5 min.	10 min.	20 min. & as stated	
solvent		<0.1		colorless
cyclopentadiene	0.8	1.4		blue
indene	36			yellow to dark blue
fluorene	13			dark blue
9-phenylfluorene	8[b]			yellow orange
9-fluorenol	>100[c]			red brown
diphenylmethane	3.6	4.8		pale yellow brown
triphenylmethane		2.7		pink
phenylacetylene	.4			violet to blue
acetophenone		.3	0.8	pink to purple
propiophenone	91			pink to brown
isobutyrophenone	.2		.6	pale pink
1,2-dibenzoylethane	72[d]			dark green to brown
acetone	<.1			colorless
ethyl acetate	<.1			colorless
ethyl malonate	<.1			colorless
cyclohexanone	1.5			red to purple
1,4-hydroquinone	40[e]			yellow
2,6-di-*t*-butyl-4-methyl phenol		<.1		colorless

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[a] Per cent transfer = $\left[\text{nitrobenzene radical anion}\right] \cdot 100/0.005$

[b] 0.0125 M substrate

[c] Spectrum predominantly substrate radical anion

[d] Spectrum of radical not consistent with $C_6H_5NO_2^{\overline{\cdot}}$

[e] Two recognizable radical species present

Table 19. (Continued)

Substrate	Per cent transfer[a] after			Color change in solution
	5 min.	10 min.	20 min. & as stated	
benzhydrol		<.1		colorless
xanthydrol		1.0		colorless
benzoin	>100[c]			yellow to brown
thiophenol		.1	.2 (30 min.)	colorless
3,4-dimercapto-toluene	11			pale yellow
n-butylmercaptan		.2	.3	colorless
nitromethane		.2	.4	colorless
nitroethane		.3	.6	colorless
2-nitropropane		.1	.2	colorless
nitrocyclohexane			.1	colorless
hydrazobenzene			2 (40 min.)	yellow
N-hydroxybenzene-sulfonamide	92			bright orange
diphenylamine		.1		colorless
carbazole		.1		pale yellow
indole		<.1		colorless
__-picoline-*N*-oxide		.1		pale pink
diphenylacetonitrile	2			yellow
phenylacetonitrile		.5		dark red to purple
acetonitrile		<.1		colorless
propionitrile		<.1		colorless
isobutyronitrile		<.1		colorless
benzopinacol	100			
n-butyllithium[f]	~6			

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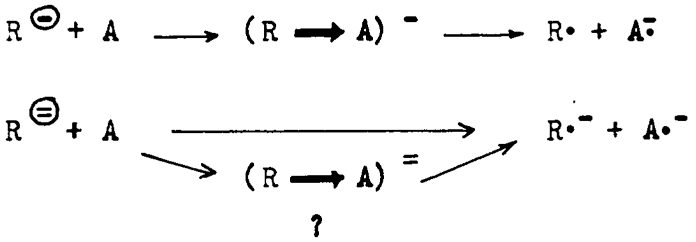
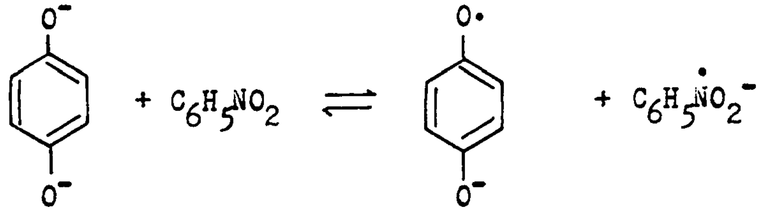
[f] 0.01 M nitrobenzene, ~1 M *n*-butyllithium in tetrahydrofuran

in these colored solutions albeit in varying amounts and since colorless solutions gave signals of reasonable intensity it seemed that the charge transfer complex was correlated to radical formation. Our observations indicate that although charge-transfer complexes need not be present in all cases where electron transfer occurs they may exist for many carbanions in the presence of nitrobenzene or other electron acceptors.

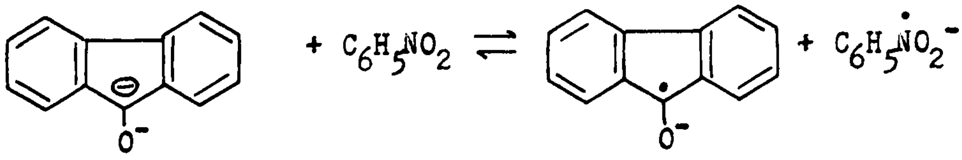


Carbanions that transferred electrons very readily were either cyclopentadiene derivatives or dianions (Table 19). Examples of the latter where two radical species could be recognized were fluorenol and hydroquinone (Figure 101).

(188)

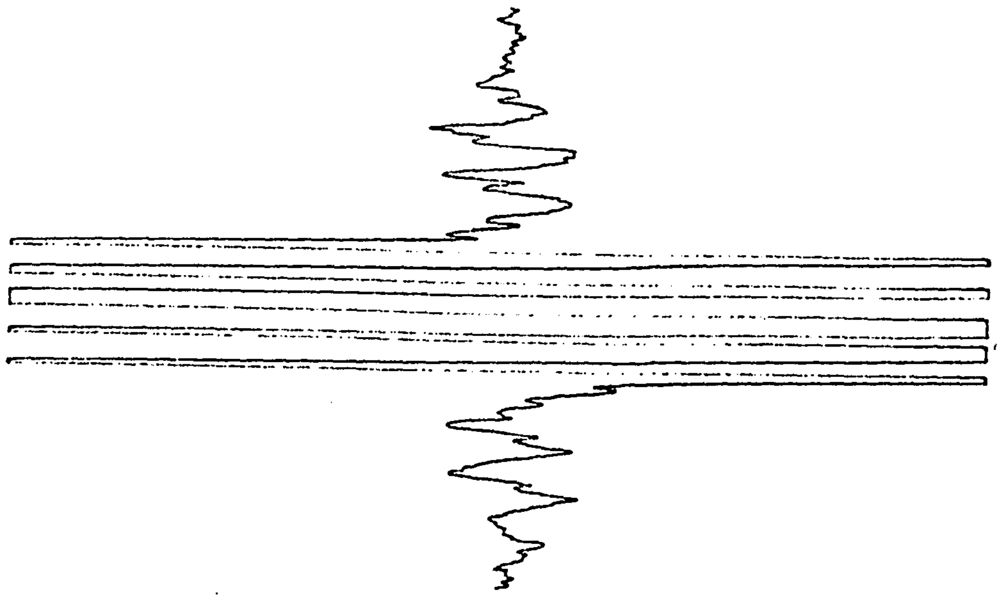


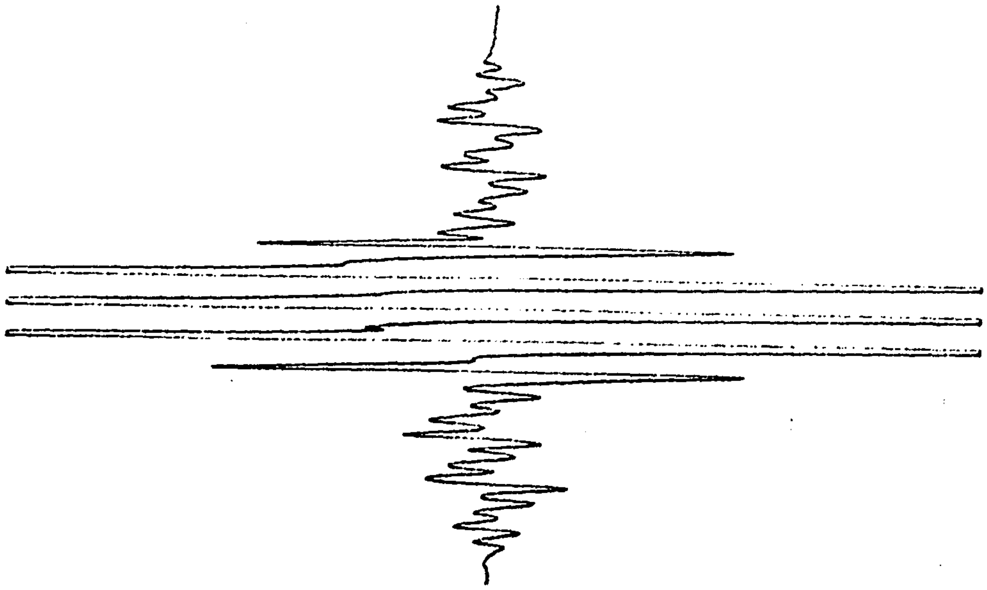
(189)



It seems reasonable that carbanions which are easily oxidized (<u>i</u>.<u>e</u>., have a low oxidation potential) should electron transfer more readily than

Figure 101. E.S.R. spectra showing the formation of two radical species by electron exchange (left, hydroquinone and nitrobenzene; right, hydroquinone and *m*-dinitrobenzene; see Tables 19, 20)





carbanions which have a high oxidation potential and are difficult to oxidize. Many carbanions which were appreciably ionized in the solvent system used did not transfer presumably because of too high an oxidation potential. Electron transfer was attempted in these cases with m-dinitrobenzene which has a lower reduction potential than nitrobenzene and hence is a better oxidizing agent (Table 20).

With m-dinitrobenzene numerous carbanions transferred to a greater extent than with nitrobenzene although the solvent systems could not be made comparable because of the large concentration of radicals produced *via* electron transfer involving solvent in dimethyl sulfoxide or t-butyl alcohol. Some cases of electron transfer were observed which gave different E.S.R. spectra not easily reconciled with the spectrum of the dinitrobenzene radical anion. Either the products of a two-electron reduction or of an addition of carbanion to the benzene ring might have produced the radical species observed. In many cases the concentration of m-dinitrobenzene radical anion decreased with time after the first observation of the signal indicating instability of the radical anion under these conditions. However in experiments where aliphatic carbanions were used as donators the radical signal appeared to be more stable.

Although in the case of nitrobenzene it could be proved that only one stable radical species was formed in the electron transfer reaction because a perfectly resolved spectrum of the nitrobenzene radical anion could be obtained (Figure 100) this could not be ascertained with certainty for m-dinitrobenzene with the information on hand. Since free radicals could be produced by electron exchange after an addition reaction a poorly resolved spectrum would be expected due to more than one radical

Table 20. Extent of electron transfer from carbanions to m-dinitrobenzene in absolute ethanol; 0.025 M substrate, 0.050 M sodium ethoxide, 0.005 M m-dinitrobenzene

Substrate	Per cent transfer[a] after 5 min. and as stated	Color change in solution
solvent	< 0.1	
cyclopentadiene	2.6, 10 (1 min.)	
indene	2[b]	purple to brown
fluorene	40 (8 min.) 80 (20 min.)	purple to black
acetophenone	2.7	pink to purple to brown
Propiophenone	4	red to purple
isobutyrophenone	.5	pale pink
1,2-dibenzoyl-ethane	2.6	brown orange (anion)
acetone	.8	pink to red
ethyl acetate	.3, 0.5 (20 min.)	pink
ethyl malonate	5	dark red to brown
1,3-indanedione	<.1, 2.4 (15 min.)	brown (anion)
2,2'-biindan - 1,1',3,3'-tetrone	<.1, 0.8 (25 min.)	purple (anion)
ethyl acetoacetate	<.1	pink
acetylacetone	<.1	colorless
2,6-di-t-butyl-4-methyl phenol	.5 (20 min.)	pale pink
hydroquinone	>100[c]	yellow to brown
thiophenol	.6, 2 (8 min.)	orange

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[a] Per cent transfer = [nitrobenzene radical anion] · 100/0.005

[b] Spectra obtained not consistent with m-dinitrobenzene radical anion apectrum

[c] Total radical concentration, maninly substrate radical anion

Table 20. (Continued)

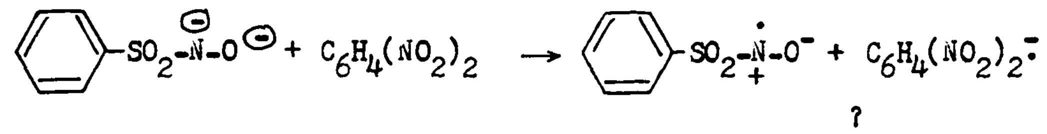
Substrate	Per cent transfer[a] after 5 min. and as stated	Color change in solution
n-butylmercaptan	12[b]	pink to pale brown
3,4-dimercapto-toluene	5[b]	pale yellow
nitromethane	2	pale brown
nitroethane	2	pale brown
2-nitropropane	.3, 2 (40 min.)	pale brown to mauve
hydrazobenzene	7.5[b] (2 min.)	
N-hydroxybenzene-sulfonamide	10[b] (10 min.)	green to yellow
benzopinacol	6.8 (3 min.)	pale yellow
dimethyl sulfone	<0.1	colorless

species present in solution. For nitromethane, 2-nitropropane, 1,3-indandione, [2,2'-biindan]-1,1',3,3'-tetrone, ethyl malonate, acetophenone and thiophenol partially resolved spectra were obtained with 10 major peaks and a total of 22-23 peaks and shoulders very similar to Figure 92 for nitroethane. The similarity in spectra for such a variety of carbanions is a strong argument in favor of one radical species in solution. For dianions a complex spectra could be expected due to two radical species in solution.

$$(190) \quad R^{\ominus} + C_6H_4(NO_2)_2 \longrightarrow R\cdot + C_6H_4(NO_2)_2^{\overline{\cdot}}$$

Different hyperfine splitting patterns were observed for 1,2-dibenzoylethane and hydrazobenzene although the 10 major peaks of m-dinitrobenzene radical anion could be recognized in the spectra. From the experiment with N-hydroxybenzenesulfonamide a spectrum was obtained which could only be reconciled with the expected spectrum of benzenesulfonamide-N-oxide radical (Figure 102).

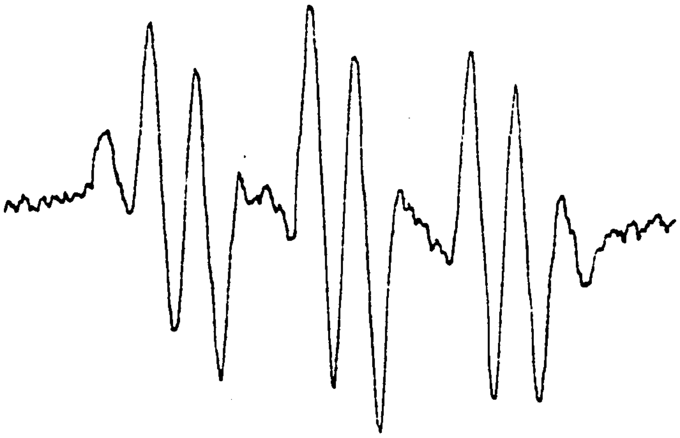
(191)

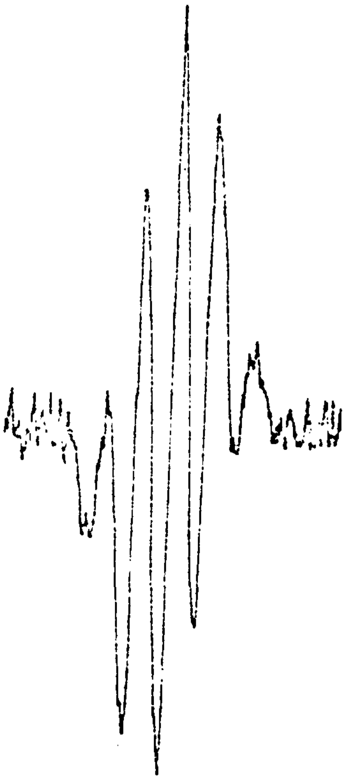


The obvious symmetry of the spectrum allowed the determination of the following splitting constants, $a_N = 12.43$ and $a_{\underline{o}-\underline{p}-H} = 3.47$ (for 3 equivalent hydrogens).

The extent of electron transfer of two series of carbanions which allowed a comparison to be made as the donator was changed from primary through to tertiary carbanion, the nitroalkanes and alkylphenones, both followed the order secondary > primary > tertiary towards nitrobenzene. The reactivity of the carbanions of alkylphenones towards oxygen has been shown to follow the order tertiary > secondary > primary in deficient base (18), the most unstable carbanion (tertiary) reacting fastest to give the most stable radical. It might be expected that electron transfer should follow the same order. The observation that a secondary carbanion transfers better than a primary carbanion is in accord with the accepted relative stability of the carbanions oxidizing to a radical. That the tertiary carbanion is a poorer or slower donator may be due to steric hindrance in the formation of a stable charge-transfer complex. The plots of the extent of electron transfer to nitrobenzene for the nitroalkanes as a function of time shown in Figure 103 indicate that the ease of

Figure 102. E.S.R. spectra of radical species thought to be benzenesulfonamide-N-oxide radical produced from N-hydroxybenzenesulfonamide in ethanol containing sodium ethoxide and *m*-dinitrobenzene (top left, a_N = 12.43, $a_{\underline{o},\underline{p}-H}$ = 3.47 gauss), free radical species thought to be iodosobenzene radical anion (top right, 1 cm. = 5.78 gauss) and iodoxybenzene radical anion (bottom, 1 cm. = 1.56 gauss) produced by electron exchange from indene in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol containing potassium *t*-butoxide





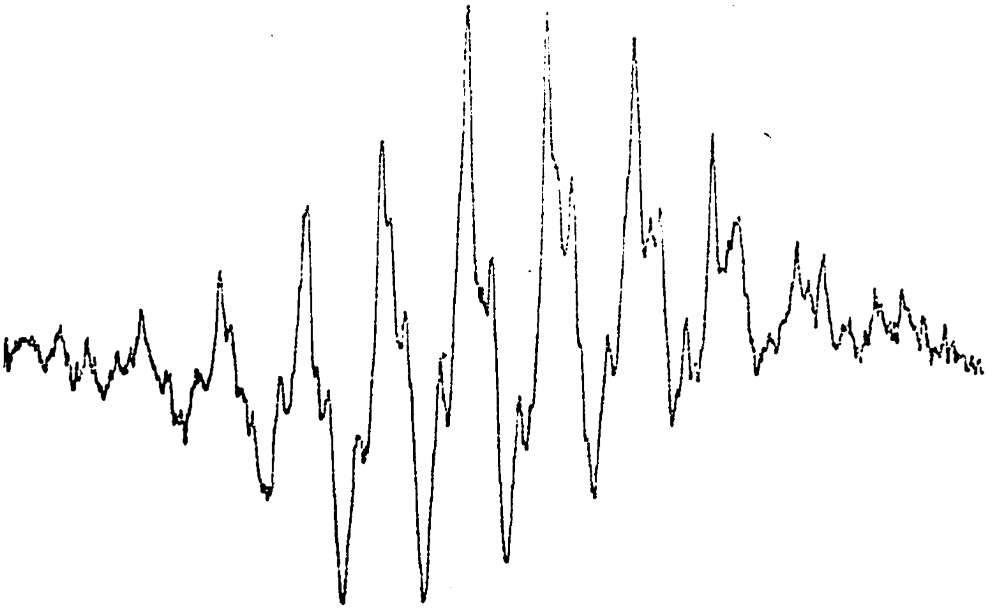
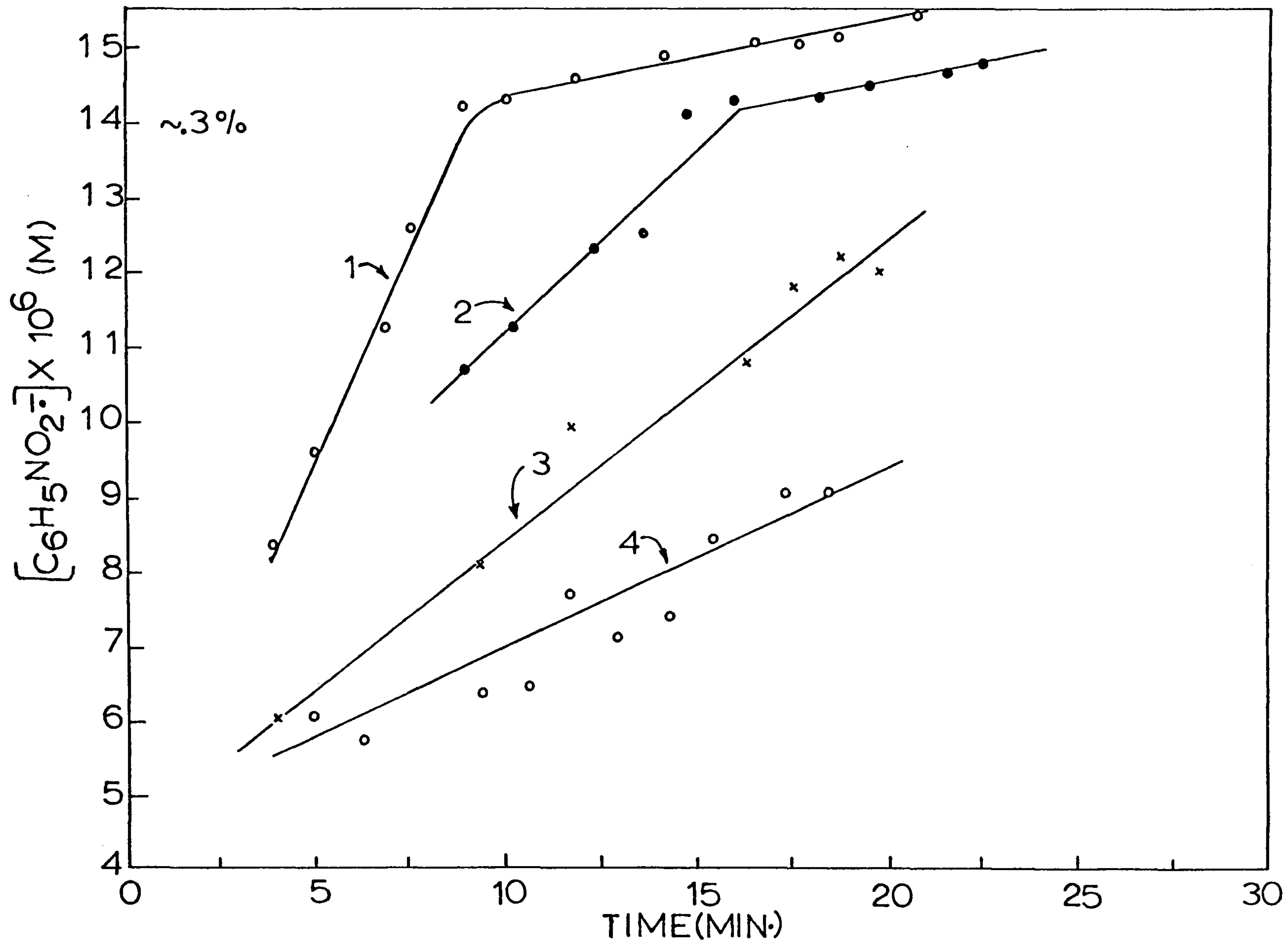


Figure 103. Extent of electron transfer from nitroalkyl carbanions to nitrobenzene as a function of time in 20% dimethyl sulfoxide - 80% *t*-butyl alcohol (0.025 M nitroalkane, 0.005 M nitrobenzene, 0.050 M potassium *t*-butoxide)

Curve 1	nitroethane
Curve 2	nitromethane
Curve 3	2-nitropropane
Curve 4	nitrocyclohexane


~.3%
$[C_6H_5NO_2^{\cdot-}] \times 10^6$ (M)
TIME(MIN.)
1
2
3
4
0
5
10
15
20
25
30
4
5
6
7
8
9
10
11
12
13
14
15

electron transfer may be a kinetically controlled reaction. With m-dinitrobenzene the primary and secondary carbanions from nitromethane and nitroethane transfer rapidly and equally well while the tertiary 2-nitropropyl carbanion transfers much more slowly, reaching approximately the same extent of transfer by 40 min. (Figure 104).

The choice of carbanions in exploring the generality of the electron transfer reaction was aimed at selecting representative carbanions of various classes of functional groups. Although the number of carbanions tried is limited the data shows that the order of the ease of electron transfer from an anion is $\geq C^{-} > -S^{-} > -O^{-} > \;>N^{-}$ for the reaction

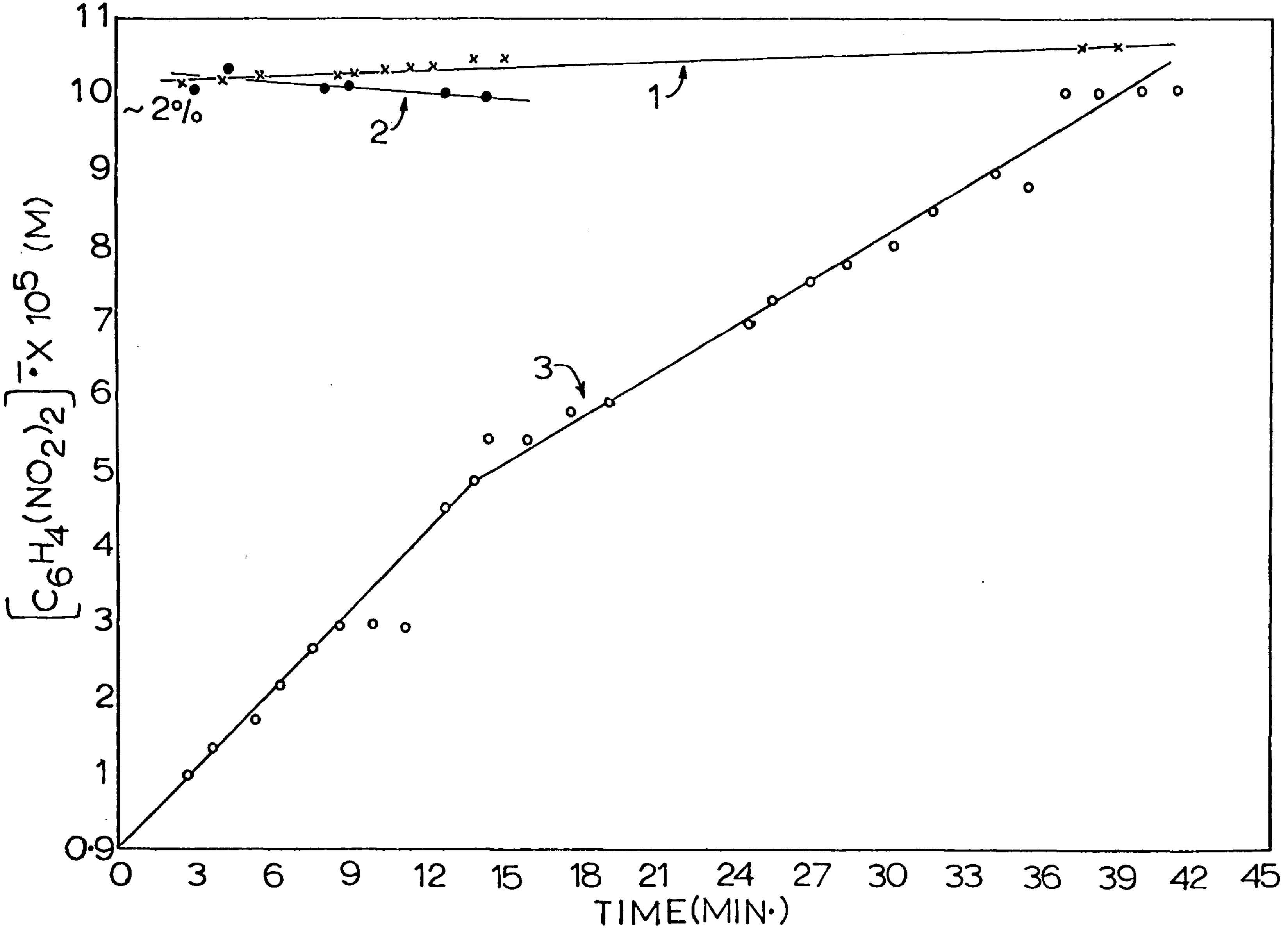
$$R^{\ominus} + A \longrightarrow R\cdot + A\cdot^{-}$$

6. Electron acceptors

The generality of electron transfer reactions as a function of the structure of carbanion was demonstrated with nitrobenzene and m-dinitrobenzene as acceptors. Quinones (26), ketones, azobenzene, heterocyclic aromatics and electron-deficient carbon double bonds (52) also have served as electron acceptors under suitable conditions in the presence of their ionized saturated analogues. It was an interesting problem to find new electron acceptors stable in highly basic solutions. It seemed reasonable to consider the one-electron reduction potential as the most important factor in predicting the ability to accept an electron from a donator in question. In general the trend for a given functional group seemed to correlate with the decrease in reduction potential in the catalytic effect exerted by substituted nitrobenzenes in the base-catalyzed oxidation of fluorene and in the ease of electron transfer by nitrobenzene and

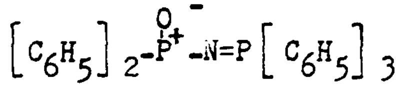
Figure 104. Extent of electron transfer from nitroalkyl carbanions to *m*-dinitrobenzene as a function of time in absolute ethanol (0.025 M nitroalkane, 0.005 M *m*-dinitrobenzene, 0.050 M sodium ethoxide)

Curve 1	nitroethane
Curve 2	nitromethane
Curve 3	2-nitropropane


$\left[C_6H_4(NO_2)_2\right]^{\overline{\cdot}} \times 10^5$ (M)
TIME(MIN·)
0·9
1
2
3
4
5
6
7
8
9
10
11
0
3
6
9
12
15
18
21
24
27
30
33
36
39
42
45
~2%
1
2
3

m-dinitrobenzene. However it was found by Russell and Strom[1] that azobenzene and azoxybenzene were not as efficient acceptors as nitrobenzene although their reduction potentials were very similar (140). Presumably charge-transfer complex formation is an important prior step to electron transfer and the ease of formation and stability of the complex should be considered. The observed examples of rapid electron exchange between alcohols and ketones indicate that structural similarities between the donor and the acceptor aid in electron transfer reactions.

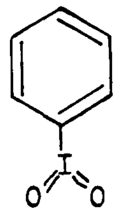
In our scouting experiments to uncover new and interesting electron acceptors it was found that azoxybenzene, triphenylphosphine oxide, diphenylphosphonimido triphenylphosphorane oxide,



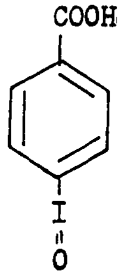
$$\left[C_6H_5\right]_2\text{-}\overset{O^-}{P^+}\text{-N=P}\left[C_6H_5\right]_3$$

and 2,2'-dipyridyl-N-oxide were found to be unsuitable and did not produce radical species under conditions where nitrobenzene transferred extensively. However small amounts of radicals were observed in trials using iodoxybenzene and p-iodosobenzoic acid.

Iodoxybenzene



Iodosobenzoic acid



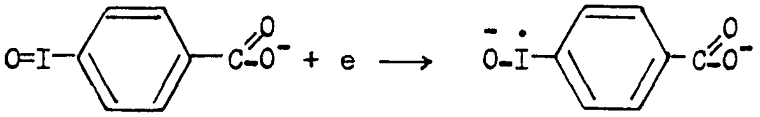
A simple 5-peak spectrum each separated by 2.72 gauss was obtained

---

[1] G. A. Russell and E. T. Strom, Dept. of Chemistry, Iowa State University, Ames, Iowa. Private communication regarding electron transfer experiments with azobenzene, May, 1963.

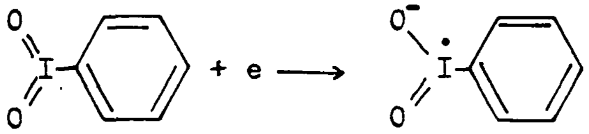
from a solution of indene and p-iodosobenzoic acid (both 0.025 M) containing 0.050 M potassium t-butoxide in 80% dimethyl sulfoxide - 20% t-butyl alcohol (Figure 102). No signal was observed for either component in base in the absence of the other. If electron transfer had generated an iodosobenzene radical anion it would be the first reported of this type.

(192)



A more complex spectrum containing 9 or 10 main peaks split into triplets was obtained for the radical species from iodoxybenzene (Figure 102) generated presumably by electron transfer from propiophenone. More information is necessary to ascertain the radical species but by analogy to nitrobenzene the iodoxybenzene radical may have been formed.

(193)



Organic radicals involving paramagnetic iodoso and iodoxy groups have not been reported in the literature although iodonium benzene is believed to react as an electron acceptor in phenylation reactions with β-diketones (95).

IV. CONCLUSIONS

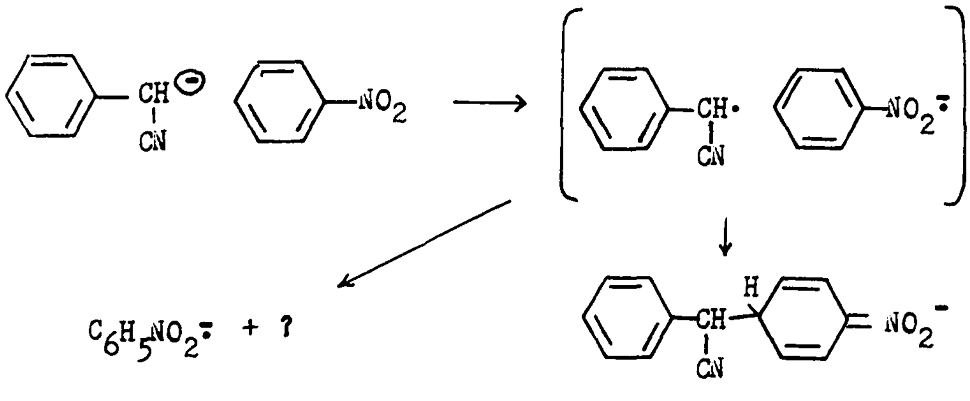
The conception that carbanion oxidation might proceed through the intermediary of free radicals is a mere encroachment into the field of typical ionic reactions compared to the potential invasion in the form of the one-electron transfer mechanism presently threatening ionic reaction strongholds. The outcome rests upon ingenuity in designing experiments and techniques for identifying short-lived intermediates in every reaction under consideration.

It is well understood that molecules will react to give products by the path of lowest energy. That this pathway more often involves free radicals than commonly realized may eventually be proved in the future. For the present, a beginning has been made in this direction; the observations described in this thesis serve to show that free radicals are present either as intermediates or by-products in solutions containing reactive species which are known to react to yield known products. From these observations deductions can be made about the mechanisms of various product formations. Some of these are:

Nucleophilic addition reactions (see Reference 141)

e.g.

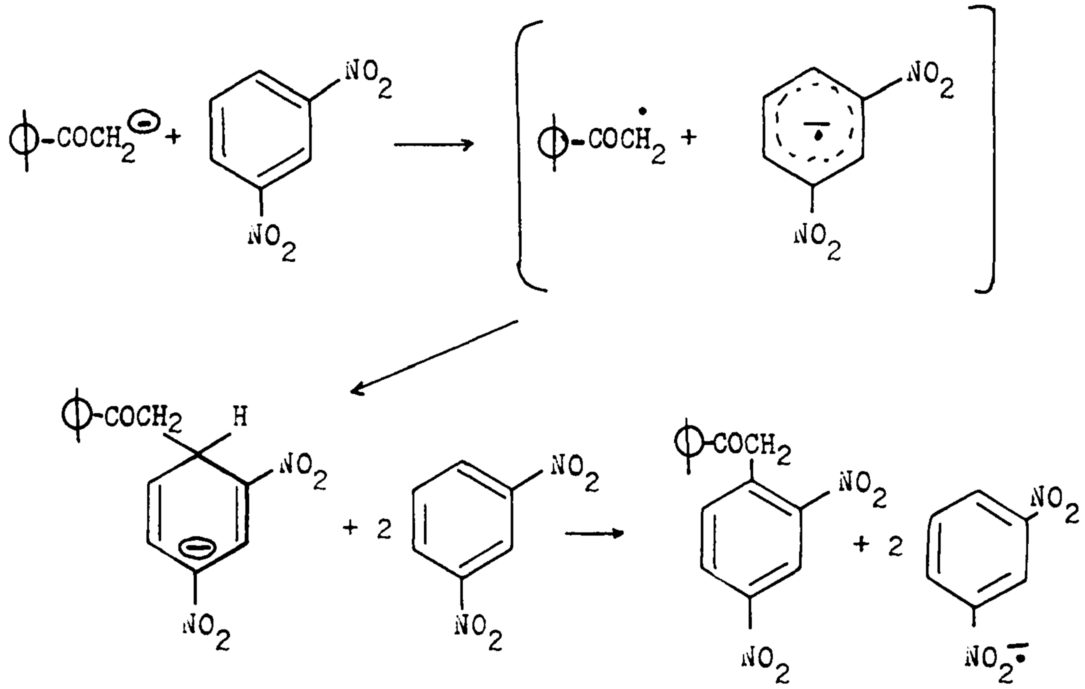
(194)



Addition products from charge-transfer complexes with m-dinitrobenzene (see References 37, 142)

e.g.

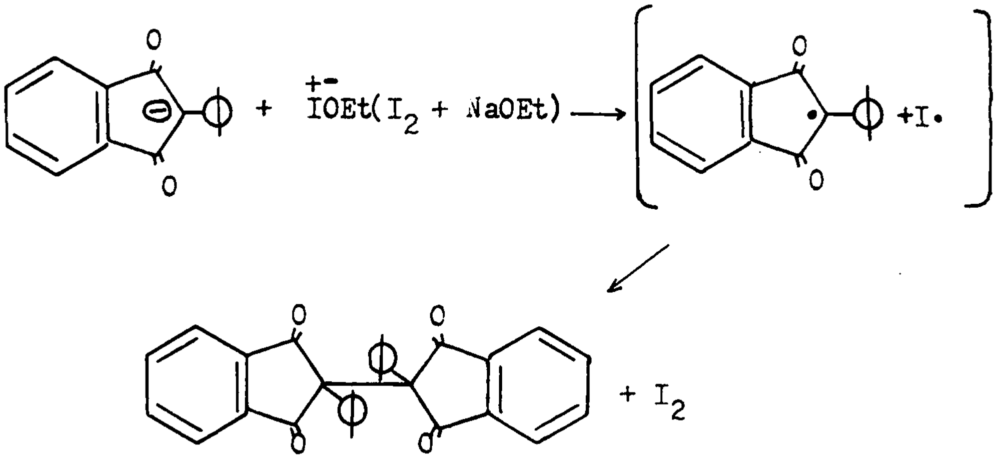
(195)



Iodine oxidation (see References 95, 143)

e.g.

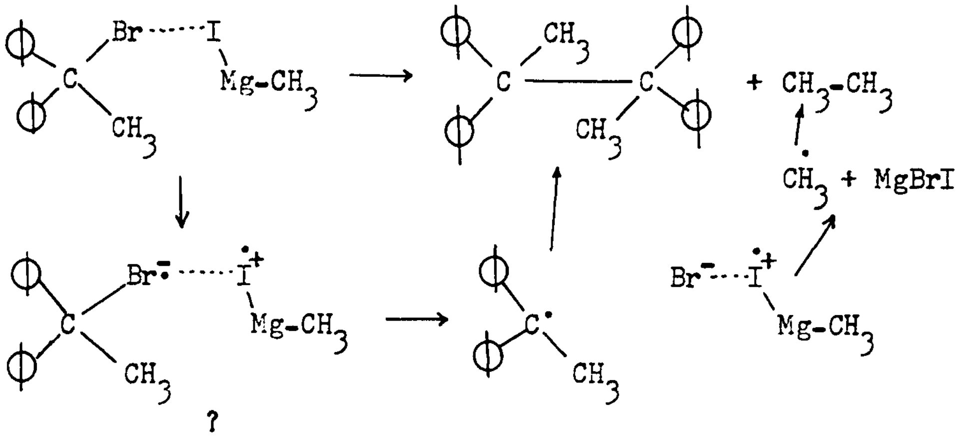
(196)



Grignard Coupling reactions (see References 144, 145, 2)

e.g.

(197)



We have reported the occurrence of free radicals observed in basic solutions containing donators in the form of carbanions and acceptors such as nitrobenzene. The simple mechanism suggested is one-electron transfer.

$$R^{\ominus} + A \longrightarrow R\cdot + A^{\bar{\cdot}}$$

No more data is available to justify a more detailed description of the general mechanism of radical formation; however, the discovery of free radicals generated by electron transfer processes between organic molecules would become more significant if the mechanism of electron transfer could be firmly established; a one or two electron transfer process can be visualized:

Two electron process

$$R^{\ominus} + A \longrightarrow \underset{\text{complex}}{\left[R \Rightarrow A \right]^{-}} \longrightarrow \underset{\substack{\text{addition} \\ \text{product}}}{R\text{-}A^{-}} \longrightarrow \underset{\substack{\text{solvent} \\ \text{cage}}}{\left[R\cdot + A^{\bar{\cdot}} \right]} \longrightarrow R\cdot + A^{\bar{\cdot}} \searrow ?$$

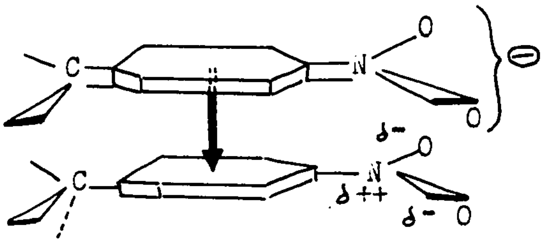
One electron process

$$R^{-} + A \longrightarrow \left[R \longrightarrow A\right]^{-} \longrightarrow \underset{\text{solvent cage}}{\left[R\cdot + A^{\overline{\cdot}}\right]} \longrightarrow A^{\overline{\cdot}} + \underset{\big\downarrow}{R\cdot}$$

dimerize, abstract hydrogen,
lose proton, oxidize, _etc._

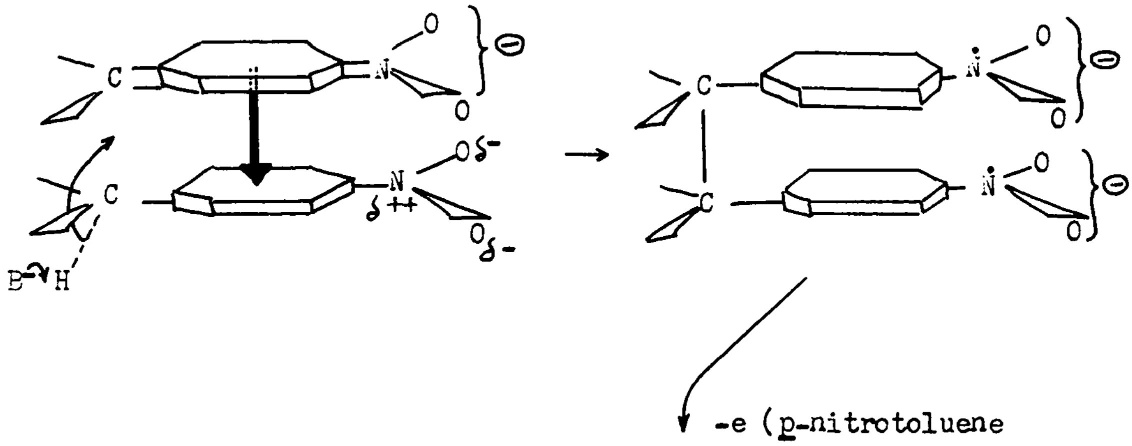
Considerable data on the chemistry of _p_-nitrotoluene in basic solution has been obtained. Since dimerization occurs in the presence of oxygen the carbanion must be relatively unreactive towards oxygen or the charge-transfer complex formation must be very rapid and non-reversible. Moreover if _p_-nitrobenzyl radicals are formed they must dimerize within the solvent cage. We have found dimerization to be very rapid in aprotic dipolar solvents which solvate cations preferentially to anions. Since there is no evidence for specific solvation of free radicals in dimethyl sulfoxide it would seem the radical and radical anion pair would be relatively unsolvated and free to react with oxygen in solution. It follows that dimerization must occur within the charge-transfer complex.

For dimerization within the charge-transfer complex the donor and acceptor molecules must be compatibly oriented. Furthermore, since a high electron density must reside on the nitro group of the _p_-nitrobenzyl carbanion, and a low electron density on the nitrogen of the nitro group of the unionized molecule these groups might be expected to exist nearest each other. These factors may determine the following orientation for "maximum π-orbital overlap".



XXXVI

The formal dimerization of *p*-nitrobenzyl carbanion and *p*-nitrotoluene to produce *p,p'*-dinitrobibenzyl involves the loss of two electrons and one proton. The time sequence of electron or proton removable is a matter of speculation with no analogies to call upon. Possibly the proton removal is synchronous with electron transfer as shown.



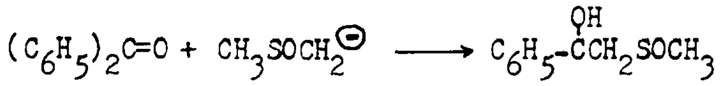
-e (*p*-nitrotoluene

p,p'-dinitrobibenzyl radical anion

-e (*p*-nitrotoluene)

p,p'-dinitrobibenzyl

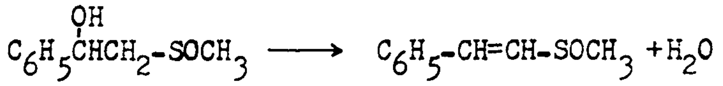
The study which began as an investigation into the mechanism of dimerization of p-nitrotoluene in the presence of oxygen has led to oxidation reactions which provide stilbene derivatives from numerous tolyl derivatives (e.g., methyl p-toluate to p,p'-dicarboxystilbene), ketones (when no α-hydrogens are present) from substituted methylenes, and carbinols from tertiary carbanions. These products can also be achieved by other oxidative pathways. However a number of new reactions have been discovered, e.g., dimethyl sulfoxide adduct formation,



$$(C_6H_5)_2C{=}O + CH_3SOCH_2^{\ominus} \longrightarrow C_6H_5\text{-}\overset{OH}{C}CH_2SOCH_3$$

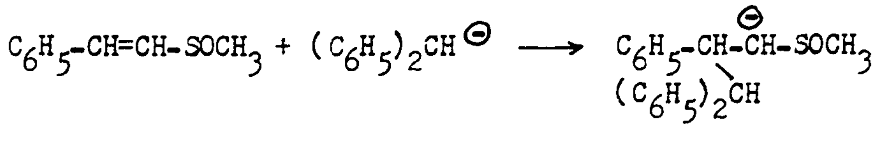
asymmetric three-carbon condensation (93),

(198)



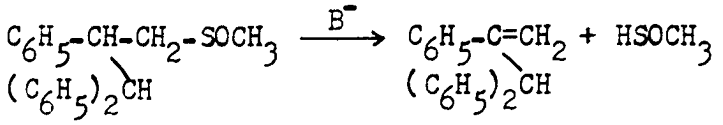
$$C_6H_5\overset{OH}{C}HCH_2\text{-}SOCH_3 \longrightarrow C_6H_5\text{-}CH{=}CH\text{-}SOCH_3 + H_2O$$

(199)



$$C_6H_5\text{-}CH{=}CH\text{-}SOCH_3 + (C_6H_5)_2CH^{\ominus} \longrightarrow C_6H_5\text{-}\underset{(C_6H_5)_2CH}{CH}\text{-}\overset{\ominus}{C}H\text{-}SOCH_3$$

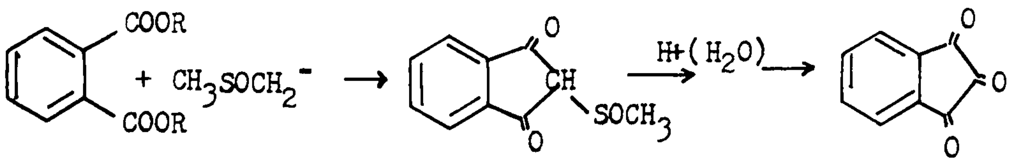
(200)



$$C_6H_5\text{-}\underset{(C_6H_5)_2CH}{CH}\text{-}CH_2\text{-}SOCH_3 \xrightarrow{B^-} C_6H_5\text{-}\underset{(C_6H_5)_2CH}{C}{=}CH_2 + HSOCH_3$$

and ninhydrin formation,

(201)



The study of the reactions of p-nitrotoluene in basic solutions in the absence of air has led to the discovery of electron transfer reactions from anions, e.g., carbanions to unsaturated molecules, particularly containing nitrogen.

$$R^{\ominus} + A \longrightarrow R\cdot + A^{\overset{-}{\cdot}}$$

where A = nitrobenzene, azobenzene, phenazine,
fluorenone, perchlorofulvalene, *etc*.

The applications of these observations are under current investigation and will undoubtedly receive increased attention in the future.

V. EXPERIMENTAL

A. Methods

The experiments specifically mentioned in tables by "run" numbers refer to the page number in one of three research notebooks, A, B or C, with subscripts designating the first, second or third experiment on the page.

All plots of oxygen absorbed as a function of time are calculated as the ratio of moles oxygen at S.T.P. absorbed per mole starting material. All oxidations were performed at 740 mm. pressure. Since the apparatus was not thermostated oxidation temperatures varied during the year from 24° - 30° C., although the temperature during an experiment varied insignificantly. Sometimes very fast oxidations caused an increase in temperature of the oxidizing solution.

The method of measuring the rate of oxidation was a volumetric constant-pressure method essentially the same as used by Moye (3). All oxidations were performed in a creased 125 ml. flask, well agitated by a wrist-action shaker designed for this purpose (Figure 105). The flask was built with a second small ground glass opening which was fitted with a 10 ml. bulb with a curved neck. The addition of the basic solution from the bulb into the solution of substrate in the flask was brought about by turning the bulb up. At this moment the shaker was started and instant mixing occurred. In all experiments the substrate was completely dissolved in the solvent before the basic solution was added. The rate of oxidation was followed until an insignificant rate of oxygen absorption was observed. If intermediate products were desired oxidation was stopped

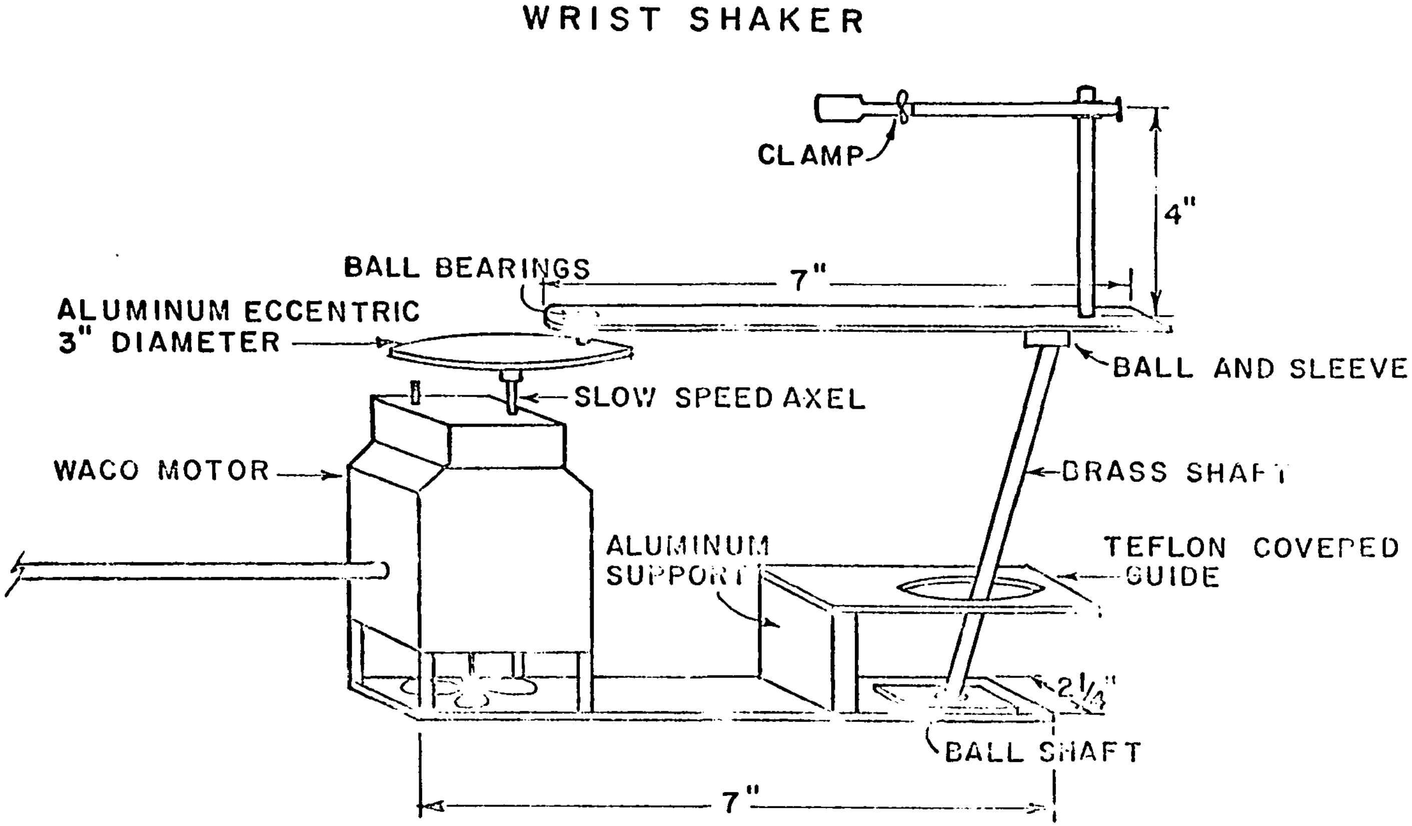


Figure 105. Wrist-action shaker used to agitate solutions for oxidation experiments

earlier and quenched by pouring the solution into water. For very slow oxidations a relay-controlled constant-levelling device was used designed for this purpose (Figure 106).

The relay was activated by a small capacitor clipped around the manometer tube at the top level of the mercury column. When the mercury column fell below a given level the relay activated the slow speed motor which turned the rod threaded through the mercury bulb support. The mercury bulb was raised by the threaded rod as the oxygen pressure dropped in the system due to oxygen absorption. An electric stop-switch was built on the guide rod to prevent the bulb from rising too high when the oxygen had been entirely used in the system. The bulb support could be returned to a low position by removing the rod and turning it top to bottom.

The oxidations of methyl p-toluate in the shaker were performed in the usual fashion. The experiments in a solution stirred with a magnetic stirring bar were similar to that used by Moye (3). For the reactions under 4 atmosphere oxygen pressure a Parr hydrogenation apparatus was used adapted for very rapid shaking. Instant mixing of the base with the substrate under oxygen after the apparatus was sealed and under pressure was brought about by introducing carefully into the pressure bottle containing solvent and methyl p-toluate a thin-walled test-tube like container (a small sealed drying tube served very well) which contained a solution of the base; the tube instantly shattered and the solutions were mixed when the shaker was started. The high speed stirrer was run at speeds of approximately 10,000 r.p.m. which vigorously foamed the solution. Oxygen was passed through the solution continuously, remaining approximately 30-40 mm. above atmospheric pressure.

AUTOMATIC MERCURY-BULB LEVELLING DEVICE

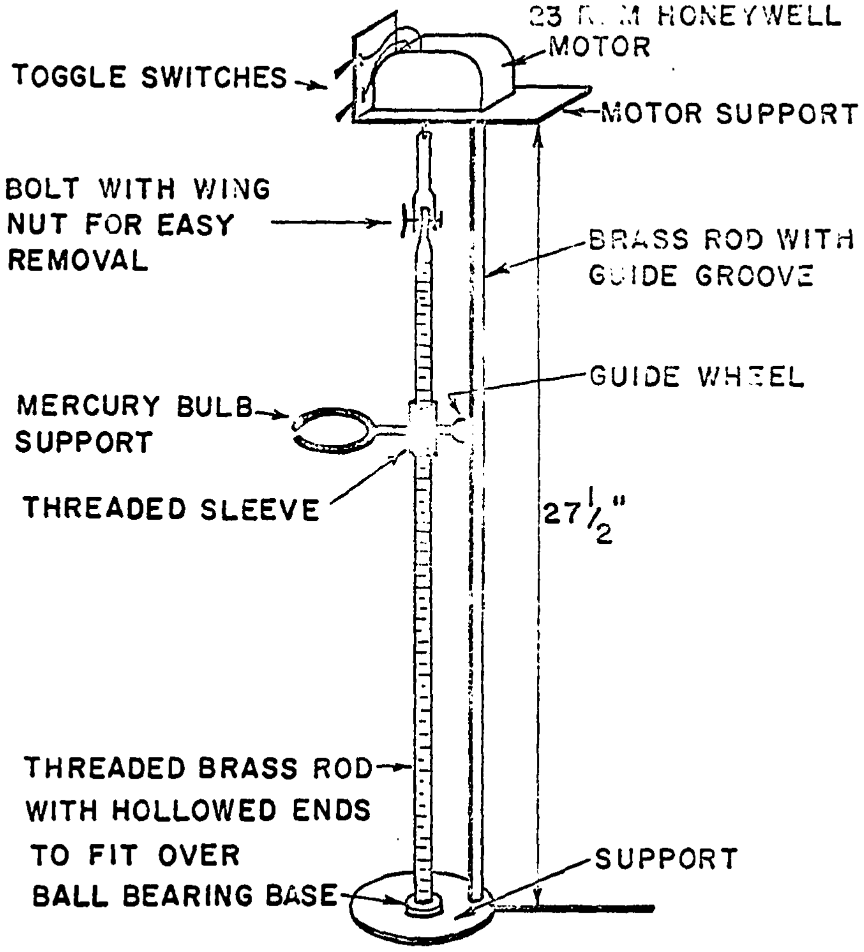


Figure 106. Relay-controlled mercury-bulb levelling apparatus used for slow oxidation experiments

For the isolation of products from the methyl p-toluate oxidations the oxidized solution was boiled in 10% sodium hydroxide for approximately 2 hr., acidified with hydrochloric acid and allowed to stand for complete precipitation of acid. The precipitate was filtered and dried at 120°; the aqueous solution was extracted with large quantitites of benzene. The average molecular weights for these acids as well as for those isolated from the oxidations of the other substituted toluene derivatives were determined by dissolving the acids in a known amount of aqueous sodium hydroxide and by back-titrating potentiometrically with standard hydrochloric acid.

The p-nitrotoluene spontaneous dimerization experiments were carried out in a 3-necked 1 liter flask in the absence of air. The solution of p-nitrotoluene in t-butyl alcohol was degassed by freezing under vacuum in a dry-ice acetone bath. The reaction was run under the vapor pressure of t-butyl alcohol (about 30-40 mm.) to eliminate the trace amounts of oxygen possibly included in nitrogen gas. A solution of potassium t-butoxide was added from a 50 ml. flask connected via a curved neck which could be turned in an upward position at zero time. A magnetic stirring bar agitated the solution. After a given time the reaction was quenched by degassed water introduced quickly through tubing from a vessel containing deaerated water. Since the flask was under partial vacuum, by simply opening a suitable stop-cock water could be siphoned rapidly into the flask.

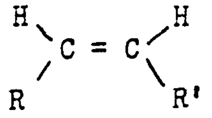
After the aqueous solution was treated with air or oxygen the products could be obtained since p,p'-dinitrobibenzyl precipitated and p-nitrotoluene could be obtained by benzene extraction. In the series of experiments in the presence of nitrobenzene, the precipitate was boiled in benzene and p,p'-dinitrobibenzyl recovered from the solution. An unidentified red material insoluble in hot benzene remained behind. This material had the following I.R. absorption peaks:

2.75-3.10 μ, broad peak possibly due to water or oxime O-H stretch at 2.74-2.86 μ (Bellamy, Reference 146);

6.26 μ, narrow peak, $>C=C<$ stretch; 6.62 and 7.48 μ, broad nitro group absorptions (all three absorptions are present in nitroaromatics);

6.89 μ, fairly intense; 7.14 μ, fairly weak; these peaks are the most distinctive peaks in the spectrum and always appear for the material. They do not correspond to absorptions for $-C=N-$, $-C=\overset{O}{N}-$, $-N=N-$, $-N=\overset{O}{N}-$; the only group which absorbs in this range is $=N-N=O$ (Bellamy, Reference 146).

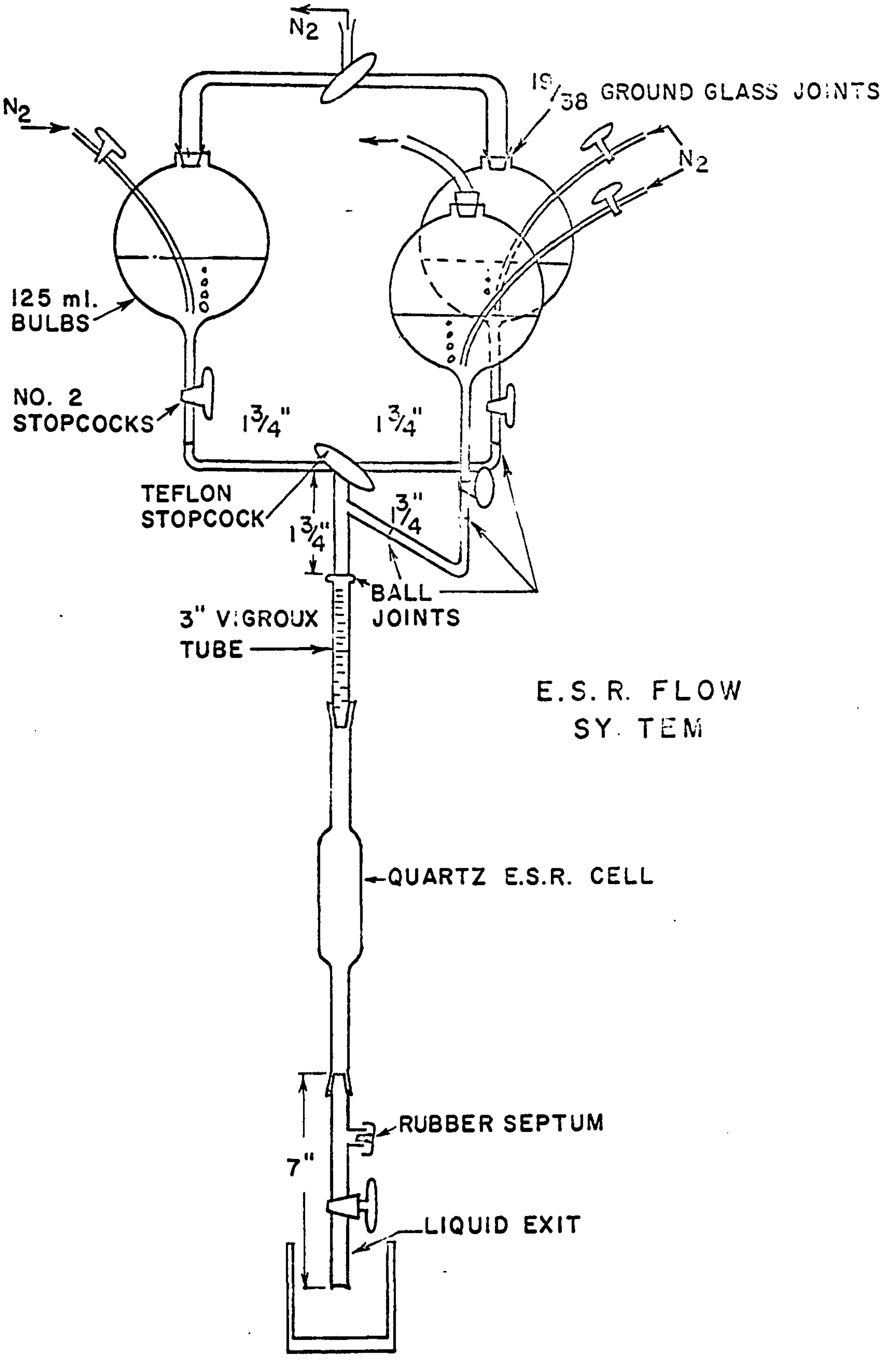
6.38-6.94 μ, $>C=C<$ stretch; 7.04-7.14 μ;



stretch and deformation

The E.S.R. flow experiments were performed with an apparatus as outlined in Figure 107. Solutions of p-nitrotoluene and potassium t-butoxide in separate bulbs were continuously degassed during experiments with prepurified nitrogen. Before the experiments were begun the E.S.R. cell and all tubes leading to the cell were filled with degassed solvent through the bottom rubber septum by means of a hypodermic syringe and needle with the bottom stop-cock closed. This procedure if done carefully removed all bubbles of air in the tubes and cell. After degassing the solutions for 20-30 min. the solutions were allowed to mix and flow through the T-stop-cock and through the E.S.R. cell. For the rate experiments this flow was maintained for 30 sec. and stopped by closing

Figure 107. Flow system used for initial rate measurements of spontaneously formed p-nitrotoluene radical anion


N2
N2
19/38 GROUND GLASS JOINTS
N2
125 ml. BULBS
NO. 2 STOPCOCKS
1 3/4"
1 3/4"
TEFLON STOPCOCK
1 3/4"
3"
1 1/4
BALL JOINTS
3" VIGROUX TUBE
E.S.R. FLOW SYSTEM
QUARTZ E.S.R. CELL
RUBBER SEPTUM
7"
LIQUID EXIT

the T-stop-cock. The build-up in radical concentration was followed on the recorder either by scanning through a given peak up field and down field or by stopping the scan on the top of a given peak and recording the increase in intensity.

In _t_-butyl alcohol thorough washing was required to remove all reactants and products from the cell and approach tubes. This was arranged by allowing degassed solvent to flow through the cell from the extra bulb connected to the approach tube below the T-stop-cock. The quantity used was arbitrary but usually amounted to 40-50 ml.

The connecting ball-joints were chosen for flexibility and minimum strain on the cavity during manipulation of stop-cocks, _etc_. These joints were found satisfactory with ethyl or _t_-butyl alcohol but dimethyl sulfoxide passed through them readily and extensive leaking occurred under the usual conditions of silicon-grease application. The size of flasks and tubing were the maximum allowable for the available space. The Vigroux tube was designed to aid in mixing the solutions but its effectiveness could not be ascertained. At maximum flow rate the time from mixing to passage through cell was approximately 6 sec. for _t_-butyl alcohol as determined by timing the flow of a known volume of solution through the known volume of the cell and approach tube.

A number of the early electron transfer experiments were performed in this system but the method seemed inefficient and often inaccurate for routine experiments due to cleaning problems. A small mixing cell was designed shown in Figure 108 wherein two solutions could be separately degassed through rubber septums with a hypodermic needle and mixed after a given time of degassing (usually 20-30 min.). With practice the E.S.R.

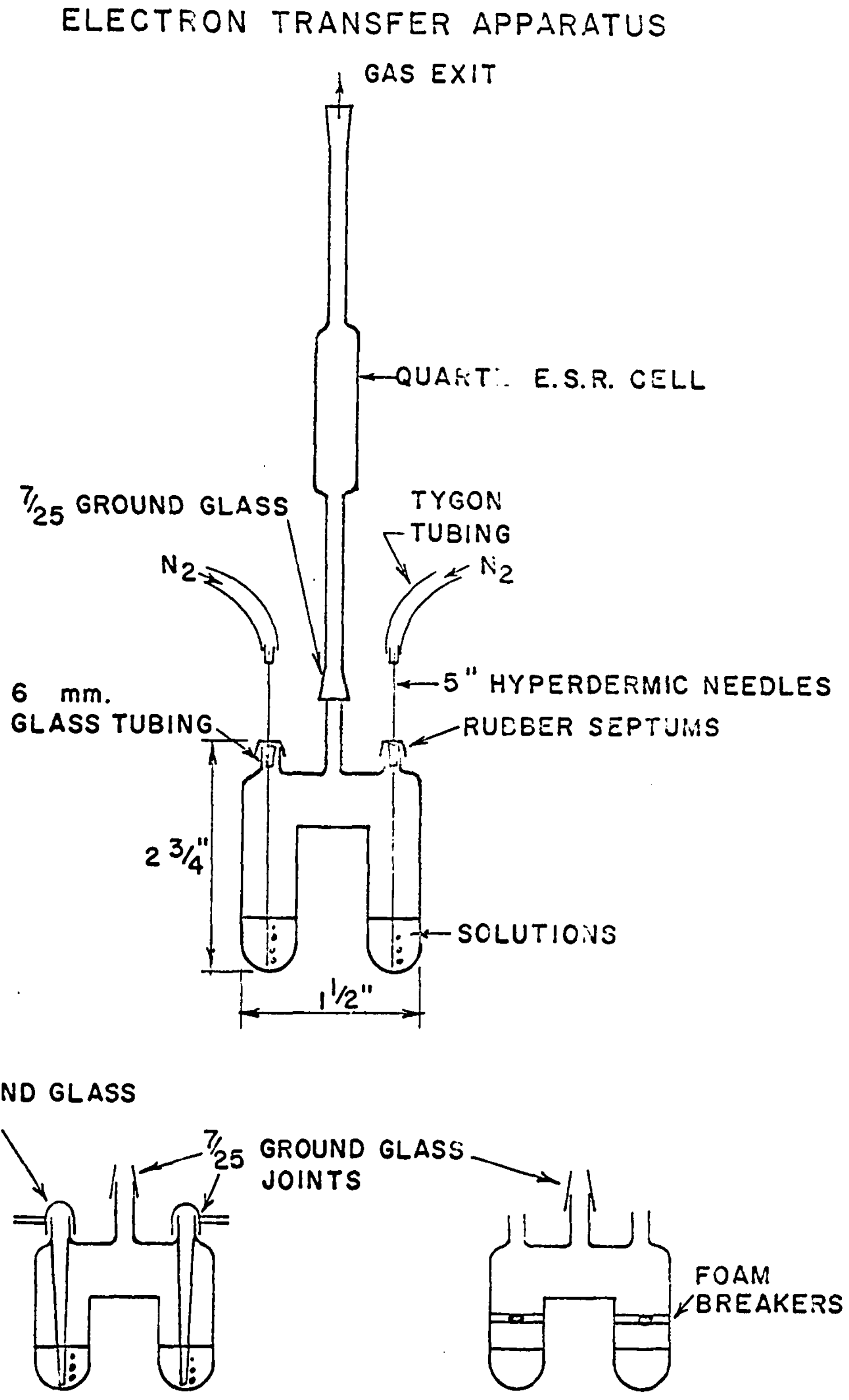


Figure 108. Degassing arrangement and mixing cells used in electron transfer experiments

cell could be closed under a slight positive nitrogen pressure and filled after mixing. The cell and stopper were held in place by rubber bands. The mixing chamber and cell were well cleaned with water, acetone and benzene and room dried after every experiment. Rubber septums were either renewed after every experiment or reused 2-3 times after washing in water, acetone and benzene and room dried.

Ground glass caps were also used instead of rubber septums which could be closed by turning 90° from the open position shown in the diagram. The 80% dimethyl sulfoxide - 20% t-butyl alcohol foamed considerably on degassing and foam breakers (essentially a top wall with a hole) were designed which prevented the prior mixing of solutions by foaming. The mixing tube with the rubber septums had the advantage that solids could be weighed directly in the vessel and dissolved under nitrogen whereas the ground glass caps were necessary when more corrosive solutions were used, e.g., n-butyllithium solutions.

B. Solvents

The source of t-butyl alcohol varied according to availability. Bulk quantities sold by Eastman, Baker and Matheson Coleman & Bell were used. Since the same oxidation rates were observed for t-butyl alcohol which was dried over granular sodium sulfate or dried over calcium hydride and distilled, liter quantities of commercial t-butyl alcohol were stored over sodium sulfate and used as needed.

Dimethyl sulfoxide obtained from Eastman or Aldrich was slightly colored and had an odor. It was vacuum distilled before use at approximately 60-80°. The solvent obtained from Crown Zellerbach in small quantities as free samples was the best grade obtainable in our experience with regard to color, odor and water content (upon addition of calcium hydride no evolution of gases was observed). Bulk quantities of dimethyl sulfoxide were sold in polyethylene containers with caps containing paper or plastic fillers. This chemical had a slight color as well as an odor. Upon addition of potassium t-butoxide even in the presence of t-butyl alcohol a purple color developed which turned to brown on standing. The bulk dimethyl sulfoxide was distilled before use.

Hexamethylphosphoramide was used as received from Tennessee Eastman. It was colorless and had a sweet amine odor. Upon addition of calcium hydride very little gas was evolved. The chemical was stored over calcium hydride and removed when needed.

Commercially available "analytical reagent" grade pyridine (Mallinckrodt) was kept over potassium hydroxide pellets and used as received.

"Analytical" grade Mallinckrodt benzene was used as solvent for oxidation experiments as well as for most extractions. Since the "chemically pure" grade of benzene from the same source, when used for extractions, left behind on evaporation a small amount of foul-smelling liquid, it was not used.

Small amounts of various solvents used were commercially available and dried over granular sodium sulfate before use.

C. Bases

The potassium t-butoxide used in this study was either in a solution of t-butyl alcohol made by the reaction of clean potassium with excess t-butyl alcohol at room temperature or commercially available dry potassium t-butoxide obtained from MSA Research. Exposure to air was avoided as much as possible in the manipulation of the base or basic solution.

A solution of lithium t-butoxide in t-butyl alcohol was made by the reaction of clean lithium wire with excess t-butyl alcohol at room temperature.

Benzyltrimethylammonium methoxide (Triton B) was available from Matheson Coleman & Bell as a 40 per cent solution in methanol.

D. Chemicals

Most chemicals used were commercially available and many were used without purification. Numerous compounds were inherited from previous workers in the group or were available from the organic chemicals storage. Table 21 lists the sources and/or melting points or boiling points.

Table 21. Chemicals

Chemical	Purity and source
p-nitrotoluene	M.P. 50.5-51°
p-nitrotoluene (practical)	Eastman
p-nitroethylbenzene	Aldrich
p-nitrocumene	B.P. 132° (3) n_D^{20} 1.5369 (20)
o-nitrotoluene	Matheson
o-nitroethylbenzene	Matheson Coleman & Bell
o-nitrocumene	n_D^{20} 1.5251 (20)
p,p'-dinitrobibenzyl	Aldrich

Table 21. (Continued)

Chemical	Purity and source
p,*p*'-dinitrostilbene	Moye (3)
2,4-dinitrotoluene	Eastman
2,4,6-trinitrotoluene	Moye (3)
o-dinitrobenzene	Aldrich
m-dinitrobenzene	Matheson
p-dinitrobenzene	Eastman
sym-trinitrobenzene	Moye (3)
2,4-dinitrobromobenzene	chemical storage
2,4-dinitrochlorobenzene	Eastman
bis-(*p*-nitrophenyl)-methane	Eastman
bis-(2,4-dinitrophenyl)-methane	M.P. 174-5° (3)
bis-2,3-(*p*-nitrophenyl)-butane	Moye (3)
tris-(*p*-nitrophenyl)-methane	Moye (3)
5-nitro-*o*-toluenesulfonic acid	Eastman
o-bromo-*p*-nitrotoluene	Aldrich
o-amino-*p*-nitrotoluene	Eastman
o-methyl-*p*-nitrotoluene	Aldrich
m-cyano-nitrobenzene	Maumee
nitromesitylene	Eastman
p-nitrobenzyl alcohol	Eastman
p-nitrobenzaldehyde	Matheson Coleman & Bell
p-nitrophenylacetonitrile	M.P. 115-6° (3)
p-nitrobenzyl phenyl ether	Williamson (20)
p-nitrophenylacetic acid	Eastman
p-nitrobenzyl bromide	Matheson Coleman & Bell
methyl *p*-nitrophenylacetate	M.P. 52-3° (147)
4-nitropyridine-N-oxide	Chemische Fabrik

---

[a] Synthesized from *p*-nitrophenylacetic acid in methanol containing a drop of sulfuric acid

Table 21. (Continued)

Chemical	Purity and source
9-nitroanthracene	M.P. 143.5-5° (3)
9-nitroanthrone	M.P. 138-9°, chemical storage
m-nitrobenzonitrile	Eastman
m-trifluoromethylnitrobenzene	Maumee
p-cyanonitrobenzene	Eastman
p-chloronitrobenzene	chemical storage
p-bromonitrobenzene	Eastman
p-dimethylaminonitrobenzene	Eastman
m-methoxynitrobenzene	Eastman
5-nitroacenaphthene	Eastman
nitrosobenzine	Aldrich
pentachloronitrobenzene	Aldrich
m-aminonitrobenzene	Paragon Testing Laboratories
6-nitroquinoline	Eastman
nitromethane	Eastman
nitroethane	Eastman
2-nitropropane	Eastman
2,3-diphenylindenone	Aldrich
tetraphenylcyclopentadiene	Aldrich
9-fluorenol	Moye (3)
indene	Aldrich
fluorene	M.P. 113-4°
2-nitrofluorene	M.P. 156-7° (3)
2,7-dinitrofluorene	M.P. 298-300°, Aldrich
2-hydroxyfluorene	M.P. 168-9°, Aldrich
3-hydroxyfluorene	M.P. 134.5-5.5°, Aldrich
9,9-bifluorene	M.P. 239-244°, Aldrich
1,2-benzofluorene	M.P. 192.5-3.5°, Aldrich
2,3-benzofluorene	M.P. 212-3°, Aldrich
3,4-benzofluorene	M.P. 122.5-3.5°, Aldrich

Table 21. (Continued)

Chemical	Purity and source
2,7-dibromofluorene	M.P. 196°[b] (143)
anthraquinone	Eastman
anthrone	Aldrich
9,9-bianthrone	M.P. 245-250°
2,6-di-t-butyl-4-methylphenol	Aldrich
hydroquinone	Matheson Coleman & Bell
cyclohexanone	Eastman
benzhydrol	Eastman
diphenylacetonitrile	recrystallized
phenylacetonitrile	distilled
benzopinacol	M.P. 171-2°
fluorenone pinacol	M.P. 180-1°
acetonitrile	distilled
propionitrile	Eastman
isobutyronitrile	Eastman
diphenylpicrylhydrazyl	Eastman
phenylacetylene	Aldrich
α-methylnaphthalene	Eastman
β-methylnaphthalene	Eastman
9,10-dihydrophenanthrene	Aldrich
phenanthrene	Aldrich
9,10-dihydroanthracene	Aldrich
p-phenyltoluene	Aldrich
diphenylmethane	Matheson Coleman & Bell
triphenylmethane	Matheson Coleman & Bell
4,6,8-trimethylazulene	Eastman
acenaphthene	Eastman

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[b] Synthesized by bromination of fluorene in acetic acid in air

Table 21. (Continued)

Chemical	Purity and source
xanthydrol	Matheson Coleman & Bell
xanthene	Aldrich
xanthone	Aldrich
acridine	Aldrich
acridan	Aldrich
acridone	Eastman
N-hydroxybenzenesulfonamide	Eastman
1,2,N,N'-tetraphenylethylenediamine	M.P. 138-150°[c] (149)
4-benzylpyridine	Aldrich
4-methylacetophenone	Eastman
p-toluic acid	Eastman
p-toluenesulfonic acid	Matheson Coleman & Bell
tetrachloro-*p*-xylene	Aldrich
p-bromotoluene	Eastman
methyl *p*-toluate	Matheson Coleman & Bell
p-tolunitrile	Eastman
p-toluamide	Eastman
methyl *p*-toluenesulfonate	Eastman
di-*p*-tolyl sulfone	Eastman
di-*p*-tolyl sulfoxide	Aldrich
4-methylbenzophenone	Eastman
4,4'-dimethylbenzophenone	Eastman
phenyl *p*-tolyl sulfone	(93)
4-methylazobenzene	(93)
α-picoline	distilled
β-picoline	distilled
γ-picoline	distilled

---

[c] Made by sodium reduction of benzalaniline (mixture of meso and dl-forms)

Table 21. (Continued)

Chemical	Purity and source
α-picoline-N-oxide	Matheson Coleman & Bell
β-picoline-N-oxide	Matheson Coleman & Bell
γ-picoline-N-oxide	Matheson Coleman & Bell
2,4,6-collidine	distilled
2,4-lutidine	Eastman
bis-(4-pyridyl)-ethane	Aldrich
bis-(4-pyridyl)-ethylene	Aldrich
p-iodosobenzoic acid	Eastman
iodoxybenzene	Aldrich
benzoin	Matheson Coleman & Bell
9-phenylfluorene	Moye (3)
ethyl malonate	Matheson Coleman & Bell
1,3-indandione	Aldrich
2,2'-biindan -1,1',3,3'-tetrone (Bindone)	Aldrich
acetophenone	Matheson
propiophenone	Eastman
isobutyrophenone	Eastman
hydrozobenzene	Eastman
azobenzene	Matheson Coleman & Bell
azoxybenzene	Eastman
benzidine	Coleman & Bell
diphenylamine	Matheson Coleman & Bell
pyrrole	Eastman
p-aminophenol	Matheson Coleman & Bell
phenothiazine	Matheson Coleman & Bell
phenothiazine-S-oxide	Matheson Coleman & Bell
indole	Aldrich
3,4-dimercaptotoluene	Aldrich
n-butylmercaptan	Eastman

Table 21. (Continued)

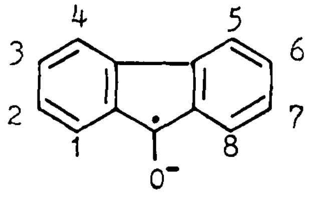
Chemical	Purity and source
n-butyllithium	Foote Mineral
bis-1,2-(4-methylpyridinium iodide)-ethane	M.P. 320-2° d.[d] (150)
bis-1,2-(4-methylpyridinium iodide)-ethylene	M.P. 215-220 d.[d] (150)
diphenylphosphonimido triphenylphosphorane oxide	Trona

[d] Synthesized from *bis*-1,2-(4-pyridyl)-ethane and ethylene and methyl iodide

VI. APPENDIX

A. Ketyls

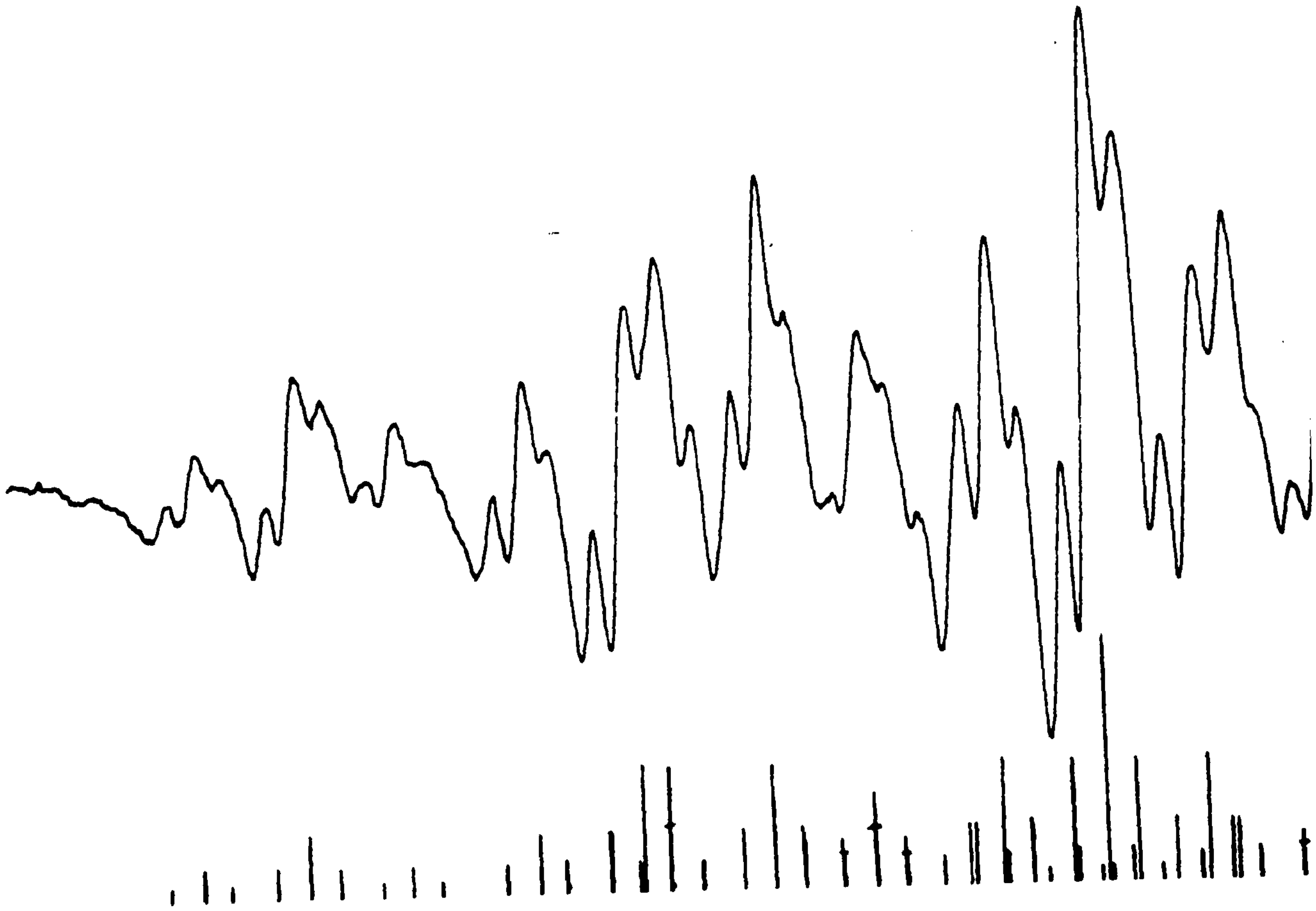
The 5-peak E.S.R. spectrum of the fluorenone ketyl radical anion



could readily be obtained from basic solutions of fluorenol in dimethyl sulfoxide or *t*-butyl alcohol exposed to air, by reduction of fluorenone by glucose in base or by potassium in tetrahydrofuran or by cleavage of fluorenone pinacol in basic solution. A partially resolved spectrum in 20% dimethyl sulfoxide - 80% *t*-butyl alcohol containing potassium *t*-butoxide and a trace of fluorenone is shown in Figure 109. The synthetic spectrum was constructed from the proton splitting constants: $a_1 = 3.65$, $a_2 = 2.61$, $a_3 = 0.31$ and $a_4 = 0.24$ gauss arrived at by inspection. The splitting constants a_1 and a_2 are similar enough to yield a 5-peak spectrum on low resolution but on better resolution peaks due to a_1, a_2 and a_3 protons appear (Figure 110). The triplets due to the a_4 protons are very difficult to resolve. It seems reasonable to assign splitting constants a_1 and a_2 to hydrogens 1, 3, 6 and 8 which are ortho and para to the ketyl function. Whether protons 1 and 8 or 3 and 6 interact to give the larger splitting constant is not known.

A spectrum of 2,7-dibromofluorenone ketyl in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol is given in Figure 111 generated by glucose reduction. The spectrum can be very well described by the parameters, $a_1 = 3.67$,

Figure 109. E.S.R. spectrum of fluorenone ketyl radical anion in 20% dimethyl sulfoxide - 80% t-butyl alcohol generated from 0.025 M fluorenol by 0.05 M potassium t-butoxide and a trace of fluorenone in the absence of air; a_H = 3.65, 2.61, 0.81 and 0.24 gauss



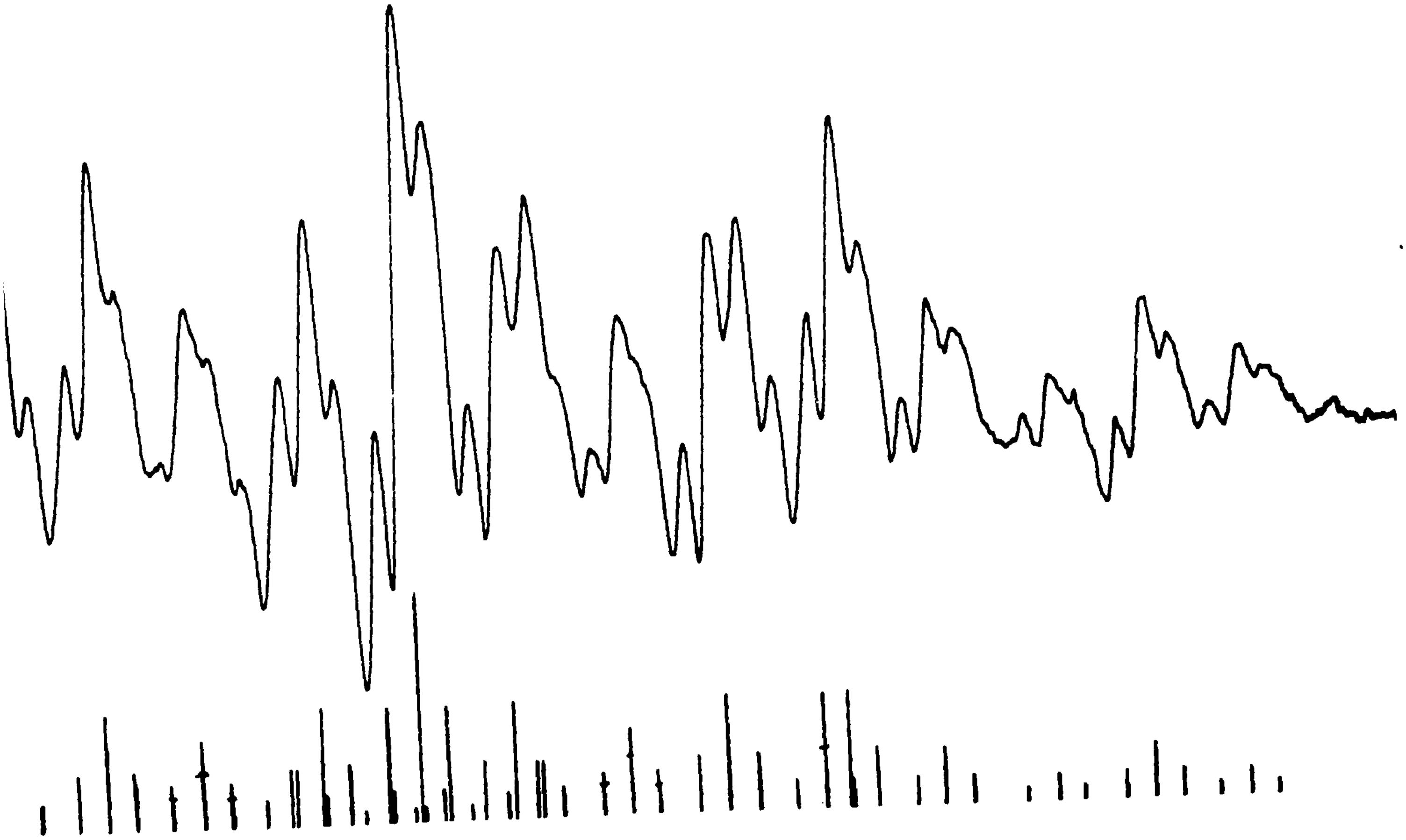
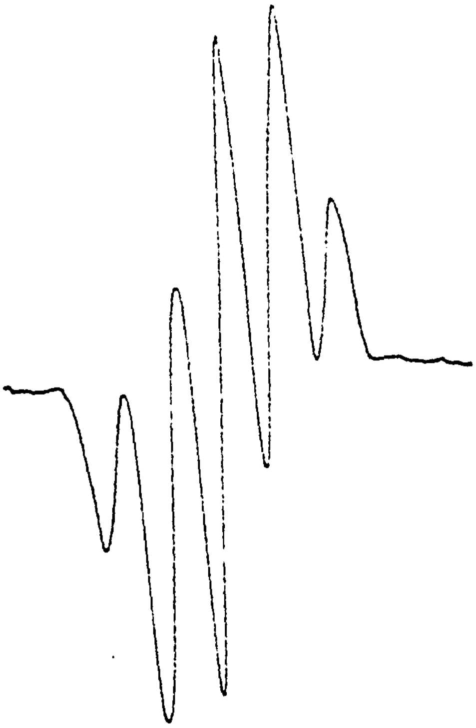


Figure 110. Low resolution spectra of fluorenone ketyl radical anion in 20% dimethyl sulfoxide - 80% _t_-butyl alcohol containing potassium _t_-butoxide (same as Figure 109; top, 1 cm. = 3.89 gauss; bottom, 1 cm. = 1.56 gauss)



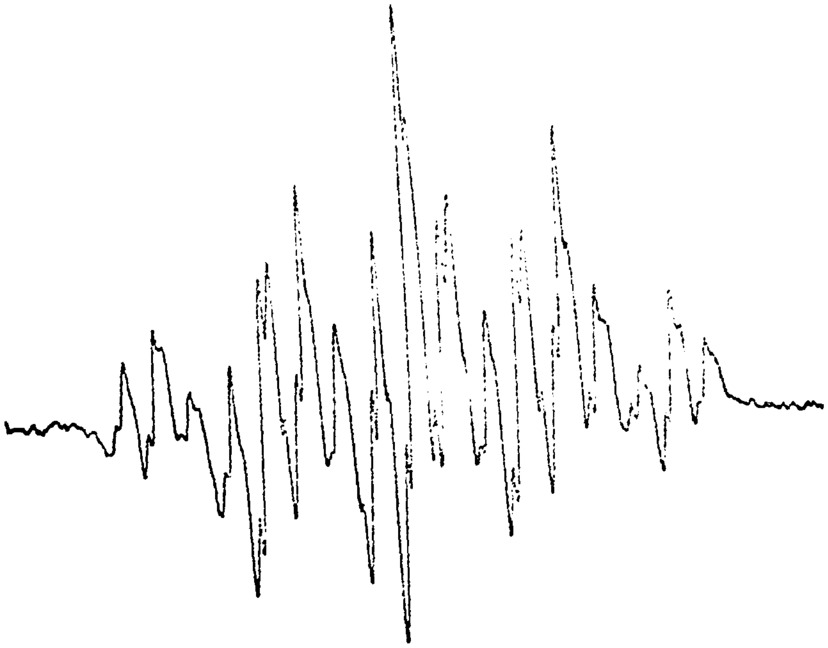
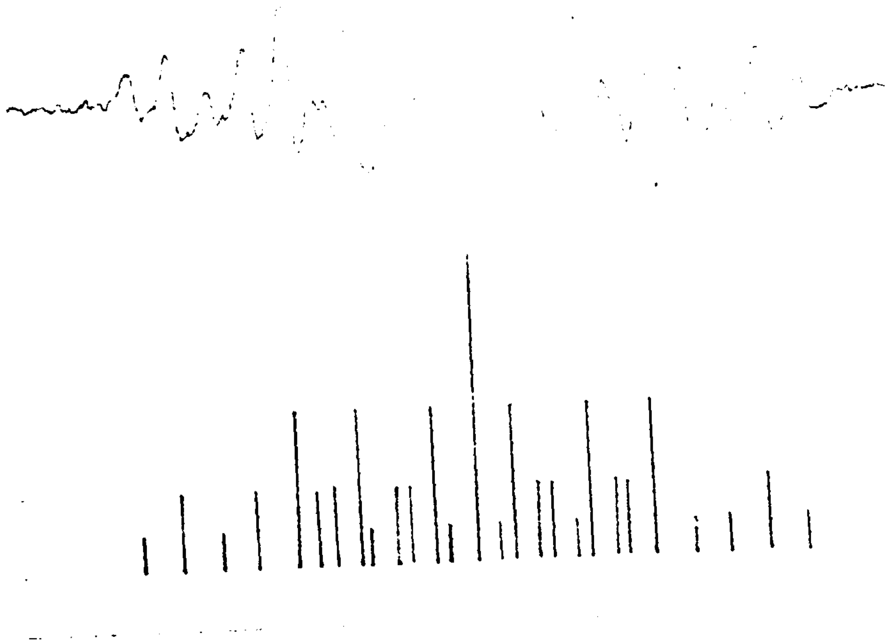
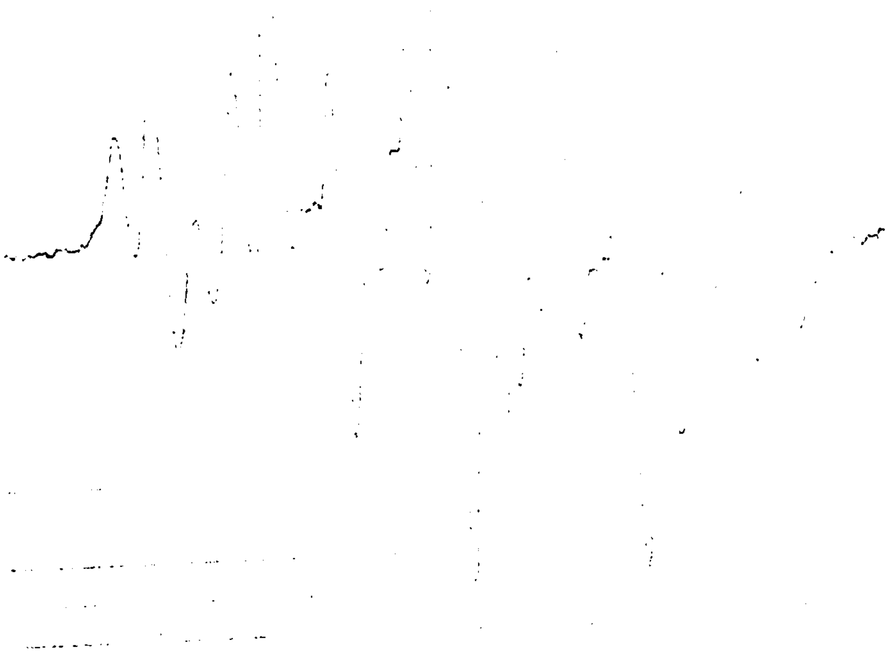


Figure 111. E.S.R. spectra of 2,7-dibromofluorenone ketyl (top) in 80% dimethyl sulfoxide - 20% t-butyl alcohol and fluorenone ketyl (bottom) in dimethyl sulfoxide - t-butyl alcohol for comparison (1 cm. = 1.56 gauss)



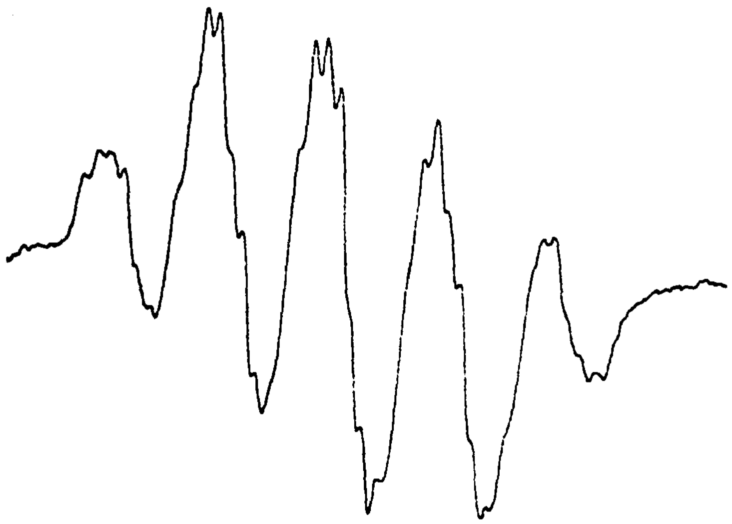


a_2 = 2.36 and a_3 = .803. A partially resolved spectrum of the fluorenone ketyl is included for comparison. No evidence of the triplets due to the a_4 proton splitting was observed and on this basis the splitting constant of 0.24 gauss can be assigned to protons 2 and 7 in the fluorenone ketyl. A further assignment of 0.81 gauss to protons 4 and 5 follows. The protons 2, 4, 5 and 7 are "meta" to the ketyl function and would be expected to have small splitting constants.

The fluorenone ketyl radical ion was formed by the dissociation of the pinacol by base in various solvents. The spectra changed for different solvent and base systems as indicated in Figure 112 (top); the most dramatic effect was found in t-butyl alcohol containing potassium t-butoxide. The spectrum seemed to give no indication of two splitting constants for the ortho- and para-hydrogens, very small meta splitting constants and an overall larger total line width (Table 22). In t-butyl alcohol containing Triton B in methanol a spectrum having similarities to both that in dimethyl sulfoxide and in pure t-butyl alcohol was obtained (Figure 112, bottom; Table 22). The splitting constants could not be readily obtained by inspection of the spectrum recorded for fluorenone ketyl in benzene containing Triton B - methanol (Figure 113). From these spectra it can be concluded that t-butyl alcohol had a relatively large solvent effect on the proton splitting constants of the fluorenone ketyl radical anion.

The best resolution of the xanthone ketyl (Figure 113) would not uncover more peaks than the easily resolved 5 triplets with splitting constants 4.48 and 1.08 gauss. The sequence of intensities for the 5 main peaks were in accord with 1:2:3:2:1 and it had to be concluded that there

Figure 112. E.S.R. spectra of fluorenone ketyl in *t*-butyl alcohol - potassium *t*-butoxide (top) and in *t*-butyl alcohol - Triton B - methanol (bottom) generated from the pinacol in the absence of air (1 cm. = 2.38 gauss)



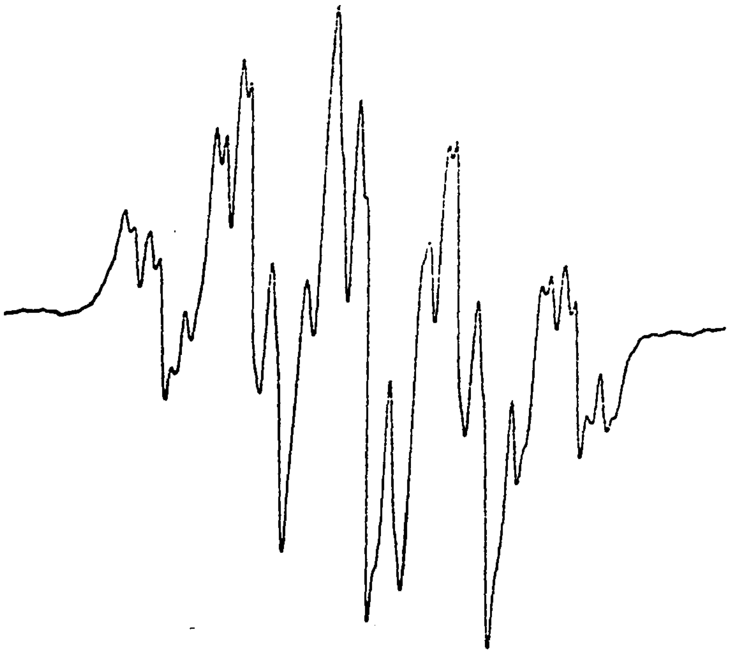


Table 22. Hyperfine splitting constants for fluorenone ketyl

Solvent[a]	Base[b]	$a_{o,p\text{-}H}$ (gauss)	$a_{m\text{-}H}$ (gauss)	Total line width (gauss)
20% DMSO-80% *t*-BuOH	*t*-BuOK	3.65, 2.61	0.81, 0.24	15.31
80% DMSO-20% *t*-BuOH	*t*-BuOK	3.53, 2.37	0.78	17.0
t-BuOH	*t*-BuOK	3.53[c]	0.39[c]	18.56
t-BuOH (MeOH)	Triton B	3.70, 2.86	0.76, 0.15	17.61
benzene (MeOH)	Triton B			18.09

[a] DMSO = dimethyl sulfoxide; *t*-BuOH = *t*-butyl alcohol; MeOH = methanol

[b] *t*-BuOK = potassium *t*-butoxide; Triton B = benzyltrimethylammonium methoxide in methanol

[c] 4 Equivalent hydrogens

were 4 equivalent protons in the radical. Furthermore two additional equivalent protons produced the triplets but two protons on the radical did not interact with the free electron. No assignment of splitting constants could be made but it seemed likely that protons 1, 3, 6 and 8 interacted to produce the larger splitting constant (4.48 gauss) and must be equivalent.

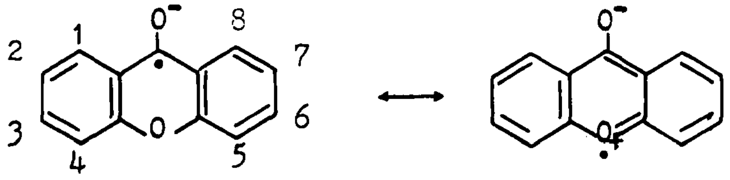
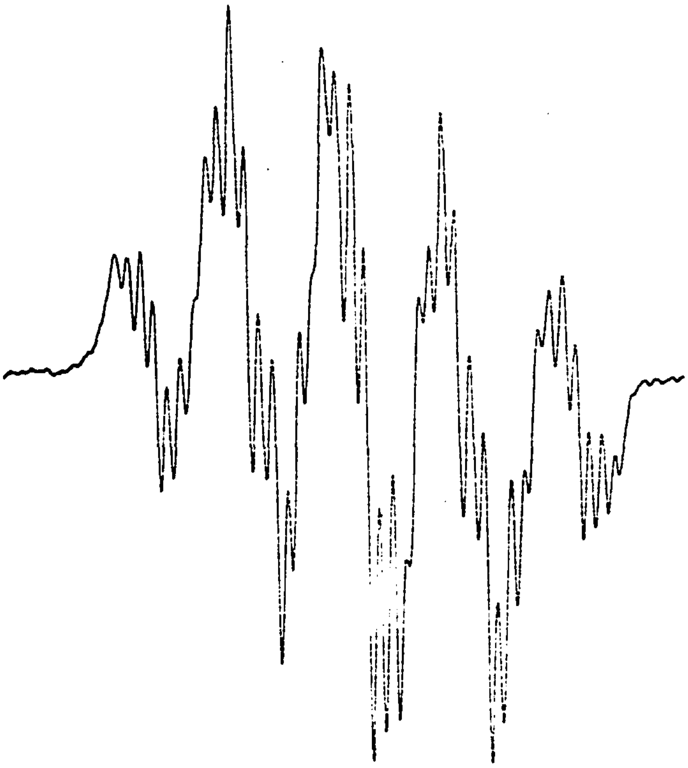
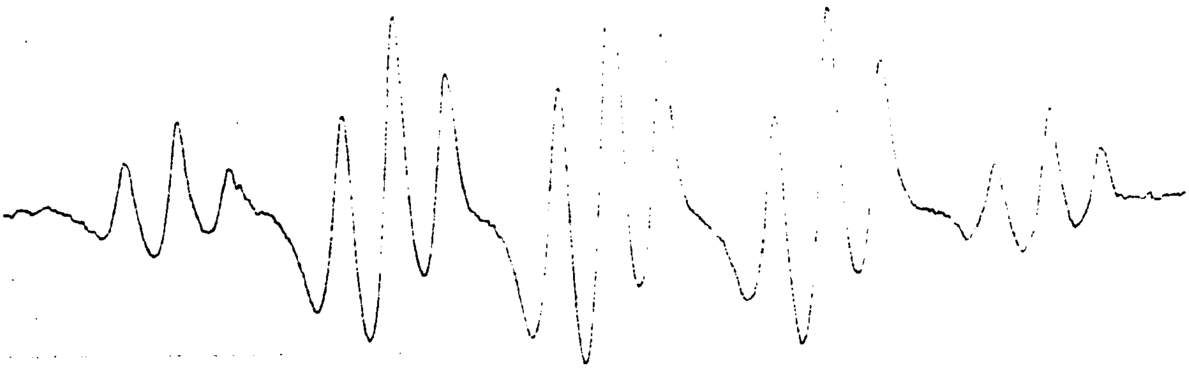
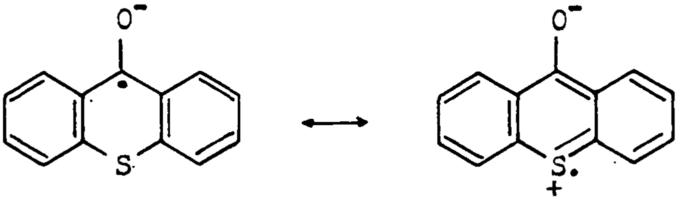


Figure 113. E.S.R. spectra of fluorenone ketyl in benzene containing Triton B - methanol (top) produced from the pinacol to be compared to spectra in Figure 112 (1 cm. = 2.38 gauss) and of xanthone ketyl in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol generated by xanthydrol-xanthone electron exchange in the presence of potassium *t*-butoxide (1 cm. = 1.56 gauss)





Protons 4 and 5 could produce the smaller interactions (1.08 gauss) due to a high odd electron density on the ether oxygen. The observation of an E.S.R. spectrum of a very similar radical has recently been published (62).



XXXVII

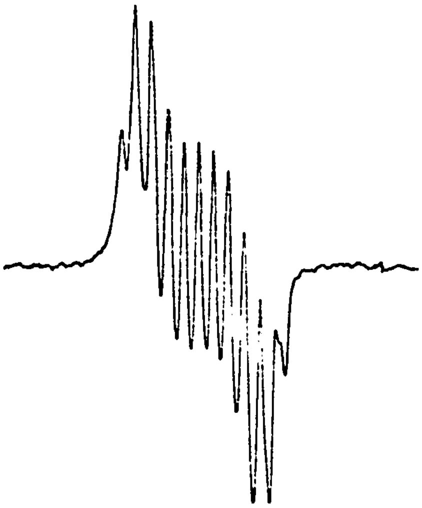
A series of peaks in 5 groups separated by 3.5 gauss were recorded in good agreement with our findings, indicating a larger contribution to the resonance hybrid from Structure XXXVII for thiazanthone than for xanthone. Each group could be resolved into 18 lines. As in the case for fluorenone ketyl it is apparent that high resolution will uncover four different splitting constants for the thiaxanthone ketyl and hence probably for xanthone ketyl as well.

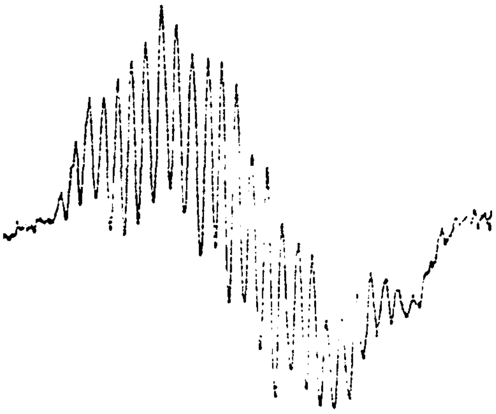
The ketyls of 2,3-diphenylindenone and tetraphenylcyclopentadienone were made by a glucose reduction but the signal of approximately 5.5 and 3 gauss respectively in both cases could not be resolved. The ketyls of 1,2-, 2,3- and 3,4-benzofluorenones were made by the same method (Figure 114). Partially resolved complex spectra were obtained and splitting constants were not evaluated.

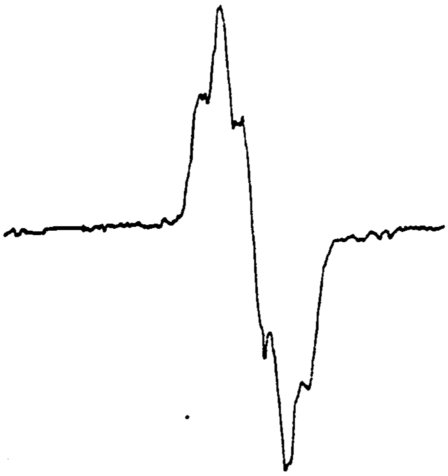
B. New Free Radicals

In addition to the numerous free radicals studied which have not been reported in the literature the radical anions of m-cyanonitrobenzene,

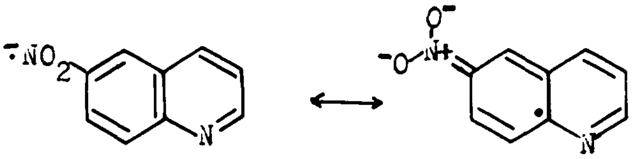
Figure 114. E.S.R. spectra of benzofluorenone ketyl radical anions in dimethyl sulfoxide - *t*-butyl alcohol; 1,2- top left (1 cm. = 5.73 gauss), 2,3- top right (1 cm. = 3.89 gauss) and 3,4- bottom (1 cm. = 5.73 gauss) generated by glucose reduction in the presence of potassium *t*-butoxide







m-trifluoromethylnitrobenzene and 6-nitroquinoline were made by electron transfer. A well resolved spectrum containing 22 peaks in 10 groups was obtained for m-cyanonitrobenzene very similar to that observed for m-dinitrobenzene (Figure 115). m-Trifluoromethylnitrobenzene gave a more complex spectrum with a broader line width (Figure 116). 6-Nitroquinoline radical anion gave a spectrum of 5 peaks qualitatively in agreement with two equivalent nitrogen atoms in the radical (Figure 115).



XXXVIII

A spectrum of a free radical which could be the radical anion of [Δ 2,2'-biindan] -1,1',33'-tetrone was obtained by an iodine oxidation in basic solution of [2,2'-biindan] -1,1',3,3'-tetrone (Figure 117).

(202)

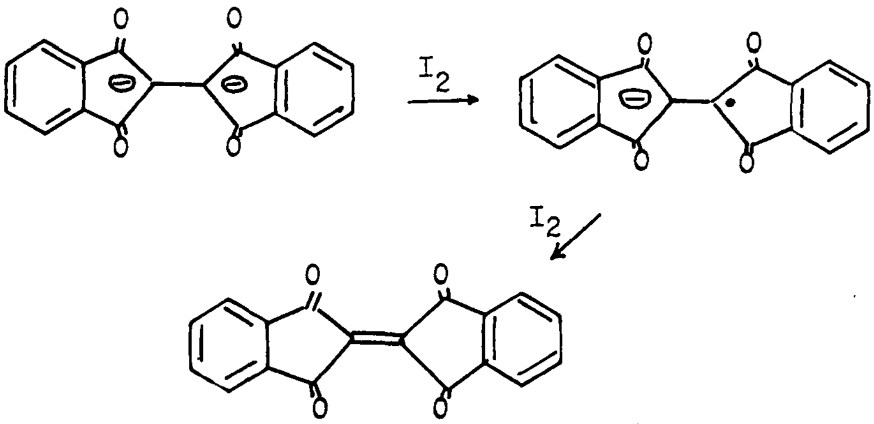
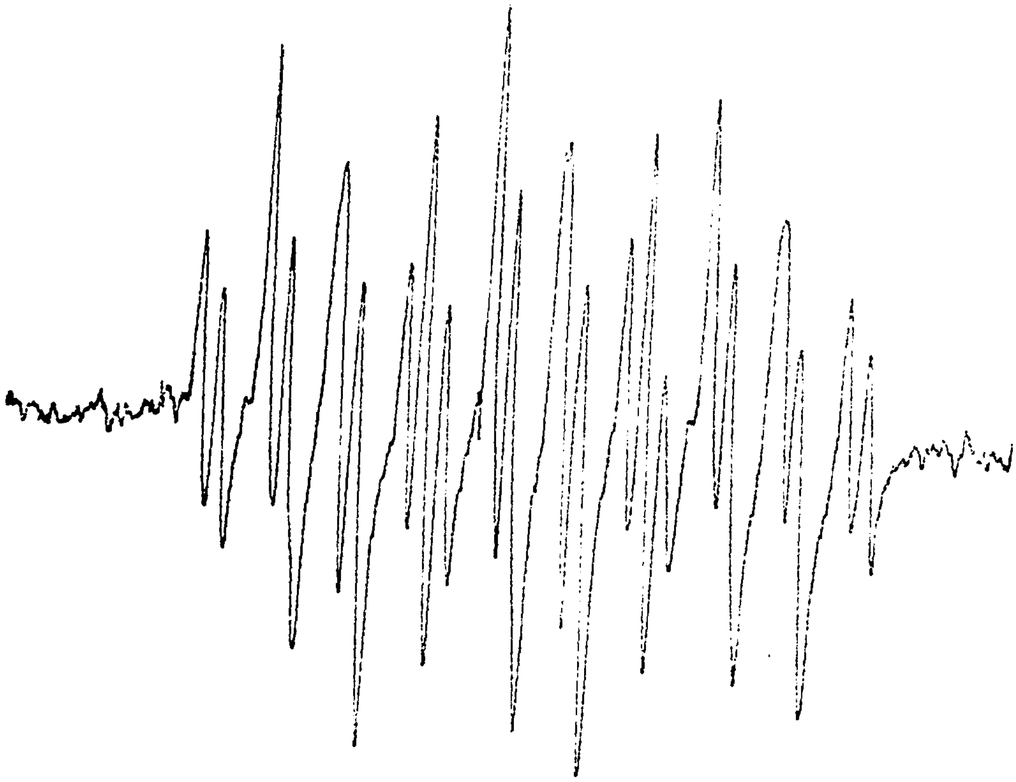
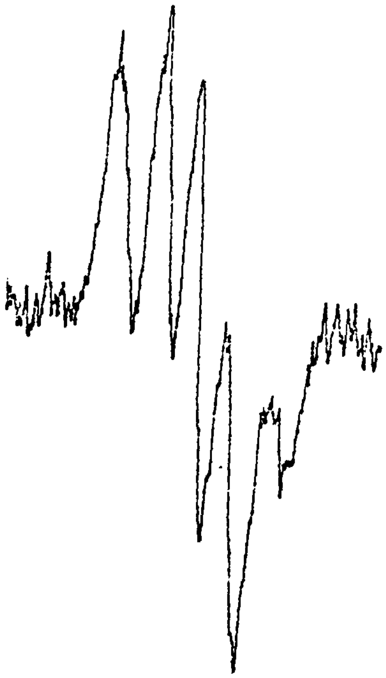


Figure 115. E.S.R. spectra of m-cyanonitrobenzene and 6-nitroquinoline radical anions produced by electron transfer from 0.025 M indene in the presence of 0.005 M substrate and 0.050 M sodium ethoxide in ethonol (top, 1 cm. = 3.89 gauss; bottom, 1 cm. = 5.78 gauss)





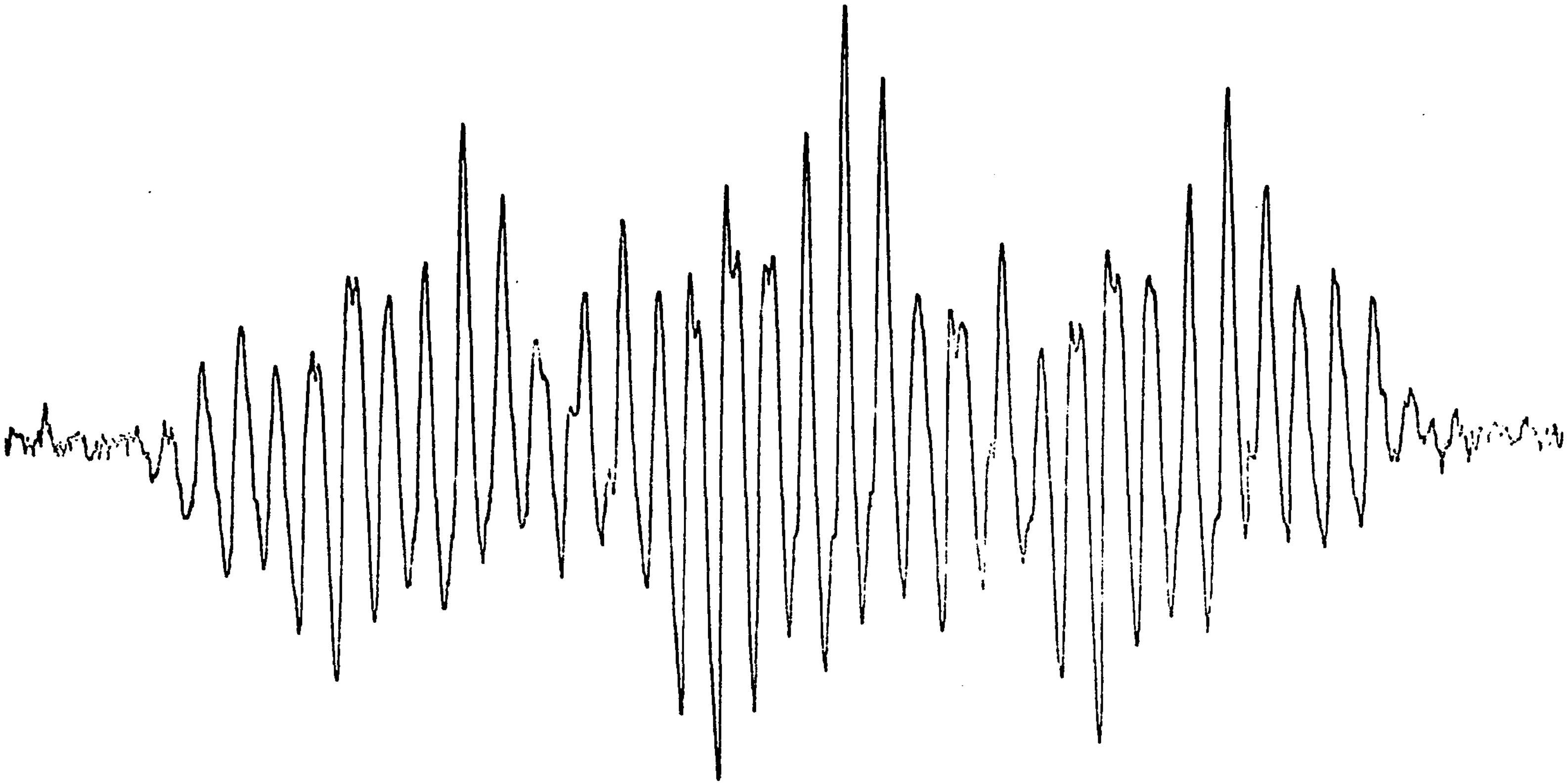


Figure 116. E.S.R. spectrum of m-trifluoromethylnitrobenzene formed via electron transfer from 0.025 M indene in ethanol containing 0.05 M sodium ethoxide (1 cm. = 2.38 gauss)

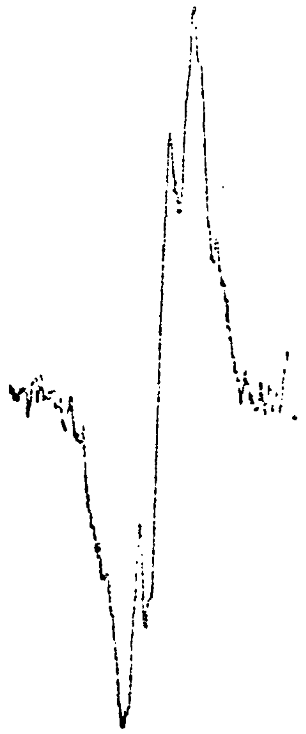
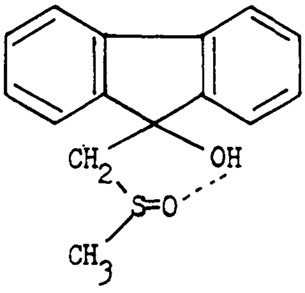


Figure 117. E.S.R. spectrum obtained by the iodine oxidation of 2,2'-biindan -1,1',3,3'-tetrone in ethanol containing sodium ethoxide (1 cm. = 3.89 gauss)

C. Dimethyl Sulfoxide Adducts

The oxidation of fluorene in 80% dimethyl sulfoxide - 20% t-butyl alcohol produced the dimethyl sulfoxide adduct of fluorenone (see Products as a function of solvent) with melting point 155.5-6.5° and I.R. spectrum containing peaks for carbon-oxygen stretch, hydrogen-bonded hydroxyl and sulfoxide. The N.M.R. spectrum was consistent with the structure



Carbon-hydrogen analysis (Schwarzkopf Microanalytical Laboratory) obtained was the following:

	found	calculated
carbon	69.19%	69.9%
hydrogen	5.61%	5.47%
sulfur	12.34%	12.42%

The adduct could be isolated by pouring the solution from the oxidation of fluorene into water and extracting the aqueous solution with benzene (no precipitates formed in the aqueous solution) followed by evaporation of the benzene at room temperature. The adduct was obtained in semi-crystalline form but could be dissolved in chloroform and recrystallized from chloroform-cyclohexane. Prolonged oxidations gave unidentified products which would not crystallize. The same adduct could be made from fluorenone under similar conditions in dimethyl sulfoxide in the presence of potassium t-butoxide, but fluorenone could be recovered unchanged from dimethyl sulfoxide in the absence of potassium t-butoxide (Table 23). In the presence of deficient base the yield of adduct was approximately twice the amount of potassium t-butoxide present in solution.

Similar dimethyl sulfoxide adducts could be synthesized from benzophenone and anthraquinone. No color change was observed in the experiment with benzophenone but a bright pink solution was obtained with anthraquinone. A small amount of unreacted anthraquinone was filtered from the aqueous solution; the adduct was soluble under these conditions and was obtained from a benzene extract. The benzophenone adduct precipitated from the aqueous solution. The I.R. and N.M.R. spectra showed the peaks recorded in Tables 24 and 25. Carbon-hydrogen analyses were:

	benzophenone adduct		anthraquinone adduct	
	found	calculated	found	calculated
carbon	69.6%	68.89%	66.91%	67.1%
hydrogen	5.95%	6.12%	5.14%	4.93%
sulfur	12.36%	12.20%	11.75%	11.2%

A xanthone adduct could not be made in 80% dimethyl sulfoxide - 20% t-butyl alcohol after treatment in the usual manner for 6.5 hr. or after warming the solution at 60-70° for 15 min. Unreacted xanthone was recovered although the solution was dark blue during the experiment.

An attempted experiment with anthrone in the absence of air gave no dimethyl sulfoxide adduct but all the material recovered melted at 230-240° with sublimation; the melting point and an I.R. spectrum were consistent with the structure of 9,9'-bianthrone. Since the reaction was attempted in a solution under nitrogen there remains the interesting possibility that the dimer was formed when the solution containing the reactants was poured into water saturated with air.

Table 23. Dimethyl sulfoxide adduct formation in 80% dimethyl sulfoxide - 20% t-butyl alcohol

Run	Ketone[a] (mmoles)	t-BuOK[b] (mmoles)	time	Product	
				Ketone[c] (%)	Adduct (%)
75_1-A	1.42 (F)	0	1 day	92 (80-1°)	
75_3-A	1.54 (F)	1.5	5 min.		65.5 (135-7°)
83_1-A	1.64 (F)	.33	5 min.	40 (75-6°)	29.5 (153-5°)
83_2-A	1.69 (F)	.33	20 min.	35.5 (76-7°)	37 (149-153°)
83_3-A	1.77 (F)	.33	1 hr.	17 (72-5°)	45 (140-151°)
83_4-A	1.67 (F)	.33	4 hr.	trace	30 (143-150°)
150-A	5.19 (B)	5.7	15 min.	0	93 (110-120°)[d]
145_1-A	2.0 (A)	4	1 hr.[e]	filterable amount	29.5 (152-3° d.)
			3 hr.[e]	small amount	44 (156-6.5° d.)[f]

[a] F = Fluorenone; B = benzophenone; A = anthraquinone

[b] t-BuOK = potassium t-butoxide

[c] Recovered starting ketone

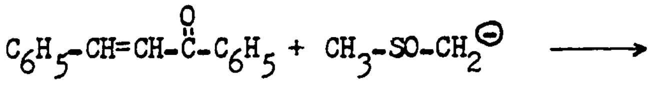
[d] After recrystallization from chloroform-cyclohexane, M.P. 146-146.7°

[e] Half portions were poured into water

[f] After recrystallizations from chloroform-cyclohexane, M.P. 158-8.3° d.

In an attempt to obtain information on the site of addition of the methylsulfinyl carbanion in the case of an α,β- unsaturated ketone, benzalacetophenone was tried under the usual conditions.

(203)



$$C_6H_5\text{-}CH{=}CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}C_6H_5 + CH_3\text{-}SO\text{-}CH_2^{\ominus} \longrightarrow$$

Table 24. I.R. data for dimethyl sulfoxide adducts[a]

Adduct	-OH (sharp)	-OH (broad)	C-H	C=O	C=C	S=O (broad)
fluorenone	2.77	2.95	3.34		6.21	9.28, 9.84
benzophenone	2.79[b]	2.96	3.35		6.26	9.49, 9.87
(in KBr wafer)		3.12				9.46, 9.80
anthraquinone	2.8[b]	2.98	3.34	6.0	6.23	9.39, 9.92

[a] Wave length in μ

[b] Shoulders

Table 25. N.M.R. data for dimethyl sulfoxide adducts[a]

Adduct	Methyl	Methylene	Alcohol	Aromatic
fluorenone	7.61	7.01	5.18	
benzophenone	7.45	6.45 (quartet)	4.52	9.17
anthraquinone	7.57	7.03 (quartet)	4.06	

[a] Position of peaks in τ units

The solution turned bright red on addition of base and a white precipitate was recovered after pouring the solution into water after 5 min. which melted indefinitely at 80-100° (benzalacetophenone is yellow and melts at 55-7°). After 0.5 hr. or 3.5 hr. in the basic solution material was obtained which still melted within the same range, 85-90°. Higher melting white crystals were obtained after recrystallization from ethanol (~170° and ~190°). The I.R. showed carbonyl and conjugated double-bonded carbon groups but no sulfoxide bands; the N.M.R. was too complex to be helpful. This study was not completed.

The same treatment with p-nitrobenzaldehyde afforded only p-nitrobenzoic acid (identified by I.R., melting point and mixed melting point) in the absence of air. This observation agreed with the structural assignment made to the radical species formed spontaneously in the basic solution of p-nitrobenzaldehyde, namely, t-butyl p-nitrobenzoate radical anion. The ester radical anion would be expected to oxidize and hydrolyze rapidly in aqueous solutions saturated with air.

D. pK_a's of Weak Acids

Since this study in part involved an investigation into the reactivity of various functionally different carbanions towards oxygen it seemed that a table of readily available pK_a values for organic weak acids should be recorded for the sake of completeness. A convenient compilation was found in Bordwell's "Organic Chemistry" (151). In Table 26 selected pK_a values and the ease of oxidation are listed.

This series of pK_a's also provides for an estimation of the acidities of a number of compounds we have been able to ionize as evidenced by the reaction of the carbanion with oxygen. Since diphenylmethane (pK_a 35, McEwen's scale) oxidized faster than dimethyl sulfoxide, the latter probably has a pK_a greater than 35. The pK_a's for methyl p-toluate, p-tolunitrile, phenyl p-tolyl sulfone, p-tolyl sulfoxide, 4-methylbenzophenone and 4-methylazobenzene must be between 25 and 35 since fluorene (pK_a 25) oxidizes in t-butyl alcohol but the above mentioned do not. The

Table 26. pK_a's of weak acids and ease of oxidation of carbanions in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol containing potassium *t*-butoxide

Weak acid	pK_a[a]		Oxidation	Reference	$R^{\ominus}\xrightarrow{O_2}R\cdot$
methane		84S	no		
cumene	37M		no		
toluene		59S	no		
2-methylanthracene		57S	?		
cycloheptatriene		45S	?		
2-methyl-naphthalene			v. slow	this work	v. good
1-methyl-naphthalene			v. slow	this work	v. good
diphenyl-methylethylene			?		
diphenylmethane	35M		yes	this work	v. good
diphenyl-1-naphthylmethane	34M				
triphenylmethane	33M		yes	this work	v. good
diphenylbi-phenylmethane	31M				
9-phenylxanthene	29M				
xanthene	29M		yes	this work	v. good
1,2,3-triphenyl-cyclopropene		28S	?		
aniline	27M		yes	(93)	?

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[a] Most pK_a's are taken from Bordwell's "Organic Chemistry" (151), McEwen (152) and Streitwieser *et al.* (153); Streitwieser's values are listed in a separate column because a revised pK_a scale was suggested (153). Apparently the pK_a scale of McEwen's was too compressed for pK_a values above 20; some values have been taken from Streitwieser's earlier publication (154); M = McEwen, S = Streitwieser and B = Bordwell

Table 26. (Continued)

Weak acid	pK_a		Oxidation	Reference	$R^{\ominus}\xrightarrow{O_2}R\cdot$
p-toluidine	27M		yes[b]		
p-anisidine	27M		yes[b]		
fluorene	25M	31S	yes	this work	v. good
4,5-methylene-phenanthrene		25,31S			
perinaphthene		16-25S			
diphenylamine	23M		yes[b]		
indene	21M	23S	yes	this work	v. good
phenylacetylene	21M		no[b]		v. good
acetone	20B		slow	(18)	poor
t-butyl alcohol	19M		no	this work	v. poor
acetophenone	19M		yes	(18)	fair
9-phenylfluorene	18.5 (155)		yes	(3)	v. good
p-nitroaniline	18.5B		no[b]		
cyclopentadiene	14 (156)	17S	yes	(3)	v. good
bis-p-nitrophenyl-methane	15.8B		slow	this work	poor
2,4-dinitroaniline	15.3B		no[b]		v. poor
acetamide	15B		no[b]		v. poor
pyrrole	15B		yes[b]		fair ?
tris-p-nitrophenyl-methane	14.7B		slow	this work	poor
bis-p-nitrophenyl-amine	14.5B		no[b]		v. poor
imidazole	14.2B		no[b]		poor

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[b] G. A. Russell and F. J. Smentowski, Dept. of Chemistry, Iowa State University, Ames, Iowa. Private communication regarding the oxidation of nitranions, 1961-2

Table 26. (Continued)

Weak acid	pK_a	Oxidation	Reference	$R^{\ominus}\xrightarrow{O_2}R\cdot$
p-nitrophenyl-acetonitrile	13.4B	no	(3)	v. poor
bis-methylsulfonyl-methane	13B	no	(18)	v. poor
fluoradene	11-12, 10S	yes	(157)	v. good
nitromethane	11.0B	slow	(109)	fair
malononitrile	11.0B			
ethyl acetoacetate	11.0B	no	(18)	v. poor
benzenesulfonamide	11.0B	no^b		v. poor
ethanethiol	10.5B	yes	(12)	good
cyanamide	10.4B	no^b		v. poor
phenol	10.0B	slow		
succinimide	9.6B	no^b		
hydantoin	9.12 (158)		(158)	
acetylacetone	8.9B	no	(18)	
2-thiohydantoin	8.5 (159)		(159)	
m-nitrophenol	8.4B			
triacetylmethane	5.8B			
dinitromethane	4.0B			
aci-nitromethane	3.2B			
trinitromethane	1B			
tris-methylsulfonyl-methane	0B	no	(18)	v. poor

pK_a's of the methylnaphthalines must be in the order of 36 (on McEwen's scale) since they ionize and oxidize in hexamethylphosphoramide but react very slowly in 80% dimethyl sulfoxide - 20% *t*-butyl alcohol (cumene pK_a 37, does not oxidize in hexamethylphosphoramide).

A wider range of pK_a units than given by McEwen for very weakly acidic hydrocarbons as suggested by Streitwieser et al. (153) agrees with our findings concerning the ease of ionization and oxidation of hydrocarbons; i.e., very qualitatively if diphenylmethane (pK_a 35) ionizes and oxidizes readily in our solvents cumene (pK_a 37) would probably be expected to ionize and oxidize as well albeit more slowly. However if as Streitwieser suggests the scale should be revised to have fluorene pK_a 31 (i.e., diphenylmethane $pK_a \approx 40$) and toluene pK_a 59 (i.e., cumene $pK_a \approx 59$) the larger difference in pK_a values would account for our inability to ionize and oxidize hydrocarbons like toluene, ethylbenzene and cumene.

VII. REFERENCES

1. J. Q. Adams and S. W. Nicksic, J. Am. Chem. Soc., 84, 4355 (1962).
2. D. Bryce-Smith, J. Chem. Soc., 1603 (1956).
3. A. J. Moye, The Autoxidation of Resonance Stabilized Carbanions, unpublished Ph.D. thesis, Library, Iowa State University of Science and Technology, Ames, Iowa, 1961.
4. A. C. Cope, H. L. Holmes and H. O. House, The Alkylation of Esters and Nitriles in R. Adams, editor, "Organic Reactions", Vol. 9, Ch. 4, John Wiley & Sons, Inc., New York, N. Y., 1957.
5. C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor and A. E. Brodhag, J. Am. Chem. Soc., 78, 1653 (1956).
6. W. von E. Doering and R. M. Haines, J. Am. Chem. Soc., 76, 482 (1954).
7. Y. Sprinzak, J. Am. Chem. Soc., 80, 5449 (1958).
8. A. J. Parker, Quart. Revs., 16, 163 (1962).
9. H. E. Zaugg, B. W. Horrom and S. Borgwardt, J. Am. Chem. Soc., 82, 2895 (1960).
10. D. J. Cram, B. Rickborn, C. A. Kingsbury and P. Haberfield, J. Am. Chem. Soc., 83, 3678 (1961).
11. I. M. Kolthoff and J. F. Coetzee, J. Am. Chem. Soc., 79, 1852 (1957).
12. T. J. Wallace and A. Schriesheim, J. Org. Chem., 27, 1514 (1962).
13. T. J. Wallace, A. Schriesheim and W. Bartok, J. Org. Chem., 28, 1311 (1963).
14. W. Bartok, D. D. Rosenfeld and A. Schriesheim, J. Org. Chem., 28, 410 (1963).
15. H. O. Pritchard, Chem. Revs., 52, 529 (1953).
16. A. A. Oswald, B. E. Hudson, Jr., G. Rodgers and F. Noel, J. Org. Chem., 27, 2439 (1962).
17. M. Avramoff and Y. Sprinzak, J. Am. Chem. Soc., 85, 1655 (1963).
18. G. A. Russell, A. J. Moye, and K. Nagpal, J. Am. Chem. Soc., 84, 4154 (1962).

19. H. R. Gersmann, H. J. W. Nienwenhuis and A. F. Bickel, J. Chem. Soc., 279 (1962).

20. R. C. Williamson, Jr., Polar Effects in Free Radical Reactions, unpublished Ph.D. thesis, Library, Iowa State University of Science and Technology, Ames, Iowa, 1963.

21. J. Wertz, Chem. Revs., 55, 922 (1955).

22. D. H. Whiffen, Quart. Revs., 12, 250 (1958).

23. K. H. Hausser, Chimia, 14, 153 (1960).

24. R. G. Shulman, Electron and Nuclear Spin Resonance in H. Eyring, C. J. Christensen and H. S. Johnston, editors, "Annual Review of Physical Chemistry", Vol. 13, p. 325, Annual Reviews, Inc., Palo Alto, California, 1962.

25. G. K. Fraenkel, Paramagnetic Resonance Absorption in A. Weissberger, editor, "Technique of Organic Chemistry", Vol. 1, Part 4, Ch. 42, Interscience Publishers, Inc., New York, N. Y., 1960.

26. D. J. E. Ingram, "Free Radicals as Studied by Electron Spin Resonance", Butterworths, London, England, 1958.

27. M. A. Battiste, J. Am. Chem. Soc., 84, 3780 (1962).

28. E. Muller and I. Muller-Rodloff, Ber., 69B, 665 (1936).

29. R. Breslow, W. Bahary and W. Reinmuth, J. Am. Chem. Soc., 83, 1763 (1961).

30. S. M. Blinder, M. L. Peller, N. W. Lord, L. C. Aamodt and N. S. Ivanchukov, J. Chem. Phys., 36, 540 (1962).

31. T. Hayashi, K. Maeda, S. Shida and K. Nakada, J. Chem. Phys., 32, 1568 (1960).

32. J. Pannell, Mol. Phys., 5, 291 (1962).

33. A. N. Holden, C. Kittel, F. R. Merritt and W. A. Yager, Phys. Rev., 77, 147 (1950).

34. G. M. Coppinger, Tetrahedron, 18, 61 (1962).

35. J. Pannell, Chemistry & Industry, 1797 (1962).

36. E. J. Land and G. Porter, J. Chem. Soc., 3540 (1961).

37. D. H. Geske and A. H. Maki, J. Am. Chem. Soc., 82, 2671 (1960).

38. A. H. Maki and D. H. Geske, J. Am. Chem. Soc., 83, 1852 (1961).

39. A. H. Maki and D. H. Geske, J. Chem. Phys., 33, 825 (1960).

40. R. L. Ward, J. Chem. Phys., 32, 410 (1960).

41. R. L. Ward, J. Am. Chem. Soc., 83, 1296 (1961).

42. L. H. Piette, P. Ludwig and R. N. Adams, J. Am. Chem. Soc., 84, 4212 (1962).

43. T. Kauffmann and S. Hage, Angerw. Chem., 2, 156 (1963).

44. L. Holleck and R. Schindler, Z. Electrochem., 60, 1138 (1956).

45. G. Kresse and H. Manthey, Chem. Ber., 89, 1412 (1956).

46. A. K. Hoffmann, W. G. Hodgson and W. H. Jura, J. Am. Chem. Soc., 83, 4675 (1961).

47. J. C. Baird and J. R. Thomas, J. Chem. Phys., 35, 1507 (1961).

48. G. M. Coppinger and J. D. Swalen, J. Am. Chem. Soc., 83, 4900 (1961).

49. J. R. Thomas and C. A. Tolman, J. Am. Chem. Soc., 84, 2930 (1962).

50. R. L. Ward, J. Am. Chem. Soc., 84, 332 (1962).

51. Y. Matsunaga and C. A. McDowell, Proc. Chem. Soc., 175 (1960).

52. G. A. Russell, E. G. Janzen and E. T. Strom, J. Am. Chem. Soc., 84, 4155 (1962).

53. T. L. Chu, G. E. Pake, D. E. Paul, J. Townsend and S. I. Weissman, J. Phys. Chem., 57, 504 (1953).

54. A. R. Forrester and R. H. Thomson, Proc. Chem. Soc., 360 (1962).

55. E. M. Kosower and E. J. Poziomek, J. Am. Chem. Soc., 85, 2035 (1963).

56. W. M. Schwarz, E. M. Kosower and I. Shain, J. Am. Chem. Soc., 83, 3164 (1961).

57. E. Weitz, Angew. Chem., 66, 658 (1959).

58. R. L. Ward, J. Am. Chem. Soc., 83, 3623 (1961).

59. N. M. Atherton, F. Gerson and J. N. Murrell, Mol. phys., 5, 509 (1962).

60. P. H. Rieger, I. Bernal, W. H. Reinmuth and G. K. Franenkel, J. Am. Chem. Soc., 85, 683 (1963).

61. H. E. Simmons, R. D. Vest, D. C. Blomstrom, J. R. Roland and T. L. Cairns, J. Am. Chem. Soc., 84, 4746 (1962).

62. E. T. Kaiser and D. H. Eargle, Jr., J. Am. Chem. Soc., 85, 1821 (1963).

63. S. I. Weissman, Z. Electrochem., 64, 47 (1960).

64. A. C. Aten, J. Dieleman and G. J. Hoijtink, Discussions Faraday Soc., No. 29, 182 (1960).

65. R. L. Ward and S. I. Weissman, J. Am. Chem. Soc., 76, 3612 (1954).

66. M. T. Jones and S. I. Weissman, J. Am. Chem. Soc., 84, 4269 (1962).

67. G. J. Hoijtink, E. De Boer, P. H. Van der Meij and W. P. Weijland, Rec. trav. chim., 75, 487 (1956).

68. J. Jagur, M. Levy, M. Feld and M. Szwarc, Trans. Faraday Soc., 58, 2168 (1962).

69. D. E. Paul, D. Lipkin and S. I. Weissman, J. Am. Chem. Soc., 78, 116 (1956).

70. D. L. Maricle, Anal. Chem., 35, 683 (1963).

71. R. S. Mulliken and W. B. Person, Donor-Acceptor Complexes in H. Eyring, C. J. Christensen and H. S. Johnston, editors, "Annual Review of Physical Chemistry", Vol. 13, Annual Reviews, Inc., Palo Alto, California, 1962.

72. G. Briegleb and J. Czekalla, Angew. Chem., 72, 401 (1960).

73. G. Briegleb, "Electronen-Donator-Acceptor-Komplexe", Springer Verlag, Berlin, 1961.

74. S. P. McGlynn, Chem. Revs., 58, 1113 (1958).

75. J. N. Murrell, Quart. Revs., 15, 191 (1961).

76. D. Bijl, H. Kainer, and A. C. Rose-Innes, J. Chem. Phys., 30, 765 (1959).

77. L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson and W. E. Mochel, J. Am. Chem. Soc., 84, 3374 (1962).

78. O. W. Webster, W. Mahler and R. E. Benson, J. Am. Chem. Soc., 84, 3678 (1962).

79. S. S. Danyluk and W. G. Schneider, Can. J. Chem. 40, 1884 (1962).

80. H. Kainer and A. Überle, Chem. Ber., 88, 1147 (1955).

81. J. W. Eastman, G. Engelsma and M. Calvin, J. Am. Chem. Soc., 84, 1339 (1962).

82. I. Isenberg and S. L. Baird, J. Am. Chem. Soc., 84, 3803 (1962).

83. D. H. Anderson, R. M. Elofson, H. S. Gutowsky, S. Levine and R. B. Sandin, J. Am. Chem. Soc., 83, 3157 (1961).

84. J. F. Garst and R. S. Cole, J. Am. Chem. Soc., 84, 4352 (1962).

85. T. Abe, Bull. Chem. Soc. Japan, 34, 21 (1961).

86. T. Abe, Bull. Chem. Soc. Japan, 34, 1776 (1961).

87. R. Foster and R. K. Mackie, Tetrahedron, 18, 1131 (1962).

88. R. E. Miller and W. F. K. Wynne-Jones, J. Chem. Soc., 2375 (1959).

89. D. F. Evans, J. Chem. Soc., 1351 (1957).

90. W. IJ. Aalbergsberg, J. Gaaf and E. L. Mackor, J. Chem. Soc., 905 (1961).

91. H. R. Gersmann and A. F. Bickel, J. Chem. Soc., 2711 (1959).

92. A. K. Colter and S. S. Wang, J. Am. Chem. Soc., 85, 114 (1963).

93. G. A. Russell, E. G. Janzen, H.-D. Becker and F. Smentowski, J. Am. Chem. Soc., 84, 2652 (1962).

94. K. Conrow and P. C. Radlick, J. Org. Chem., 26, 2260 (1961).

95. F. M. Beringer, S. A. Galton and S. J. Huang, J. Am. Chem. Soc., 84, 2819 (1962).

96. W. E. Bachmann, J. Am. Chem. Soc., 53, 2758 (1931).

97. D. Blake, G. E. Coates and J. M. Tate, J. Chem. Soc., 618 (1961).

98. C. Tamborski, F. E. Ford and E. J. Soloski, J. Org. Chem., 28, 181 (1963).

99. A. Streitweiser, Jr. and W. C. Langworthy, J. Am. Chem. Soc., 85, 1757 (1963).

100. G. A. Russell and E. G. Janzen, J. Am. Chem. Soc., 84, 4153 (1962).

101. D. J. Cram and C. K. Dalton, J. Am. Chem. Soc., 85, 1268 (1963).

102. M. F. Hawthorne and G. S. Hammond, J. Am. Chem. Soc., 77, 2549 (1955).

103. H. E. De La Mare, J. K. Kochi and F. F. Rust, J. Am. Chem. Soc., 85, 1437 (1963).

104. D. B. Denney, J. Am. Chem. Soc., 78, 590 (1956).

105. J. K. Kochi, J. Am. Chem. Soc., 85, 1958 (1963)

106. J. W. Ladbury and C. F. Cullis, Chem. Revs., 58, 403 (1958).

107. W. A. Waters, Quart. Revs., 12, 277 (1958).

108. B. S. Thyagarajan, Chem. Revs., 58, 439 (1958).

109. G. A. Russell, J. Am. Chem. Soc., 76, 1595 (1954).

110. E. J. Corey and M. Chaykovsky, J. Am. Chem. Soc., 84, 866 (1962).

111. C. G. Swain and E. R. Thornton, J. Am. Chem. Soc., 83, 4033 (1961).

112. H. Kwart and P. S. Francis, J. Am. Chem. Soc., 77, 4907 (1955).

113. A. G. Green and J. Baddiley, J. Chem. Soc., 93, 1721 (1908).

114. O. Diels, Ber., 34, 1758 (1901).

115. F. Ullmann and H. Bleier, Ber., 35, 4273 (1902).

116. W. C. Lothrop and P. A. Goodwin, J. Am. Chem. Soc., 65, 363 (1943).

117. J. Thiele and A. Wanscheidt, Ann., 376, 269 (1910).

118. J. W. Cook, A. Dansi, C. L. Hewett, J. Iball, W. V. Mayneford and E. Roe, J. Chem. Soc., 1319 (1935).

119. S. V. Anantakrishnan and E. D. Hughes, J. Chem. Soc., 1607 (1935).

120. John E. Leffler and Ernest Grunwald, "Rates and Equilibria of Organic Reactions", John Wiley and Sons, Inc., New York, N. Y., 1963.

121. Jack Hine, "Physical Organic Chemistry", 2nd ed., McGraw-Hill Book Company, Inc., New York, N. Y., 1962.

122. W. G. Toland, Jr., J. B. Wilkes and F. J. Brutschy, J. Am. Chem. Soc., 75, 2263 (1953).

123. A. Michael and A. Adair, Ber., 11, 116 (1878).

124. H. Meyer, Ann., 433, 327 (1923).

125. S. Bance, H. J. Barber and A. M. Woolman, J. Chem. Soc., 1 (1943).

126. P. Kattwinkel and R. Wolffenstein, Ber., 37, 3222 (1904).

127. P. Kattwinkel and R. Wolffenstein, Ber., 34, 2423 (1901).

128. K. B. Wiberg, J. Am. Chem. Soc., 77, 2519 (1955).

129. E. H. Rodd, "Chemistry of Carbon Compounds", Vol. 3, Part B, Elsevier Publishing Company, New York, N. Y., 1956.

130. C. G. Le Fevre and R. J. W. Le Fevre, J. Chem. Soc., 196 (1937).

131. J. Meinsenheimer, Ann., 323, 205 (1902).

132. D. H. Geske and J. L. Ragle, J. Am. Chem. Soc., 83, 3532 (1961).

133. J. Hine, "Physical Organic Chemistry", McGraw-Hill Book Company, Inc., New York, N. Y., 1956.

134. F. W. Bergstrom, I. M. Granara and V. Erickson, J. Org. Chem. 7, 98 (1942).

135. M. T. Jones, J. Chem. Phys. 35, 1146 (1961).

136. F. M. Schimmel and F. W. Heineken, Physica, 23, 781 (1957).

137. H. Wieland and S. Gambarjan, Ber., 39, 1500 (1906).

138. H. Wieland, Ber., 48, 1091 (1915).

139. E. W. Stone and A. H. Maki, J. Chem. Phys., 36, 1944 (1962).

140. Kurt Schwabe, "Polarographic und Chemische Konstitution Organischer Verbindungen", Akademie Verlag, Berlin, 1957.

141. R. B. Davis, L. C. Pizzini and E. J. Bara, J. Org. Chem., 26, 4270 (1961).

142. R. Foster and R. K. Mackie, Tetrahedron, 19, 691 (1963).

143. F. M. Beringer, S. A. Galton and S. J. Huang, Tetrahedron, 19, 809 (1963).

144. R. C. Fuson and Wm. E. Ross, J. Am. Chem. Soc., 55, 720 (1933).

145. H. F. Miller and G. B. Bachmann, 57, 766 (1935).

146. L. J. Bellamy, "The Infra-red Spectra of Complex Molecules", 2nd ed. John Wiley & Sons, Inc., New York, N. Y., 1960.

147. Sir I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds", Oxford University Press, New York, N. Y., 1953.

148. N. Campbell, W. W. Easton, J. L. Rayment and J. F. K. Wilshire, J. Chem. Soc., 2784 (1950).

149. R. Jaunin, Helv. Chim. Acta, 39, 111 (1956).

150. E. D. Bergmann, F. E. Crane, Jr. and R. M. Fuoss, J. Am. Chem. Soc., 74, 5979 (1952).

151. Frederick G. Bordwell, "Organic Chemistry", The Macmillan Company, New York, N. Y., 1963.

152. W. K. McEwen, J. Am. Chem. Soc., 58, 1124 (1936).

153. A. Streitwieser, Jr., W. C. Langworthy and J. I. Brauman, J. Am. Chem. Soc., 85, 1761 (1963).

154. A. Streitwieser, Jr., Tetrahedron Letters, No. 6, 23 (1960).

155. C. H. Langford and R. L. Burwell, Jr., J. Am. Chem. Soc., 82, 1503 (1960).

156. R. E. Dessy, Y. Ikuzumi and A. Chen, J. Am. Chem. Soc., 84, 2899 (1962).

157. H. Rapoport and G. Smolinsky, J. Am. Chem. Soc., 82, 934 (1960).

158. L. W. Pickett and M. McLean, J. Am. Chem. Soc., 61, 423 (1939).

159. J. T. Edward and S. Nielsen, J. Chem. Soc., 5075 (1957).

VIII. ACKNOWLEDGMENTS

I would like to attribute my successful completion of the requirements for an advanced degree at this university to the fortunate association with Dr. Glen A. Russell who allowed me freedom of choice of research area, provided ample funds for research and opportunity for stimulating discussions; to the members of my committee, Drs. F. R. Duke, Orville L. Chapman, George H. Bowen and Geo. Burnet who were very kind and encouraging; to Dr. G. E. Dunn and Dr. H. Gesser who first interested me in research; to Anthony J. Moye whose work provided a foundation on which this study is built; to the competitive atmosphere of the graduate student group.

I would like to acknowledge the challenges and suggestions made by Frank Smentowski and Roger Williamson; the cooperation of E. Thomas Strom in phases of research involving E.S.R.; the instruction by Dr. Roy King in the use of the E.S.R. spectrometer; the tool- and cookie-providing helpfulness of Richard Kriens; the synthesis and/or purification of various compounds by Anthony J. Moye, E. J. Geels and R. Danilof; the help provided by Harvey Meyer who built the original shaking and mercury-bulb levelling apparatus; to Glenn Keuhn who as an N.S.F. participating student studied a problem pertinent to my research.

I would like to acknowledge the contribution made by my wife, Susan, who took on the responsibility of typing this thesis.

With gratitude I acknowledge the financial assistance provided by the American Chemical Society Petroleum Research Fund, Union Carbide Company and the Procter and Gamble Company in the form of fellowships.

I am equally grateful to Dr. G. A. Russell for the provision of a post-doctoral fellowship.

"Would you tell me, please, which way I ought to go from here?"

"That depends a good deal on where you want to get to," said the Cat.

"I don't much care where -" said Alice.

"Then it doesn't matter which way you go," said the Cat.

Lewis Carroll