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Organic reactions involving electron transfer

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ORGANIC REACTIONS INVOLVING ELECTRON TRANSFER

by

Edwin James Geels

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.

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Of Science and Technology
Ames, Iowa

1965

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DEDICATION

The fear of the Lord is the beginning of knowledge.

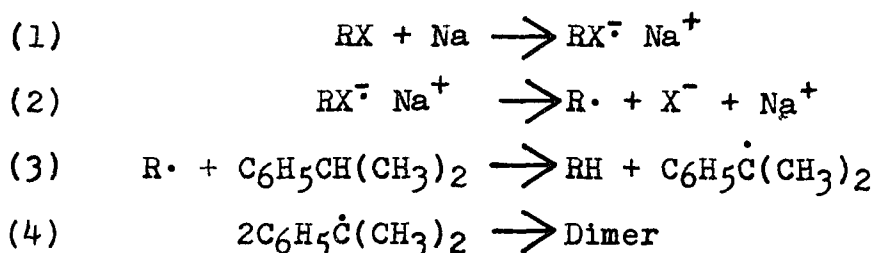
Proverbs 1:7

INTRODUCTION

Until the last decade chemistry has relegated a relatively minor role to the part of free radicals in organic reactions. This was due largely to the reactivity of free radicals which made their isolation and study quite difficult. Thus while there exist many voluminous textbooks on the subject of organic chemistry, most of them devote only a few pages to reactions involving free radical intermediates or products. However, with the advent of the electron spin resonance spectrometer, a new light has been shed on the importance of free radicals in organic chemistry as well as all other fields of chemistry. The literature of electron spin resonance (e.s.r.) of free radicals in solution has grown rapidly and it is the subject of a book (1) and several review articles (2, 3, 4, 5, 6, 7).

Since molecules containing one or more unpaired electrons are produced either by gaining one electron or by losing one electron, e.s.r. can be used for the study of one electron transfer reactions in which a free radical is either destroyed or produced. Loss of an electron by an alkali metal is a common reaction. In the Birch reduction electron transfer to an aromatic system takes place in a primary step (8). Reduction of aromatic hydrocarbons by alkali metals is common and radical-anions are formed by compounds such as naphthalene, phenanthrene, anthracene, and perylene (9). The products iso-

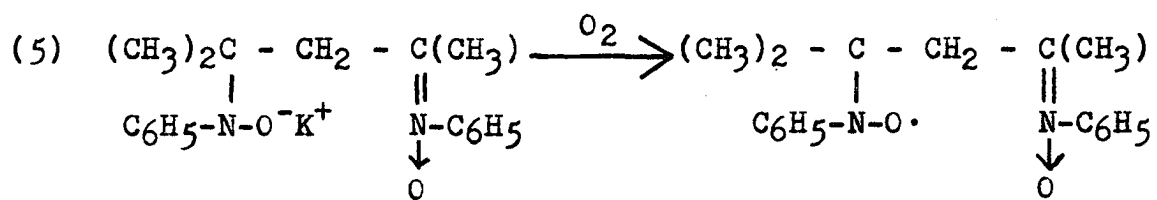
lated from some Wurtz reactions using cumene as a solvent include 2,3-dimethyl-2,3-diphenylbutane (10). This indicates a probable electron transfer reaction as shown by the following reactions.



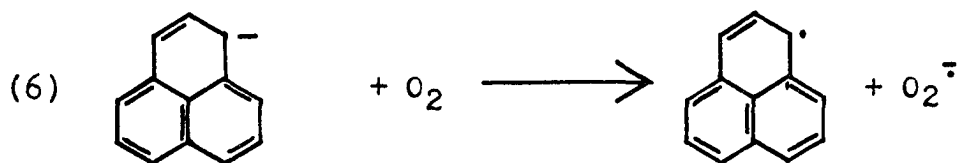
Reaction of derivatives of nitrosobenzene such as p-nitrosotoluene and p-nitrosodimethylaniline with sodium in tetrahydrofuran (THF) produces the respective radical-anions and dianions depending on the amount of alkali metal employed (11). Holmes-Walker and Ubbelohde have isolated solid paramagnetic complexes formed by transfer of electrons from lithium, sodium, or potassium to anthracene (12). Recently, Bauld has found that not only radical-dianions (13) but also radical-trianions can be prepared (14). A radical-dianion may be formed from reaction of sodium or potassium in THF with the anion of dibenzoylmethane. Other compounds found to form radical-dianions were the anions from 1-phenyl-2,3-butanedione and dimedon. A radical-trianion is formed by reaction of potassium with the dianion of benzil. Other dianions which are reduced by potassium are phenanthrenequinone which gives a five line e.s.r. spectrum and oxalate which gives a stable purple trianion exhibiting an e.s.r. singlet. The trianion of

benzil is probably converted to phenanthrenequinone trianion since both give identical e.s.r. spectra.

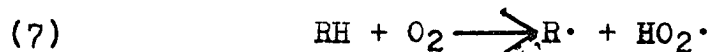
Oxygen in view of its importance to living organisms is a very important electron-transfer agent. The importance of electron transfer in carbanion autoxidations will be discussed later. Reaction of oxygen with hydrocarbons such as perylene in trifluoroacetic acid yields the perylene radical cation (15). Reaction of oxygen with the anion of the condensation product of acetone and phenylhydroxylamine yields a stable nitroxide which was isolated as red crystals (16).



The nitroxide from phenyl-9-trans-decalylhydroxylamine was isolated in a similar reaction (17). Oxygen also reacts with the anion from perinaphthene to give the perinaphthyl radical (18, 19).



However, since this reaction occurs in even the most carefully purified material with no base present, the reaction might also be written as a hydrogen atom abstraction.

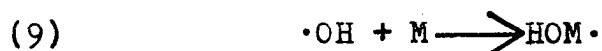
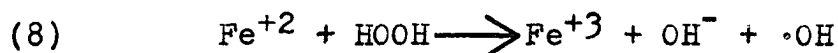


Lewis acids have also been used as electron acceptors and

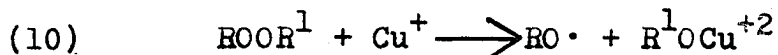
electron transfer from aromatic hydrocarbons to sulfur dioxide, antimony pentachloride, and boron trifluoride has been observed (20, 21). The discovery of free radicals in Friedel-Crafts reactions casts some doubt on the accepted reaction mechanism involving carbonium ions (22). The gradual increase in the e.s.r. absorption as the reaction proceeds suggests radical-cations as reaction intermediates or possibly as products of a side reaction. Radical-cations were formed from anthracene, naphthalene, and perylene (23, 24) and from phenylated amines (24) by electron transfer to an activated silica-alumina catalyst. The radicals were formed when the hydrocarbons were adsorbed from hexane or carbon disulfide solution. Saturation occurred at a radical concentration of 6×10^{17} spins per gram of catalyst corresponding to 2×10^{11} active sites per cm^2 of catalyst surface. In view of this work it is quite probable that radicals may be important intermediates in many reactions of aromatic hydrocarbons under cracking conditions. Rooney and Pink showed that electron transfer occurs from aromatic hydrocarbons such as anthracene, perylene, or chrysene to aluminum chloride either in carbon disulfide solution or in mixtures of the solids (25). The radicals formed are shown to be the radical-cations by comparison with their spectra in concentrated sulfuric acid. Radicals of this type are probably intermediates in the aluminum chloride catalyzed ring closures of aromatic hydro-

carbons, such as the preparation of perylene from 1,1¹-binaphthyl (26).

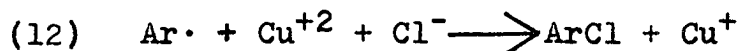
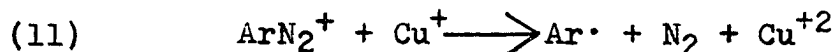
Although one electron transfer involving transition metal ions is common it was not until as late as 1946 that evidence was set forth for such a pathway in the catalysis of vinyl polymerization by peroxides (27). This catalysis was shown to be due to reactions of metal ions with the peroxides producing free radical species.



Cuprous ions react with organic peroxides in a similar manner (28).



The reduction of nitrobenzene to aniline by titanium trichloride in aqueous alcohol is thought to occur by one electron transfer from Ti^{+3} to nitrobenzene (29). The Sandmeyer reaction is also a reaction of this type in which cuprous ion transfers an electron to a diazonium ion (30).



This reaction produces free aryl radicals capable of initiating vinyl polymerization. In dilute solution up to 35% of the diazonium ions can produce aryl free radicals. The oxidation of hydrazine to nitrogen and ammonia in aqueous solution is postulated to occur by a one electron transfer to metal ions

such as Ce(IV), Fe(III), V(V), KMnO_4 , and $\text{K}_2\text{Cr}_2\text{O}_7$ (31). This is supported by the work of Adams and Thomas (32) who found that on mixing solutions of hydrazine and ceric ammonium sulfate in a fast flow system the e.s.r. spectrum of the hydrazine radical-cation (N_2H_4^+) could be observed. A similar situation is the oxidation in alkaline solution of 2,4,6-tri-t-butylphenol by potassium ferricyanide to the phenoxy radical (33).

Recently the subject of complex formation in organic chemistry has received a considerable amount of attention (34, 35). The amount of charge transfer involved in complex formation may range from weak electronic interactions to complete electron transfer with the formation of radical-ions. The first report of this was by Kainer et al. who discovered that solid adducts of p-phenylenediamine and N,N,N',N'-tetramethyl-p-phenylenediamine with tetrahalo-p-benzoquinones displayed strong e.s.r. signals (36). Other paramagnetic complexes which have been discovered are those formed from interaction of tetracyanoquinodimethane (TCNQ) with ions of the type $(\text{C}_6\text{H}_5)_3\text{-X-CH}_3^+$ where X = N, P, or As (37). Complexes of iodine with aromatic hydrocarbons have been found to be paramagnetic in one case (38) and other workers have found that bromine as well as iodine adducts formed with polyphenylethylenes and substituted biphenyls were paramagnetic (39). The e.s.r. spectra of hydrocarbon-iodine complexes were found

to be very similar to the spectra from the radical-cations of the hydrocarbons (40, 41). The e.s.r. spectrum displayed by the solid complex from triphenylamine with iodine is that of the donor cation $(C_6H_5)_3N^+$ (42).

Complex formation leading to radicals has also been observed with n-type donors. Solutions of aliphatic amines in s-trinitrobenzene give an e.s.r. absorption which is presumed to be $C_6H_3(NO_2)_3^-$ (43). Triethylamine reacts with TCNQ to give $TCNQ^-$ (44) and the iodide ion was found to transfer an electron to tetracyanoethylene (TCNE) and bromanil (45).

Although most charge-transfer complexes are diamagnetic in solution, polar solvents which can contribute to stabilization of ions sometimes cause separation of a complex into two radical ions. Thus solutions of N,N,N',N'-tetramethyl-p-phenylenediamine and p-chloranil in polar solvents exhibit an e.s.r. signal which is the sum of the absorptions from the Wurster's blue cation and the chloranil radical-anion (46, 47). When the polar solvent is changed to a non-polar solvent the color of the solution fades and the e.s.r. signal disappears.

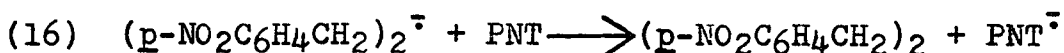
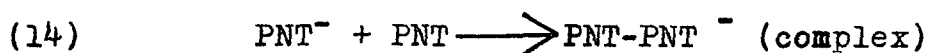
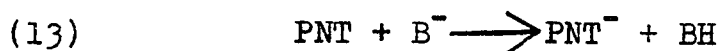
Hausser has demonstrated a temperature dependence of the electron transfer between N,N,N',N'-tetramethyl-p-phenylenediamine and diphenylpicrylhydrazyl (DPPH) in toluene and other solvents (48). An e.s.r. spectrum of the DPPH radical was seen at $-20^\circ C$, Wurster's blue cation at $-60^\circ C$ and a mixture

of the two at -40°C .

Electron transfer reactions between carbanions or nitranions and unsaturated acceptors has been extensively studied by Russell *et al.* (49). They found that high concentrations of nitrobenzene radical-anion were formed in DMSO (20%)-*t*-butyl alcohol (80%) by reaction with the carbanion or nitranion from fluorene, 9-phenylfluorene, indene, diphenylmethane, triphenylmethane, propiophenone, 3,4-dimercaptotoluene, hydrazobenzene, and N-hydroxybenzenesulfonamide. Azobenzene radical-anion was also formed in high concentration in this solvent by electron transfer from the anions of indene, diphenylmethane, triphenylmethane, acetophenone, propiophenone, isobutyrophenone, hydrazobenzene, 9,10-dihydroanthracene, and butyllithium. Propiophenone, which was found to be a good donor, also reduced phenazine, benzo[*c*]cinnoline, and benzofurazan to their radical-anions in a solution of DMSO (80%)-*t*-butyl alcohol (20%) containing potassium-*t*-butoxide.

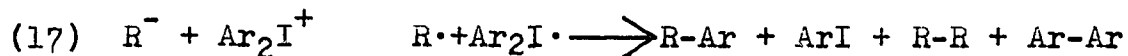
Russell and Janzen have also discovered that a number of nitroaromatics spontaneously generate radical-anions in *t*-butyl alcohol solution containing potassium *t*-butoxide (50). Included are nitroaromatics such as *p*-nitrotoluene, *p*-nitroethylbenzene, *o*-nitroethylbenzene, *o*-bromo-*p*-nitrotoluene, *p*-nitro-*o*-xylene, *o*-amino-*p*-nitrotoluene, *p*-nitrobenzyl alcohol, *p*-nitrobenzaldehyde, 2-nitrofluorene, and *p*-nitro-

acenaphthalene. The mechanism given for the formation of p-nitrotoluene (PNT) radical-anion is given by the following equations.



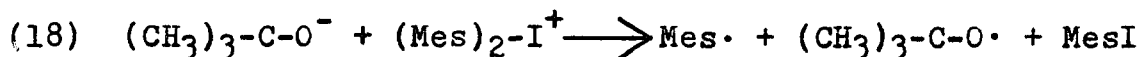
Electron transfer from a carbanion to a ketone was observed by Bachman in the formation of benzpinacol and benzoin from reaction of triphenylmethyl sodium with benzophenone and benzil (51).

Smentowski has studied the electron transfer reaction between mercaptide ions and a number of acceptors. The following decreasing order of oxidizing ability was based on the yield of disulfide which was recovered, azodicarbonamide > nitrosobenzene > maleic anhydride > acrylonitrile > nitrobenzene (52). Transfer from a nitranion was observed in the reduction of 3- and 8-methylfluoranthene and anthracene by lithium cyclohexylamide to produce the corresponding radical-anions (53, 54). Recently electron transfer was observed from a carbanion to a diphenyl iodonium salt in the alkylation of some 1,3-indandiones (55).



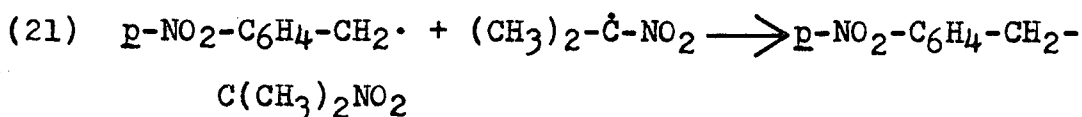
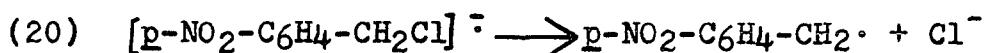
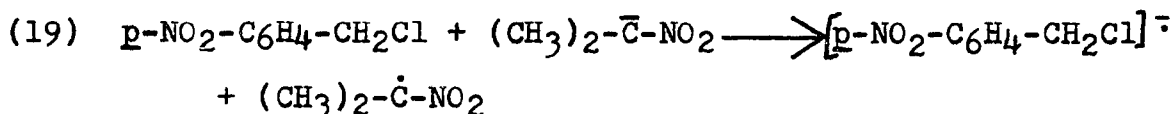
In the reaction of dimesityliodonium chloride with 1,3-indandione in t-butanol-sodium t-butoxide solution 2-t-butoxy-

2-mesityl-1,3-indandione is produced in addition to normal reaction products. This is postulated to arise by electron transfer from t-butoxide ion to the iodonium salt.



The t-butoxy radical then couples with the radical produced from the initial product 2-mesityl-1,3-indandione.

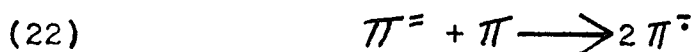
The carbon alkylation of nitroalkane salts by benzyl chlorides involves one electron transfer as an initial step (56). Mixtures of solutions of the anion from 2-nitropropane with p-nitrobenzylchloride results in an e.s.r. signal resembling that expected from the p-nitrobenzylchloride radical-anion.



Addition of a good electron acceptor such as p-dinitrobenzene inhibits formation of the radical-anion of the chloride and the percent of carbon alkylation falls from 92% when no p-dinitrobenzene is present to 2% when it is added while the amount of oxygen alkylation increases from 6% to 72% respectively.

The reaction between dianions and their unsaturated analogues has been studied by Russell et al. (57). The

reaction between the unsaturated system (π) and the dianion (π^{2-}) derived from the dihydro-compound (πH_2) usually produced large amounts of radical-anions.



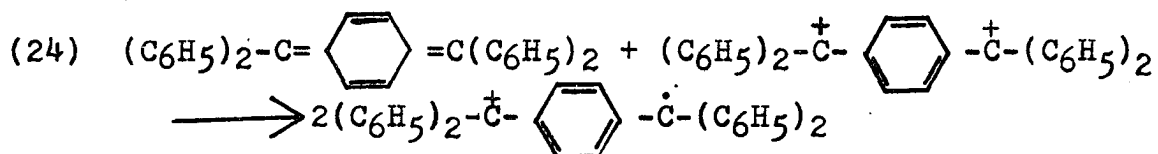
The possibility of an intermediate dimeric-dianion was also considered.



Substances undergoing electron transfer with the corresponding dianions were acridine, 2,3-diphenylquinoxaline, $\Delta^{9,9'}$ -bifluorene, anthracene, azobenzene, furil, fluoren-9-one, xanthen-9-one, and benzophenone. Other examples are the electron transfer between cyclooctatetraene dianion and cyclooctatetraene (58), between 1,4 dihydroquinone dianion and p-benzoquinone (59), and between tetraphenylethylene dianion and tetraphenylethylene (60). The transfer in the last case is very solvent dependent. Although the tetraphenylethylene radical-anion is observed in 1,2-dimethoxyethane, upon changing the solvent to ether no radical could be detected and only the dianion-unsaturated system was present. In the case of the reaction between azobenzene and its dianion, from reaction of hydrazobenzene and methylolithium, the lithium salt of the azobenzene radical-anion was actually recovered from ether solution (61).

Although transfer between dianions and unsaturated systems appears to be quite common, only one example is known of

transfer from an unsaturated system to a dicarbonium ion. This is the reaction between tetraphenyl-*p*-xylyene and the corresponding cation (62).

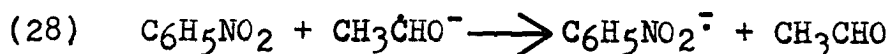
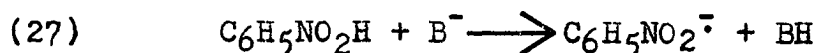
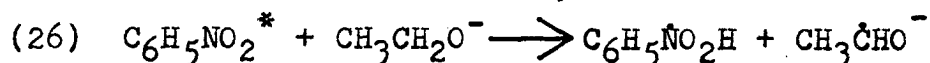
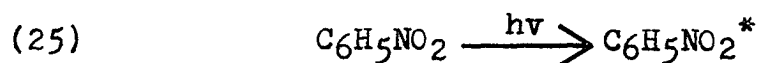


Mixture in methylene chloride of the pale yellow solutions containing the xylyene and the perchlorate salt gave a dark red solution of the radical-cation. The rate of transfer was very slow as compared to most electron transfers and was estimated to be 300 l./mole-sec.

Electron transfer between radical-ions and unsaturated systems has been carefully studied by many workers and in some cases rates of transfer were measured. The relative rate of transfer from the radical-anions of various aromatic hydrocarbons was measured and it was found that the rates decreased as the electron affinities of the hydrocarbons increased (9). The order for a series of hydrocarbons with decreasing rate is naphthalene \gg phenanthrene $>$ chrysene $>$ picene $>$ pyrene $>$ 1,2-benzanthracene $>$ anthracene $>$ perylene. Electron exchange has been studied in π - π^{\cdot} systems such as TCNE-TCNE $^{\cdot-}$ (63), N,N,N',N'-tetramethyl-*p*-phenylenediamine-Wurster's blue (64), naphthalene radical-anion-naphthalene (65), and 2,2'-bipyridine radical-anion and 2,2'-bipyridine (66).

Photoinduced electron transfer was observed by Ward when a complex of TCNE or pyromellitic dianhydride with THF was

irradiated continuously by a mercury arc lamp (67). The radicals produced were the radical-anions of TCNE and pyromellitic dianhydride. Another example of photoinitiated electron transfer is the reaction of nitrobenzene with ethoxide or methoxide ion and light to produce the nitrobenzene radical-anion (68). A probable mechanism for this transformation is given by the following series of reactions.



Electron transfer producing chemiluminescence was observed in the reaction of 9,10-diphenylanthracene radical-anion with 9,10-dichloroanthracene (69).

An example of electron transfer from a negative ion to a positive ion is given by the formation of the trimethylpyrylium radical from the reaction of trimethylpyrylium fluoborate with cyclooctatetraene (70). The salt also accepts electrons from benzophenone ketyl and anthracene anion.

Sodium triphenyltin has been found to be a good donor and transfers electrons to carbon dioxide, benzophenone, and sulfur dioxide to produce oxalate, benzophenone ketyl, and dithionite respectively (71).

Some examples of intramolecular electron transfer have been found. The first was by Weissman who observed electron

exchange between the rings of paracyclophane radical-anions such as 2,2-paracyclophane and 1,8-paracyclophane (72). Both of these had e.s.r. signals containing nine lines revealing hyperfine splitting by eight equivalent protons. Intramolecular electron exchange has also been observed in some bis(p-nitrophenyl) anions (73). Electron transfer rates (cycles/sec) obtained from e.s.r. spectra in DMSO were 9×10^6 for bis(p-nitrophenyl)sulfide, 3×10^6 for bis(p-nitrophenyl)sulfide, and 2×10^6 for 4,4'-dinitrobibenzyl.

The effect of electron transfer in polymer reactions has also assumed more importance recently. The reduction of polybenzo-p-xylylene and polyphenyl with potassium gave poly-radical-anions exhibiting a single very intense e.s.r. absorption (74). Szwarc has suggested in a review lecture that the production of living polymers by anionic polymerization may be initiated by an electron transfer process (75).



The radical-anions produced may dimerize into dianions or give dimeric radical-anions by association with monomer.



A dimeric dianion is capable of initiating anionic propagation in both directions and the formation of $^-M-M\cdot$ makes possible simultaneous anionic and radical propagation.

PART I. THE BASE-CATALYZED AUTOXIDATION
OF AROMATIC ALCOHOLS AND PHENONES

HISTORICAL

The oxidation of alcohols to aldehydes, ketones, and acids has been effected by a number of reagents. Manganese dioxide has been the oxidant used by a number of workers (76, 77, 78). The rate of oxidation and yield obtained depends on the method of preparation of the manganese dioxide (78). In the oxidation of a series of substituted alcohols only a small effect of the substituent on the rate was noticed and a free radical intermediate of the type $C_6H_5-\dot{C}HOH$ was suggested (77, 78). In the oxidation of a series of aromatic alcohols by manganese dioxide the following order of decreasing rate was observed: fluorenol > xanthidrol > benzhydrol > benzyl alcohol (77).

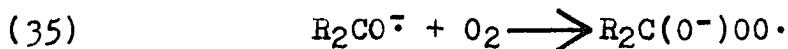
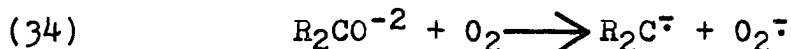
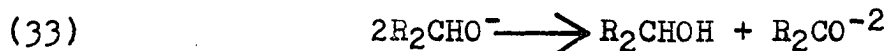
Aromatic alcohols were oxidized to aldehydes and ketones by N-bromoacetamide in benzene solution (79). Benzaldehyde, acetophenone, propiophenone, benzophenone, and deoxybenzoin were obtained in good yield by oxidation of the corresponding alcohols.

Chromium trioxide has been used in alcohol oxidations in acetic acid. The oxidation of benzpinacolyl alcohol $[(C_6H_5)_3C-CHOHC_6H_5]$ under these conditions gives in addition to the expected ketone a mixture of triphenylmethanol, tetraphenyl-ethylene, and benzaldehyde (80). A series of *m*- and *p*-substituted α -phenylethanol were oxidized by chromium trioxide and the rates of oxidation applied to the Hammett

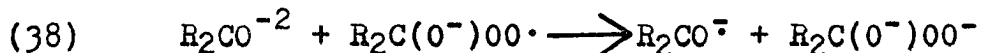
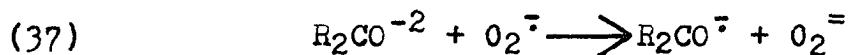
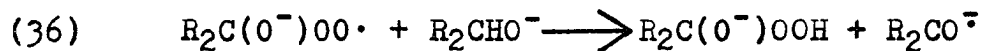
equation gave small negative rho values (81).

A number of aromatic alcohols have also been oxidized by electrolysis at a micro platinum electrode in acetonitrile solution (82).

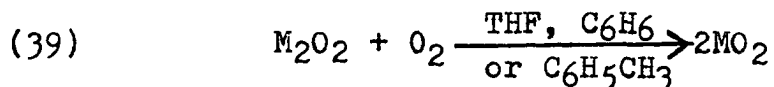
The autoxidation in basic solution of aromatic alcohols to acids and ketones is well known (83, 84). Moye has investigated the autoxidation of a number of alcohols in t-butanol containing potassium t-butoxide (85). The initial rates of oxidation in decreasing order for a number of alcohols are 9-fluorenoyl > p-nitrobenzyl alcohol > benzhydrol > benzyl alcohol. The addition of ferric ion caused considerable inhibition of the oxidation of benzhydrol and benzyl alcohol. Etienne and Fellion found that although 9-fluorenoyl and benzhydrol do not undergo autoxidation in benzene, upon the addition of sodium or potassium they lose hydrogen and rapidly absorb oxygen to give the corresponding ketones (86). LeBerre has commented on possible mechanisms for these autoxidations and particularly for the oxidation of benzhydrol (87, 88, 89, 90, 91). He concluded that the oxidation of suspensions of the sodium or potassium salts of benzhydrol in benzene or tetrahydrofuran involved dianions as intermediates and was possibly a free radical chain process (88, 91).



The possibility that the reaction also involves attack on the α -hydrogen atom was considered in addition to various propagation steps involving the dianion.



LeBerre observed in the presence of excess sodium or potassium t-butoxide that the oxygen was converted to the superoxide rather than to the peroxides (MOOH , MOOM) observed with stoichiometric amounts of base (90, 91). This was explained by an unusual reaction, the further oxidation of the peroxide to the superoxide.



RESULTS AND DISCUSSION

The oxidations described in this section were all performed in a 125 ml. creased flask which was agitated vigorously by a wrist-action shaker (Figure 1). The creased flask was built with a second small ground glass joint to which a small pear-shaped bulb with a curved neck could be attached. A solution of base could be introduced from this flask by tipping up the bulb. At the same time the shaker was started mixing the base solution with the solution of the substrate and marking the beginning of the oxidation. The course of the oxidation was followed by recording the volume of oxygen absorbed as a function of time at a constant pressure of 740 mm. of oxygen. During very slow oxidations requiring many hours for complete reaction an automatic mercury bulb leveling device was used to maintain a constant pressure (Figure 2). Although the oxidation apparatus was not thermostated the temperature varied insignificantly during any given experiment. Variation of room temperature from 24°C to 28°C caused no appreciable change in oxidation rates. All rates of oxidation given in this section are maximum rates unless otherwise noted and are calculated as the ratio of moles of oxygen absorbed at S.T.P. per mole of starting material per minute (moles O₂/mole ROH-min.).

The oxidation of a number of aromatic alcohols was

Figure 1. Wrist-action shaker used to agitate solutions for oxidations

WRIST SHAKER

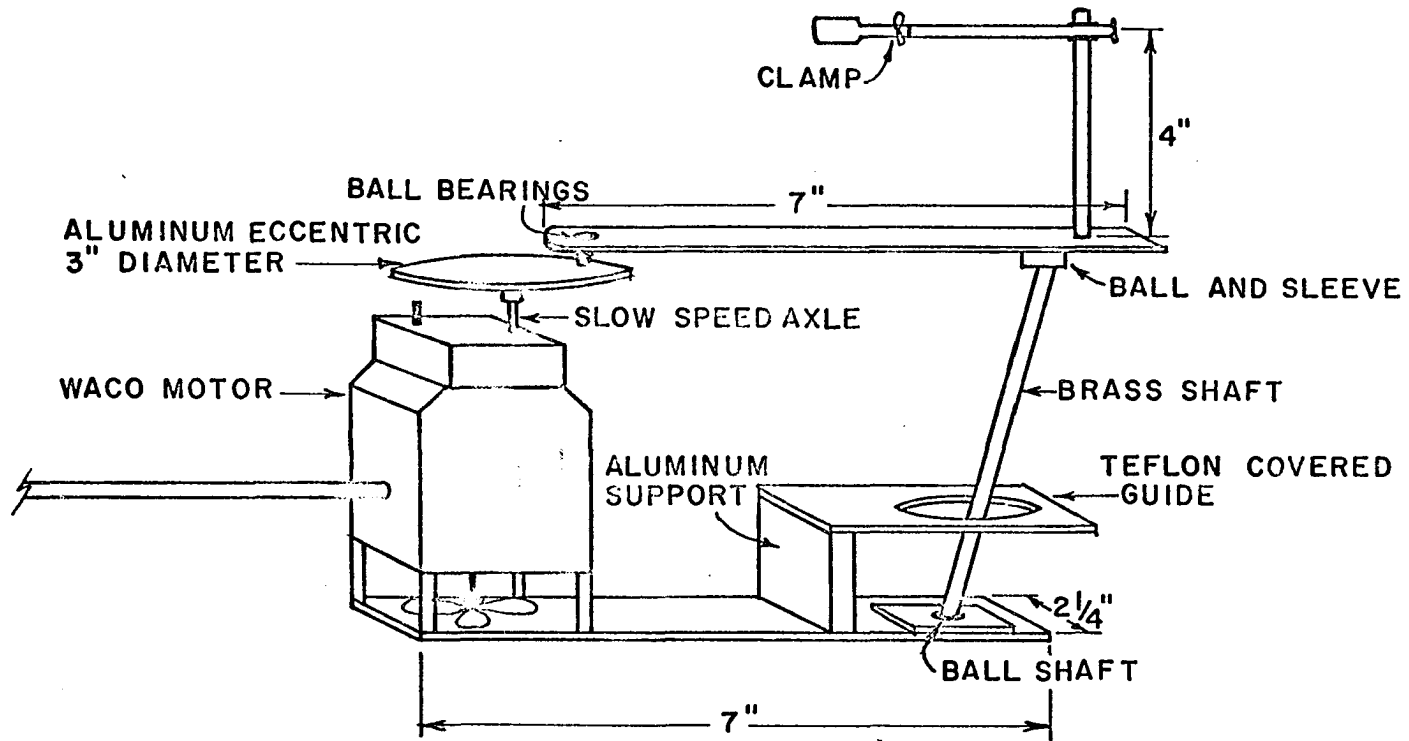
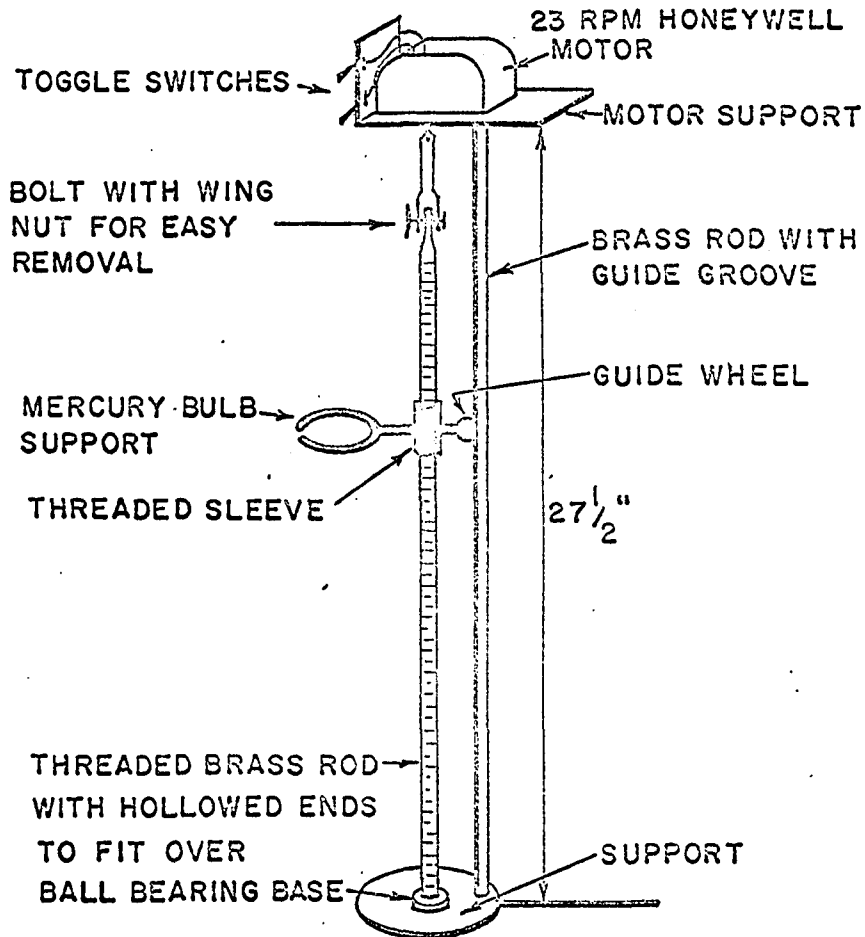


Figure 2. Relay-controlled mercury-bulb leveling device
used to maintain constant pressure in very
slow oxidations

AUTOMATIC MERCURY-BULB LEVELLING DEVICE



studied in the presence of alkoxide ions under homogeneous conditions by the use of *t*-butyl alcohol, pyridine, or DMSO as solvents. There was particular interest in obtaining evidence for or against the participation of a carbanion or a dianion in the oxidation since the formation of $(C_6H_5)_2COH^-$ or $(C_6H_5)_2CO^{-2}$ by the action of alkoxide ion appeared to be unexpected. The results are not consistent for the intervention of a carbanion in the oxidation of benzhydrol or benzyl alcohols but do suggest carbanion or dianion formation in the oxidation of the more acidic xanthenol, 9-fluorenel, and *p*-nitrobenzyl alcohol.

In solvents where the base and diarylcarbinol are soluble the ratio of superoxide to alkali metal peroxide formed at complete oxidation depends on the alkali metal involved, the amount of alkoxide present, the solvent, and upon the structure of the carbinol. The effect of the structure of the carbinol argues against the formation of the superoxide solely from further oxidation of the alkali metal peroxide and the yield of the superoxide appears to be determined by its solubility characteristics and the reactivity of the alcohol being oxidized.

Table 1 summarizes a number of oxidations of benzhydrol in the presence of bases and in the presence of a number of potential catalysts or inhibitors.

The lack of significant solvent effects as well as the

Table 1. Oxidations of benzhydrol in basic solutions

Conc. of benzhydrol, moles/l.	Conc. of $\text{KOC}(\text{CH}_3)_3$, moles/l.	Rates of oxygen absorption ^a		
		DMSO(80%)- \underline{t} -butyl alcohol(20%)	Pyridine(80%)- \underline{t} -butyl alcohol(20%)	\underline{t} -butyl alcohol
0.10	--	0.00	0.00	0.00
.06	0.18	.012	.009	.012
.12	.12	--	--	.005
.12	.24	.010	.017	.015
.12	.36	.016	--	.019
.12	.48	--	--	.023
.12 ^b	.36	.0015	--	.0007
.12	.36		--	.017 ^{c,d}
.10	.22		.018 ^e	--
.10	.22		.015 ^f	--

^aMoles oxygen/mole benzhydrol/min.

^b α -deuteriobenzhydrol.

^cAfter a pronounced induction period of 4 hrs. during which rate was 0.0001.

^d0.01 moles/l. As_2O_3 added.

^e0.01 moles/l. $\text{C}_6\text{H}_5\text{NO}_2$ added.

^f0.01 moles/l. $(\text{C}_6\text{H}_5)_2\text{CO}$ added.

lack of a significant effect of the concentration of excess base on the rates of oxidation of benzhydrol appear to exclude an oxidation mechanism involving $(C_6H_5)_2COH^{-1}$ or $(C_6H_5)_2CO^{-2}$ under the conditions employed. Significant effects of these variables were found in the oxidation of fluorene and diphenylmethane in basic solution, reactions recognized to proceed via carbanion intermediates.*

Additional evidence for the lack of carbanion or dianion intermediates is the fact that under the conditions of line 7, Table 1, α -deuteriobenzhydrol did not undergo exchange to form benzhydrol during a 24-hour period as determined by n.m.r. analysis. Unreacted alcohol recovered from the oxidation of α -deuteriobenzhydrol in DMSO-t-butyl alcohol solution showed no benzylic protons even after an oxidation period of 6 hours.

The discovery of a very large deuterium isotope effect in the oxidation of benzhydrol was at first rather surprising. The k_H/k_D ratio is 10.7 in DMSO-t-butyl alcohol and 27 in t-butyl alcohol solution. However, perusal of recent chemical literature revealed other examples of large deuterium isotope effects. In 1934 the reaction between aluminum carbide and water to produce methane was found to proceed 23 times faster in H_2O than in D_2O (92). An effect of 9.9 at 120° was

*Private communication from G. A. Russell, E. G. Janzen, and A. G. Bemis, Ames, Iowa. 1964.

observed in the reaction of methyl radicals with toluene and α,α,α -trideuteriotoluene (93). The oxidation of t-butyl-phenyl carbinol by chromium trioxide in acetic acid gave an isotope effect of 12 at 0° (94). The reaction of hydrogen atoms gave very large isotope effects in some cases. The k_H/k_D ratio for the reaction of hydrogen atoms with ethanol was found to be 17 (95) and for reaction with methanol 20 and with sodium acetate 22 (96). The base catalyzed iodination of 2-nitropropane shows large isotope effects when 2,6-substituted pyridines are used as bases (97, 98). Thus, k_H/k_D for the iodination of 2-nitropropane is 24.1 in the presence of 2,6-lutidine and 24.2 in the presence of 2,4,6-collidine. Stewart and VanDerLinden have found isotope effects of 16-17 for potassium permanganate oxidations in basic aqueous solution of a number of substituted α -trifluoromethylbenzyl alcohols (99, 100). A large k_H/k_D ratio of 7.5 was found in the ionization of $(C_6H_5)_3CH$ (D) at 25° in DMSO (80%)-t-butyl alcohol (20%).*

The existence of large deuterium isotope effects such as those mentioned above or that found in the oxidation of benzhydrol might be justified by one or more of three possible explanations. One explanation is that the reaction involves a chain mechanism with consecutive dependent steps such that

*Private communication from G. A. Russell and A. G. Bemis, Ames, Iowa. 1964.

the overall isotope effect observed is a cumulative one. A second possibility is that although there is considerable bond-breaking in the transition state there is little bond-making. This leads to a loss of bending modes in the transition state in addition to loss of stretching mode. Wiberg has calculated that in an extreme case in which the carbon-hydrogen bond had been completely broken and no new bond to hydrogen had been formed, the k_H/k_D ratio would be equal to 48 (101). Finally, the proposal which seems to receive the most support is that of quantum mechanical tunneling by hydrogen atoms or protons (102, 103, 104). Since the proton or hydrogen atom is a small particle it must be treated quantum mechanically rather than classically. As a result of this treatment tunneling through the potential energy barrier must be considered. This would be less important for deuterium than for hydrogen because of its higher mass.

The reaction of benzhydrol and benzophenone in t-butyl alcohol or DMSO (80%)-t-butyl alcohol (20%) solutions containing excess base does not yield quantities of benzophenone ketyl readily detected by e.s.r. spectroscopy, presumably because of the absence of the dianion derived from the benzhydrol. Reaction of traces of oxygen with benzhydrol in the presence of excess potassium t-butoxide did give significant concentrations of the ketyl in DMSO (100%) solution but not in t-butyl alcohol or DMSO (80%)-t-butyl alcohol (20%)

solutions.* This is consistent with the presence of the dianion in DMSO (100%) but not in the other solvents.

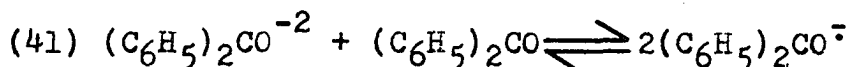
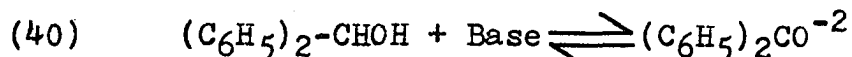
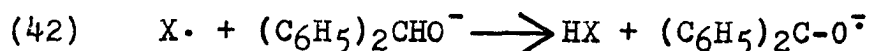
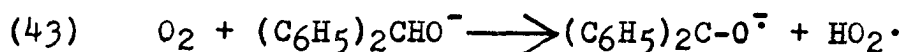


Figure 3 shows that the oxidation of benzhydrol in t-butyl alcohol solution is autocatalytic and is inhibited by arsenic trioxide. Catalysis by nitroaromatics, so characteristic of the oxidation of the carbanions derived from xanthenol and the alkylphenones was not observed.

All of the above observations point to a free radical chain oxidation not involving a carbanion or dianion. The ease of the initiation and propagation of the reaction probably results from the ease of attack of a radical species on the α -hydrogen atom of the alcoholate.



The bond dissociation energy of an alpha carbon-hydrogen bond in an alkoxide anion should be quite low because of the stability of the resulting ketyl anion. An initiation reaction attack of oxygen upon the alcoholate is quite probable.



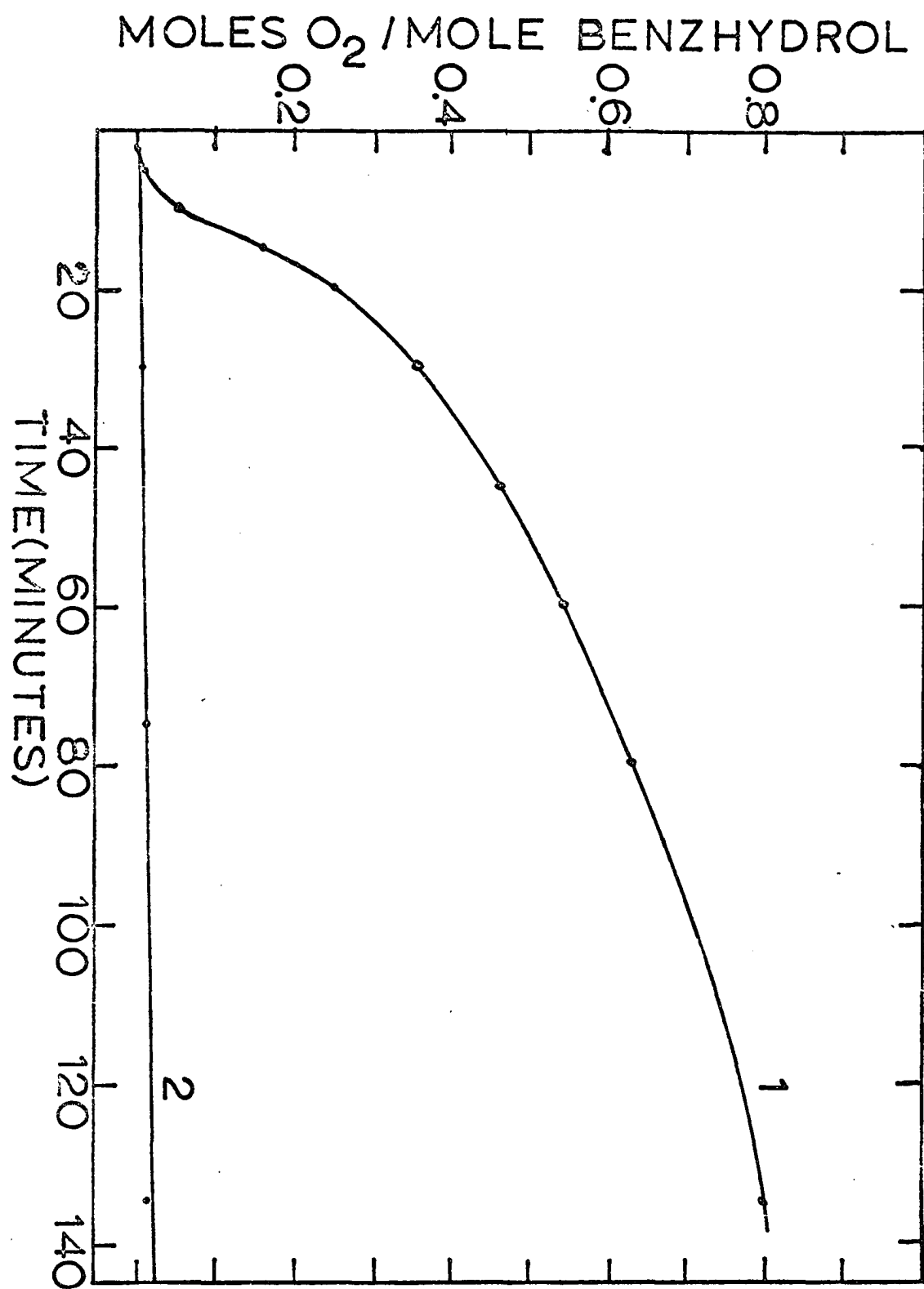
This reaction is probably even more favorable than that proposed by Russell (105) and Ingold (106) for the thermal initiation in the autoxidation of indene.

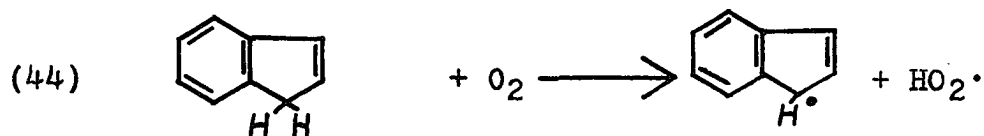
*Private communication from G. A. Russell and E. G. Janzen, Ames, Iowa. 1964.

Figure 3. Oxidation of benzhydrol (0.12 M.) in t-butyl alcohol containing potassium t-butoxide (0.36 M.)

Curve 1. No inhibitor

Curve 2. As_2O_3 (0.01 M.) present





The stoichiometry of the reaction of oxygen with benzhydrol (Table 2) varies with the concentration of base although the rates of oxidation (Table 1) are relatively independent of the concentration of base. Benzophenone is formed in excellent yield (>95%) in the presence of excess base except in DMSO (80%)-t-butyl alcohol (20%) solutions, where the benzophenone-DMSO adduct (107) is the major product. The variable stoichiometry of Table 2 results from the concurrent formation of potassium peroxide and superoxide.

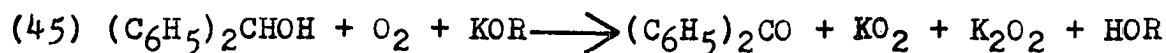


Table 2 indicates that in the presence of a slight excess of base the reaction proceeds quite cleanly to give potassium peroxide. In the presence of large excesses of potassium t-butoxide the reaction gives significant amounts of potassium superoxide which precipitate from the solution as a yellow powder.

Since the overall rate of oxidation is fairly independent of the amount of excess base (Table 1) it appears that the changing stoichiometry may reflect the formation of an insoluble complex between potassium superoxide and potassium t-butoxide. Thus, in the oxidation of 3 mmoles of benzhydrol in 25 ml. of 0.48 M. potassium t-butoxide in t-butyl alcohol solution, 4.35 mmoles of oxygen was absorbed at complete

Table 2. Oxygen stoichiometry in the oxidation of benzhydrol^a

Potassium <u>t</u> -butoxide, moles/l.	Solvent	Moles O ₂ absorbed/ mole benzhydrol (minutes)	Recovered benzhydrol, %
0.12	<u>t</u> -BuOH	0.73 (1100)	13
.20	<u>t</u> -BuOH	.91 (625)	
.24	<u>t</u> -BuOH	1.02 (425)	7
		1.13 (1100)	
.36	<u>t</u> -BuOH	1.36 (1200)	3
.48	<u>t</u> -BuOH	1.45 (1400)	
		1.16 (1400) ^b	
.24	DMSO (80%)- <u>t</u> -BuOH (20%)	1.33 (600) ^c	0
.36	DMSO (80%)- <u>t</u> -BuOH (20%)	1.65 (275)	0

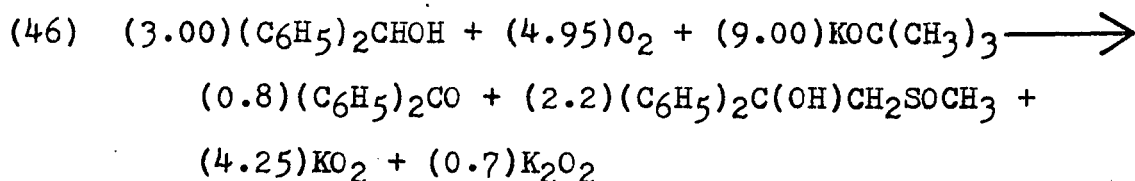
^a0.12 Molar in benzhydrol.

^bOxidation was initially 0.20 M. in KOC(CH₃)₃. After 625 min., 0.91 moles of oxygen/mole of benzhydrol had been absorbed. The base concentration was then increased to 0.48 M.

^cProduct 75% benzophenone, 25% benzophenone-DMSO adduct.

reaction and a crude precipitate formed which contained only 65% KO₂ as analyzed by the method of Seyb and Kleinberg (108). Thorough washing with t-butyl alcohol gave 0.26 g. (3.6 mmoles) of potassium superoxide of 95% purity. The remaining 0.75 mmoles of oxygen was presumably present in the form of

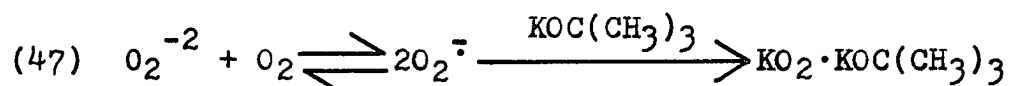
soluble potassium peroxides. In the oxidation of 0.12 M. benzhydrol in the presence of 0.36 M. potassium t-butoxide in DMSO (80%)-t-butyl alcohol (20%) solvent, 4.95 mmoles of oxygen were absorbed by 3 mmoles of benzhydrol at complete reaction. The precipitated superoxide after thorough washing with the reaction solvent weighed 0.307 g. (4.25 mmoles of superoxide) and analyzed as 103% potassium superoxide. In this case the experimental stoichiometry (277 minute reaction period) is indicated in the following equation (mmoles in parentheses).



The oxidation of benzhydrol in the presence of excess base is a good method for preparation of small quantities of very pure superoxide. Other methods for the preparation of potassium superoxide include reaction of potassium metal with oxygen (109), reaction of potassium hydroxide with oxygen at high temperatures (110), decomposition of potassium ozonide (111), and reaction of oxygen with potassium peroxide (112).

The occurrence of the last reaction in solution has been confirmed. Addition of 90% hydrogen peroxide to an excess of potassium t-butoxide in t-butyl alcohol results in a white precipitate which slowly absorbs oxygen at room temperature to yield the yellow superoxide. The reaction proceeds more

readily at the higher concentrations of excess base, apparently ruling out the autoxidation of HO_2^- as the source of the superoxide. The effect of excess base on the rate may well be connected with shifting of the following equilibrium to the right via the formation of an insoluble complex.



The formation of the potassium superoxide in the oxidation of benzhydrol has been investigated in detail. Figure 4 shows that the superoxide is an initial reaction product at high concentrations of potassium t-butoxide. After the rapid initial formation of the superoxide, additional superoxide is formed slowly at the expense of the peroxide. Table 3 lists pertinent results concerning the yields of potassium superoxide and peroxide in the autoxidation of benzhydrol and hydrogen peroxide in basic solutions.

The autocatalysis involved in the oxidation of benzhydrol appears to be connected with the formation and presence of potassium superoxide rather than benzophenone. The addition of potassium superoxide precipitated from a previous oxidation removes the autocatalysis while benzophenone has no effect. Arsenic trioxide apparently destroys the superoxide and gives rise to an induction period. The autocatalytic nature of the oxidation, the inhibition by arsenic trioxide, and the large isotope effect observed could all be consistent with extensive

Figure 4. Products of oxidation of 3 mmoles of benzhydrol (0.12 M.) in DMSO (80%)-t-butyl alcohol (20%) containing potassium t-butoxide (0.36 M.)

Curve 1. KO_2

Curve 2. K_2O_2

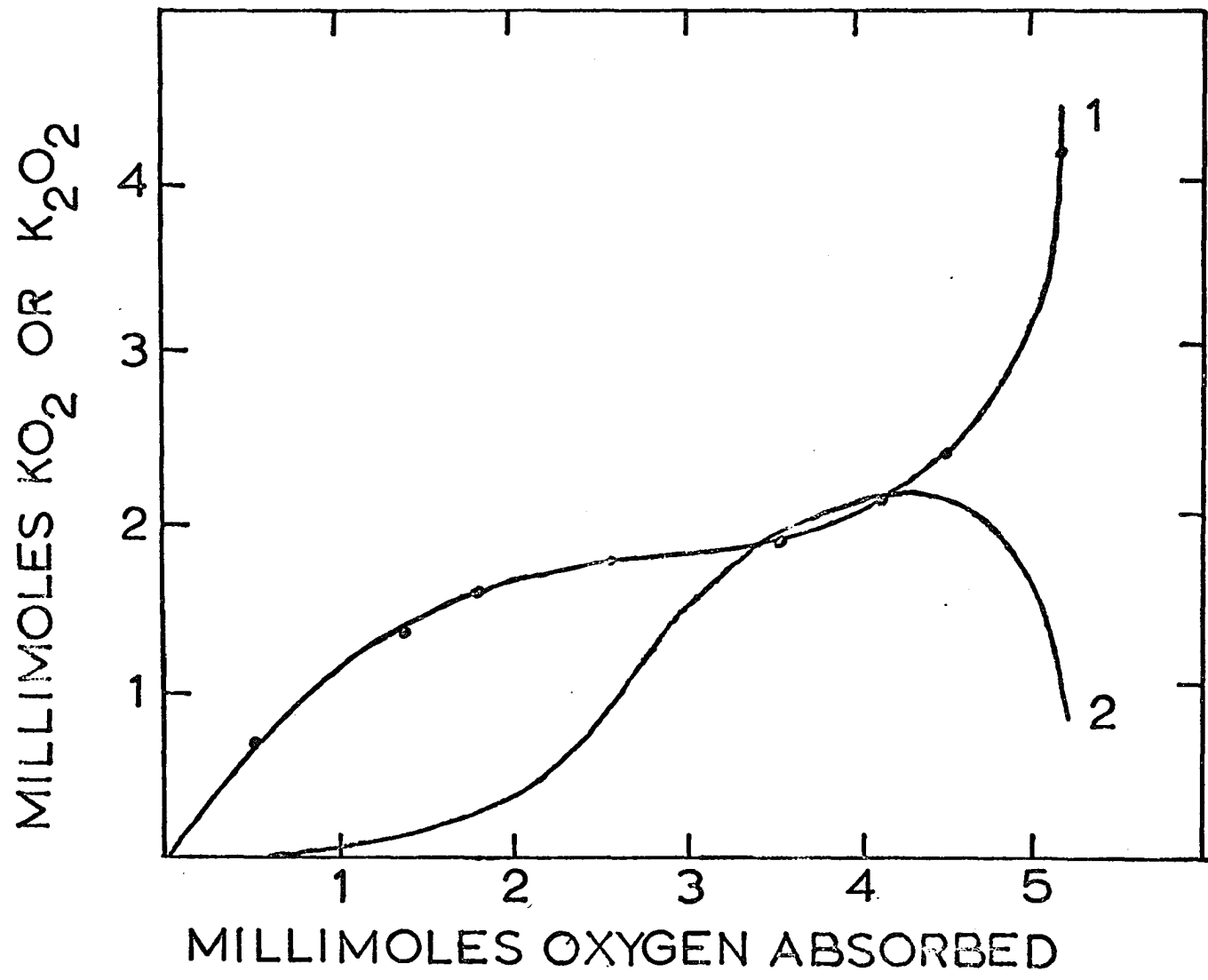


Table 3. Yields of potassium superoxide in the autoxidation of benzhydrol and hydrogen peroxide

Substrate, mmoles ^a	Time, min.	KOC(CH ₃) ₃ , mmoles ^a	O ₂ absorbed, mmoles	KO ₂ , mmoles	K ₂ O ₂ , mmoles ^b
Benzhydrol, ^c 3.0	0	9.0	0		
	10		0.53	0.69	
	20		1.41	1.28	0.13
	50		1.81	1.56	0.25
	100		3.57	1.78	1.79
	160		4.25	2.14	2.11
	220		4.53	2.32	2.21
	300	5.17	4.24	0.93	
Hydrogen peroxide, ^{d,e} 2.9	0	10	0		
	25		0.23		
	120		0.64		
	205		0.89		
	385		1.29		
	530		1.56		
	1350 ^f		2.46	5.9 ^g	
Hydrogen peroxide, ^{d,h} 2.8	0	18	0		
	25		0.80		
	200		1.82		
	1000 ^f		2.17	5.6 ⁱ	

^aInitial concentration in 25 ml. of solution.

^bBy difference, no method was found for independent determination of K₂O₂.

^cDMSO (80%)-t-butyl alcohol (20%) solvent.

^dt-Butyl alcohol solvent.

^eRate = 0.0015 moles O₂/mole H₂O₂-min.

^fOxygen absorption ceased.

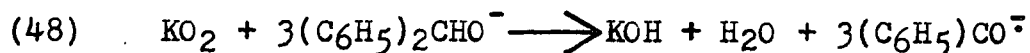
^g0.42 g. (5.9 mmoles) KO₂ analyzing 102% isolated by filtration.

^hRate = 0.033 moles O₂/mole H₂O₂-min.

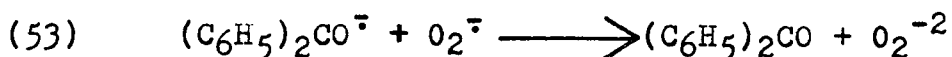
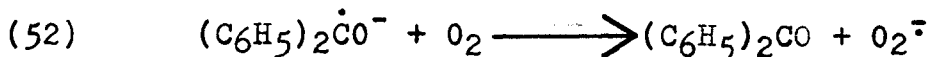
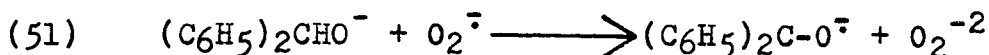
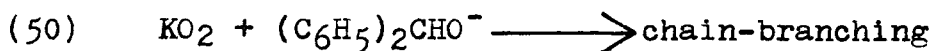
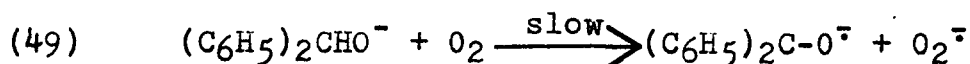
ⁱ0.40 g. (5.6 mmoles) KO₂ isolated by filtration.

chain-branching from reactions of potassium superoxide.

Chain-branching reactions of the following type are possible.



At low concentrations of base where the autocatalysis is most pronounced and the product mainly potassium peroxide, the oxidation appears to be best explained by the following sequence of reactions.



The oxidation of benzpinacol in basic solution yields benzophenone in high yield with a stoichiometry between 1 and 2 moles oxygen per mole of benzpinacol. The oxygen stoichiometry was again dependent upon the concentration of potassium t-butoxide and potassium superoxide was a product at the higher concentrations of base (Table 4). The ketyl of benzophenone is probably an intermediate and the blue color of this radical was actually observed in the oxidation of benzpinacol in DMSO (80%)-t-butyl alcohol (20%) solution. The fact that 1,1,2-triphenylethanediole oxidizes faster than benzpinacol is probably due to the greater reactivity of $\text{C}_6\text{H}_5\text{CHO}^\cdot$ produced from the former.

Table 4. Oxidation of pinacols

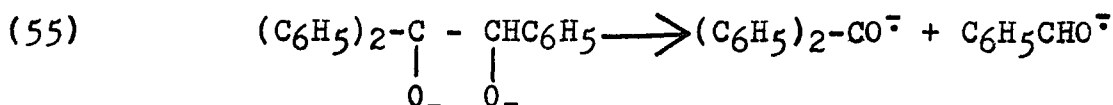
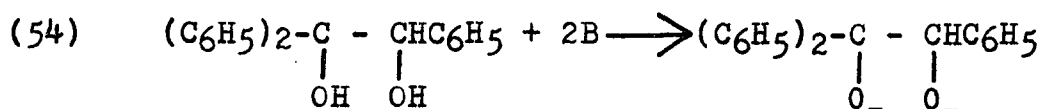
Pinacol ^b	Conc. KOC(CH ₃) ₃ moles/l.	Solvent	moles oxygen ^a mole pinacol	Rate ^c	Products
Benzpinacol	0.18	<u>t</u> -BuOH	1.04	0.16	K ₂ O ₂ , (C ₆ H ₅) ₂ CO
Benzpinacol	.36	<u>t</u> -BuOH	1.34	.32	K ₂ O ₂ , KO ₂ , (C ₆ H ₅) ₂ CO
Benzpinacol	.18	DMSO(80%)- <u>t</u> -BuOH(20%)	1.50	.23	K ₂ O ₂ , KO ₂ , (C ₆ H ₅) ₂ CO, (C ₆ H ₅) ₂ C(OH)CH ₂ - SOCH ₃
1,2-Diphenyl- ethanediol	.18	DMSO(80%)- <u>t</u> -BuOH(20%)	2.20	.10	(C ₆ H ₅) ₂ C(OH)CO ₂ H
1,1,2-Triphenyl- ethanediol	.18	DMSO(80%)- <u>t</u> -BuOH(20%)	2.20 ^d	.93	KO ₂ , K ₂ O ₂ , C ₆ H ₅ CO ₂ H, (C ₆ H ₅) ₂ CO, (C ₆ H ₅) ₂ C(OH)CH ₂ SOCH ₃

^aMaximum oxygen absorption, 300 min.

^b0.06 molar.

^cMoles oxygen per mole of pinacol per min.

^d55 min. for complete oxidation.



The 1,2-diphenylethanedione produces benzil as a primary product of the oxidation. This then rearranges in the presence of base to give benzilic acid (113).

Pertinent rate data for the oxidation of 9-fluorenone and xanthone are summarized in Table 5. The catalysis of the oxidation of xanthone by nitroaromatics (Figure 5) and the pronounced effect of solvents on the rates of oxidation of xanthone and fluorenone in the presence of potassium t-butoxide (Table 5) are in accord with a reaction involving initial ionization to a carbanion or dianion.

Consistent with the above conclusion is the observation that the ketyl of fluorenone is formed in nearly quantitative yield from a mixture of fluorenone and fluorenone in t-butyl alcohol, pyridine, or DMSO solutions in the presence of excess potassium t-butoxide. Similarly, the ketyl is readily prepared in these solvents by the reaction of a deficient quantity of oxygen with fluorenone in the presence of potassium t-butoxide or by the action of bases on the pinacol. The ketyl of xanthone is readily prepared in pyridine or DMSO (80%)-t-butyl alcohol (20%) solutions in the presence of

Table 5. Oxidation of fluorenone and xanthone

Substrate, moles/l.	Base, ^a moles/l.	Added substrate ^b	Initial rate		
			<u>t</u> -BuOH	Pyridine(80%)- <u>t</u> -BuOH(20%)	DMSO(80%)- <u>t</u> -BuOH(20%)
Xanthone, 0.12	0.36		0.10 ^c		
Xanthone, 0.06	.18		.06 ^c	0.15	0.50
Fluorenone, 0.12	.36		.25 ^c		
Fluorenone, 0.06	.18		.28	1.1	1.9
9-Deuterio- fluorenone, 0.06	.18				1.8
7-Acenaphthone, 0.06	.18			1.5	
Xanthone, 0.06	.18 ^d				.70 ^c
Xanthone, 0.06	.18 ^e				.90 ^c
Xanthone, 0.06	.18 ^f				.45
Xanthone, 0.10	.22			.15	
Xanthone, 0.10	.22	C ₆ H ₅ NO ₂		.30	
Xanthone, 0.10	.22	p-ClC ₆ H ₄ NO ₂		.35	
Xanthone, 0.10	.22	p-BrC ₆ H ₄ NO ₂		.40	
Xanthone, 0.10	.22	p-CN C ₆ H ₄ NO ₂		1.0	
Xanthone, 0.10	.22	4-nitropyridine- N-oxide		1.2	

^aPotassium t-butoxide unless otherwise specified.

^b0.005 M.

^cHeterogeneous.

^dLithium t-butoxide.

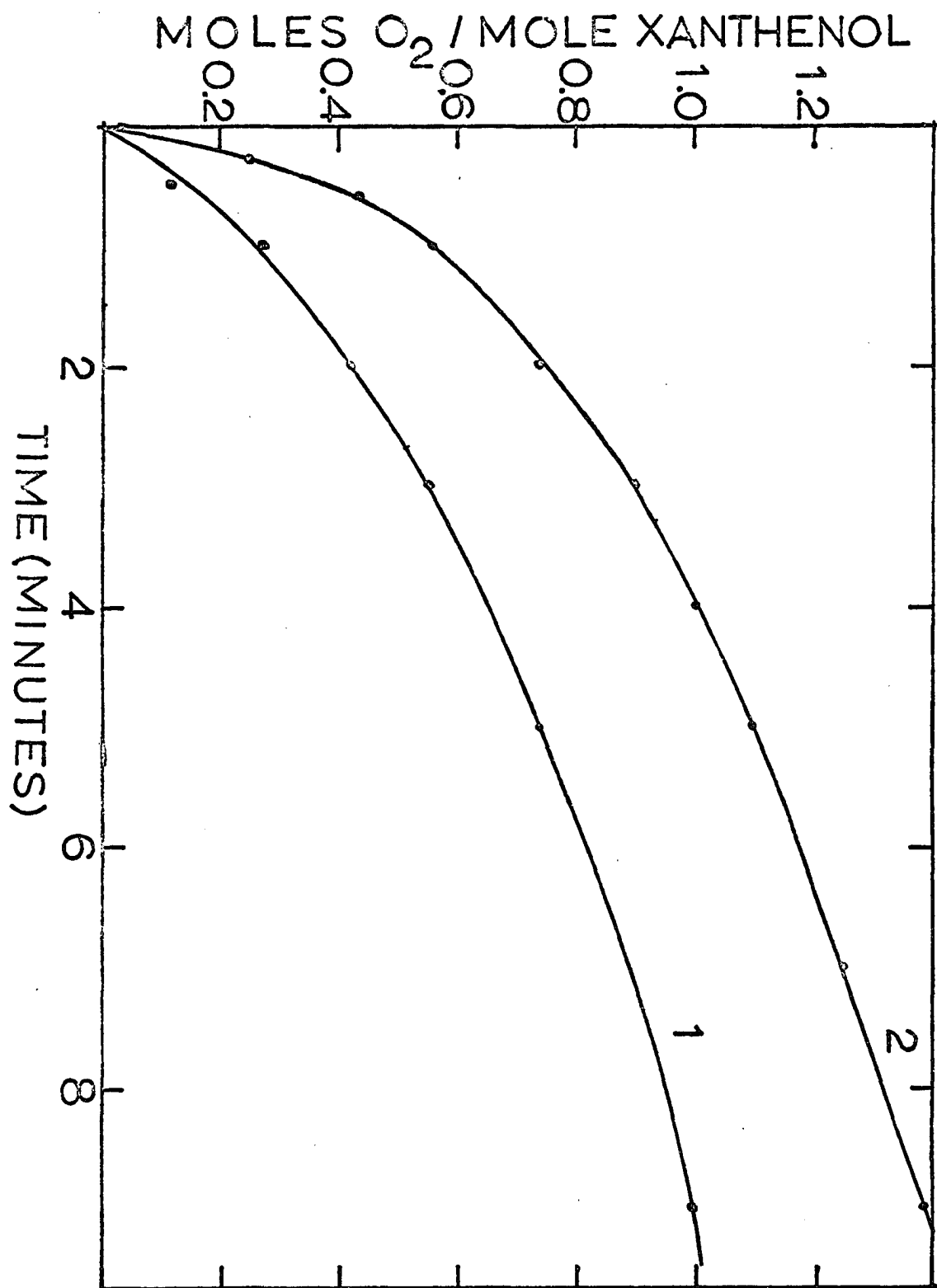
^eSodium t-butoxide.

^fRubidium t-butoxide.

Figure. 5. Oxidation of 0.12 M. xanthenol in pyridine(80%)-t-butyl alcohol(20%) containing 0.36 M. potassium t-butoxide

Curve 1. No additive

Curve 2. 0.005 M. p-cyanonitrobenzene



potassium t-butoxide by the oxidation of xanthenol or by the reaction of xanthenol with xanthone.*

Table 6 summarizes the stoichiometry and yield of products in the oxidation of fluorenol and xanthenol in basic solutions. Table 6 indicates that in the presence of lithium alkoxides the reaction proceeds to give only lithium peroxide but in the presence of the other alkali cations, and particularly potassium and rubidium, the superoxide is a major product. In the oxidation summarized in line 5 of Table 6, 0.45 g. of potassium superoxide was recovered by filtration followed by thorough washing with the reaction solvent. Analysis by oxygen evolution indicated potassium superoxide with a purity of 99%. Thus of the total 5.55 mmoles of oxygen absorbed, 5 mmoles were recovered in the form of potassium superoxide. The oxidation of xanthenol in the presence of rubidium t-butoxide absorbed 1.92 mmoles of oxygen per mole of alcohol to yield an inorganic peroxidic precipitate which hydrolyzed to rubidium hydroxide. Titration by acid indicated a composition of $\text{RbO}_{1.89}$ for the initial precipitate. The stabilities of the alkali metal superoxides are $\text{Rb, K} > \text{Na} > \text{Li}$ (114). The tendency to form the superoxide in the oxidation of fluorenol or xanthenol apparently follows the stability of

*Private communication from G. A. Russell, E. G. Janzen, and E. T. Strom, Ames, Iowa. 1964.

Table 6. Products of oxidation of fluorenol and xanthenol^a

Substrate (3 mmoles)	Solvent ^b	Base (9 mmoles)	Oxygen absorbed (min.) ^c	Products, %
Xanthenol	<u>t</u> -BuOH	KOC(CH ₃) ₃	3.2(42)	Xanthone, 99
Fluorenol	<u>t</u> -BuOH	KOC(CH ₃) ₃	3.9(42)	Fluorenone, 81
Xanthenol	Py	KOC(CH ₃) ₃	5.7(62)	
Fluorenol	Py	KOC(CH ₃) ₃	6.3(80)	
Xanthenol	DMSO	KOC(CH ₃) ₃	5.55(27)	Xanthone, 89
Fluorenol	DMSO	KOC(CH ₃) ₃	4.2(35)	9-(Methylsul- finylmethyl)9- hydroxyfluorene, 72
Xanthenol	DMSO	LiOC(CH ₃) ₃	3.0(12)	Xanthone, 87
Fluorenol	DMSO	LiOC(CH ₃) ₃	2.9(3)	Fluorenone, 71
Xanthenol	DMSO	RbOC(CH ₃) ₃	5.8(43)	Xanthone, 97
Fluorenol	DMSO	RbOC(CH ₃) ₃	4.3(20)	
Xanthenol	Py	RbOC(CH ₃) ₃	5.1(129)	Xanthone, 96
Fluorenol	Py	RbOC(CH ₃) ₃	4.3(8)	Fluorenone, 71
Xanthenol	DMSO	NaOC(CH ₃) ₃	4.1(11)	Xanthone, 95
7-Acenapthenol	DMSO	KOC(CH ₃) ₃	8.0(60)	1,8-Naphthalic anhydride, 22

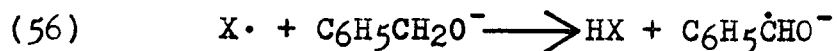
^a50 ml. of solvent except for t-butyl alcohol where 25 ml. was employed.

^bDMSO = DMSO(80%)-t-butyl alcohol(20%), Py = pyridine (80%)-t-butyl alcohol(20%).

^cFor complete oxidation.

the superoxide. The data of Table 6 indicate that at short reaction periods the ratio of inorganic peroxide to superoxide depends on the structure of the alcohol being oxidized. Since this is the case, the mechanism for superoxide formation cannot be simply that of oxidation of the peroxide.

The rates of oxidation in basic solution of a number of benzyl alcohols are summarized in Table 7. Benzoic acids were the major reaction products and a stoichiometry of between 2 and 3 moles of oxygen per mole of benzyl alcohol was observed. The oxidations of benzyl alcohols show the same characteristics as the oxidation of benzhydrol in basic solution. The rates are not particularly sensitive to solvents, a large isotope effect is observed in DMSO (80%)-*t*-butyl alcohol solution, the reaction displays autocatalysis, and 5 mole % of nitrobenzene, *p*-bromonitrobenzene, *p*-cyanonitrobenzene, or 4-nitropyridine-*N*-oxide accelerates the oxidation of *p*-bromobenzyl alcohol in pyridine (80%)-*t*-butyl alcohol (20%) by no more than 20%. Thus, the reaction appears to involve as a major initiation and propagation reaction the attack of oxygen, superoxide ion, or a peroxy radical on the α -hydrogen atom of the benzyloxy anion.



The oxidation of substituted benzyl alcohols also follows a Hammett rho-sigma relationship and a value of $\rho = 0.76$ was observed. However the oxidation of *p*-nitrobenzyl alcohol

Table 7. Rates of oxidation of benzyl alcohols^a

Alcohol	Solvent		
	DMSO(80%)- <u>t</u> -BuOH(20%)	Pyridine(80%)- <u>t</u> -BuOH(20%)	<u>t</u> -Butyl alcohol
Benzyl alcohol	0.015		0.009 ^b
<u>p</u> -Anisyl alcohol	.012		
<u>p</u> -Bromobenzyl alcohol	.022	0.070	
<u>m</u> -Nitrobenzyl alcohol	.060		
<u>p</u> -Nitrobenzyl alcohol	.850		.032 ^c
α, α -Dideuteriobenzyl alcohol	.0027 ^d		
Benzaldehyde		.01 ^e	
<u>p</u> -Nitrobenzaldehyde		1.1	
1-Phenylethanol	.008		
1-Phenylpropanol	.006		
1,2-Diphenylethanol	.005		
2,2-Dimethyl-1-phenyl propanol	.003		

^aUnless otherwise specified 0.06 M. in alcohol, 0.18 M. in potassium t-butoxide.

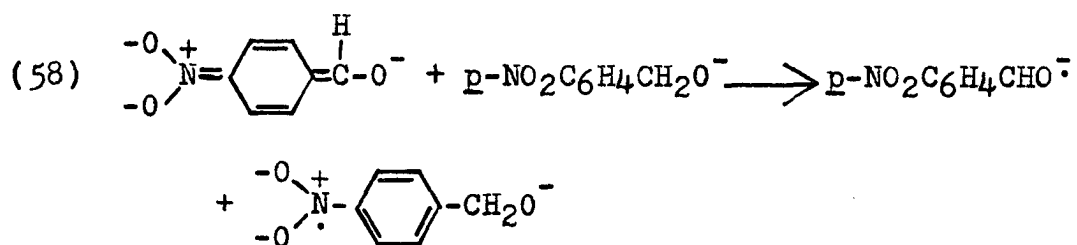
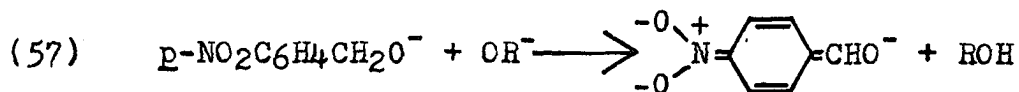
^b0.12 M. alcohol, 0.39 M. potassium t-butoxide.

^c0.17 M. alcohol, 0.34 M. potassium t-butoxide.

^dRate corrected for presence of 18% benzyl alcohol.

^e0.1 M. aldehyde, 0.22 M. potassium t-butoxide.

is an exception and probably proceeds via a carbanion intermediate since in the absence of oxygen, electron transfer to give the nitroaromatic radical-anion is observed (50).



In the presence of oxygen the following reactions could take place.

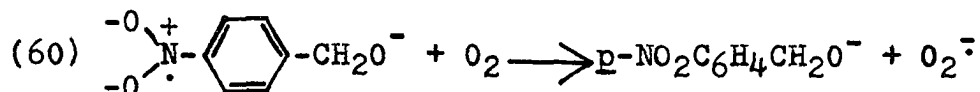
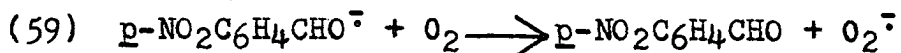
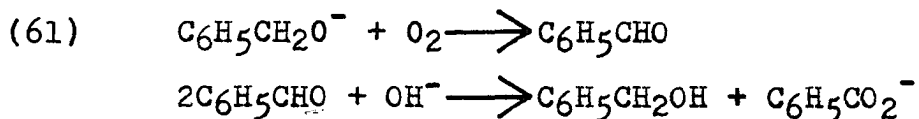


Table 7 shows that the oxidation of benzyl alcohols and benzaldehydes occur at roughly the same rate in basic systems. Thus, the formation of benzoic acids may involve benzaldehydes which undergo the Cannizzaro reaction.



Alternately, the initially formed aldehydes may form an adduct with the base which is readily attacked by oxygen or peroxy radicals to give a ketyl type intermediate.

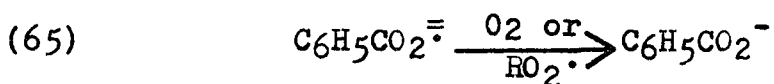
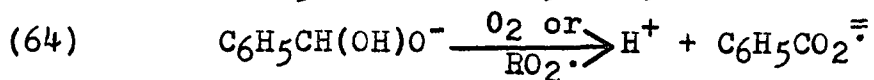
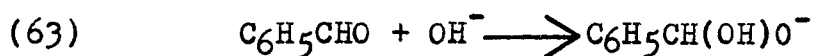


Table 7 shows that in the oxidation of a series of α -substituted benzyl alcohols ($\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{R}$) the rate of oxidation decreases with an increase in the size of the R group. Thus the rate given in a decreasing order for a number of groups is $\text{H} > \text{methyl} > \text{ethyl} > \text{benzyl} > \text{t-butyl}$. This reflects a steric hindrance to attack on the α -hydrogen atom (Reaction 56) as well as a change in the ease of ionization to the benzyloxy anion.

A radical-chain mechanism involving electron transfer reactions appears to present the best rationalization of the observations made in the study of the oxidations of aromatic alcohols. Under the reaction conditions employed it has been possible to discern two general courses for the oxidation of benzyl alcohols or diaryl-carbinols in basic solution. For benzhydrol and most benzyl alcohols the oxidation involves hydrogen atom abstraction from the alkoxide anion derived from the alcohol. For the more acidic fluorenol or xanthenol the oxidation appears to involve electron transfer from a carbanion or dianion intermediate to the attacking radicals. By choice of solvent and base it should be possible to switch from one mechanism to another with a given alcohol or to

obtain situations wherein both alkoxide and carbanion intermediates are involved in the oxidation sequence. Such a situation may well be involved in the oxidation of xanthenol in t-butyl alcohol containing potassium t-butoxide.

The oxidations involving carbanion intermediates are readily catalyzed by reagents capable of one electron oxidation whereas the oxidations involving only alkoxide ions as intermediates are susceptible to inhibition by reagents which destroy intermediate chain-branching peroxides.

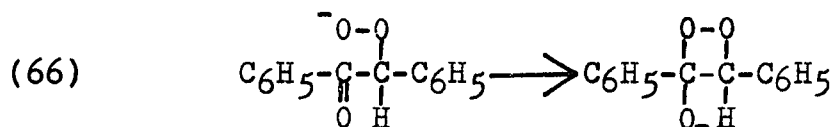
Both reactions, as well as the oxidations of benzpinacols, involve ketyl radical-anions as intermediates which in the presence of excess oxygen yield both potassium superoxide and peroxide. The stoichiometry of the reaction in the solvents employed is complicated by the stabilization of potassium superoxide in the form of an ill-defined complex with potassium t-butoxide, and by a slow, apparently heterogeneous, oxidation of potassium peroxide to the superoxide.

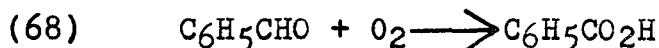
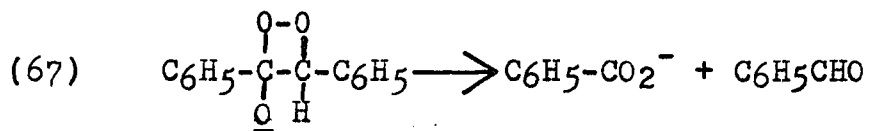
The mechanism of electron transfer from the ketyl radical-anion to molecular oxygen has not been defined. An intermediate of the type, $\text{Ar}_2\text{C}(\text{O}^-)\text{OO}\cdot$ may well be involved. However, no such evidence is known which requires this intermediate and until such evidence is presented the preferred mechanism is the transfer of an electron from the ketyl to molecular oxygen as a one-step process involving only a collisional complex.

The oxidation of benzyl alcohols or diarylcarbinols in the presence of the alkali metal *t*-butoxides in *t*-butyl alcohol, pyridine, or DMSO solutions represents not only a convenient method of preparation of benzoic acids and diaryl ketones, or their DMSO adducts, but is also a convenient method of preparing the superoxides of potassium, cesium, and rubidium in a pure form.

The autoxidation of benzoin in basic solution proceeds cleanly with the absorption of one mole of oxygen per mole of benzoin (115, 116). This reaction is commonly presumed to produce benzil (117). However, Weissberger *et al.* reported that the oxidation in ethanol containing potassium hydroxide yields 37% benzil and 64% benzoic acid (115). Weissberger later reported (116) that initially formed benzil is converted to benzoic acid if hydrogen peroxide is not carefully removed.

In *t*-butyl alcohol containing potassium *t*-butoxide Doering and Haines found that both desoxybenzoin and benzoin are readily converted to benzoic and benzylic acids when the basic solutions are shaken in oxygen and acidified as soon as the oxygen absorption ceases (83). They explained the formation of benzoic acid from desoxybenzoin as being due to the following reactions.





However, under the conditions stated in Table 7, benzaldehyde is not oxidized rapidly enough to account for the formation of benzoic acid.

The fact that hydrobenzoin and desoxybenzoin are oxidized under the reaction conditions to give the same mixture of benzoic and benzilic acids whereas the oxidation of benzoin produces considerably more benzoic acid is puzzling since it is difficult to visualize the oxidation of the diol or desoxybenzoin not involving intermediates common to the oxidation of benzoin. Pertinent rate data and yield data are given in Table 8 which indicates that the oxidation of benzoin is considerably more rapid than the oxidation of desoxybenzoin or hydrobenzoin. The rapid oxidation of benzoin does not produce potassium superoxide an observation consistent with a peroxy radical oxidation mechanism. The absence of significant amounts of benzoic acid in the oxidation of hydrobenzoin or desoxybenzoin suggests an intermediate of the type

$\text{C}_6\text{H}_5\text{CO}\overset{\text{O}\text{O}^-}{\underset{\text{O}}{\text{C}}}\text{C}_6\text{H}_5$. This does not decompose to benzoic acid but decomposes to O_2^{-2} and benzil which subsequently rearranges

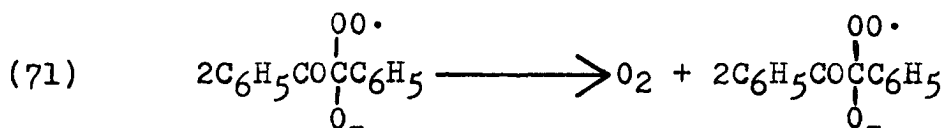
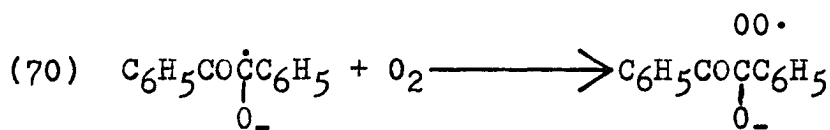
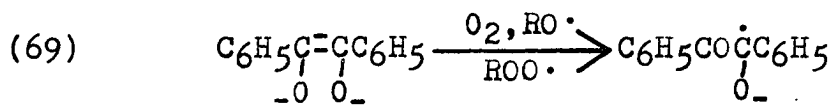
Table 8. Oxidation of benzoin, desoxybenzoin, and hydrobenzoin in DMSO(80%)-t-butyl alcohol(20%)^a

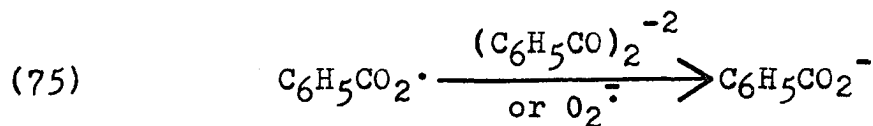
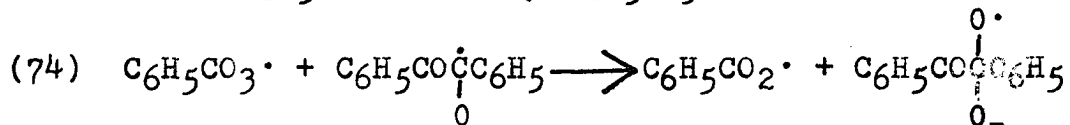
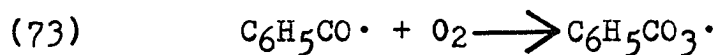
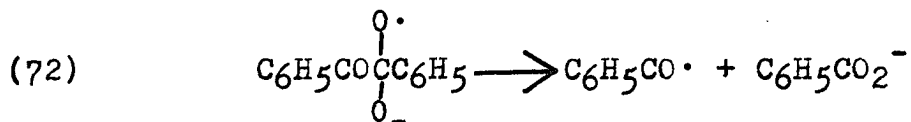
Substrate	Rate	Mole O ₂ absorbed per mole of substrate(min.)	Yield of acidic fraction, g.	Ratio, benzylic to benzoic acid ^b	Super-oxide detected
Benzoin	3.36	1.0(2)	.52	.9	no
Benzoin	3.36	1.5(720)	.55	.6	yes
Desoxybenzoin	0.84	1.4(10)	.67	7	no
Desoxybenzoin	0.84	2.0(720)	.68	7	yes
Hydrobenzoin	0.1	2.2(720)	.57	5	yes

^a3 mmoles of substrate (0.06 M.), 0.2 M. potassium t-butoxide.

^bDetermined by gas-liquid chromatography using an injector temperature of 290° and a 2 m. column of 5% SE-30 silicone grease at 165°.

to benzylic acid. For the rapid oxidation of benzoin a high radical concentration must result and the benzoic acid can occur from a radical-radical interaction.





Consistent with this suggestion is the observation of Doering and Haines (83) that the oxidation of desoxybenzoin yields benzoic acid in an exothermic reaction when desoxybenzoin in t-butyl alcohol containing potassium t-butoxide is vigorously shaken in oxygen (rapid oxidation) but yields benzylic acid when oxygen is slowly bubbled through the solution.

The reactions of desoxybenzoin with a trace of oxygen yields benzil radical anions detectable by e.s.r. spectroscopy. Figure 6 gives a typical spectrum of the radical-anion most likely formed by the following reactions.

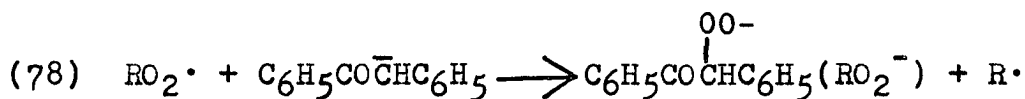
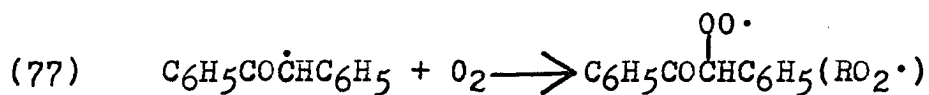
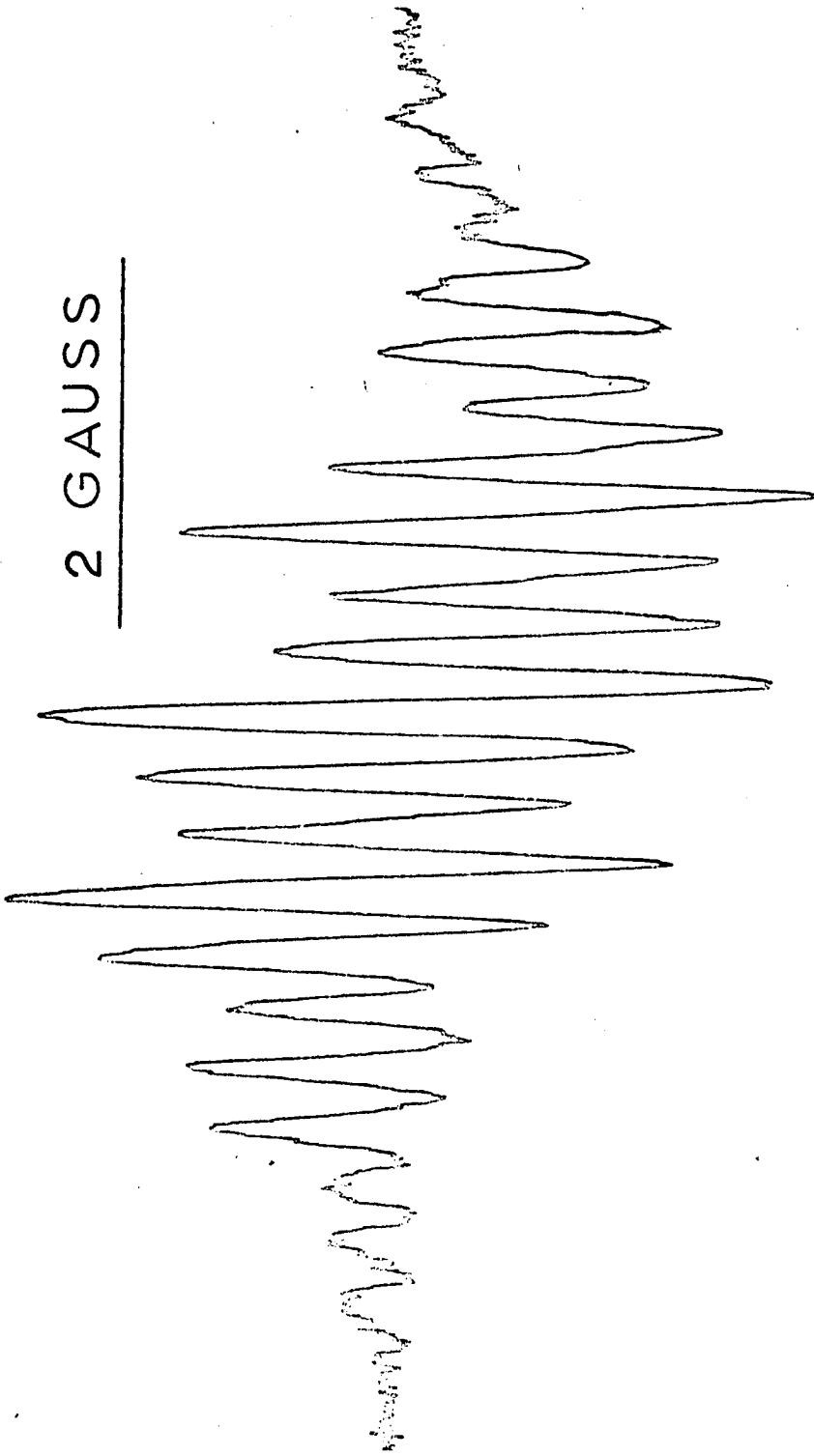
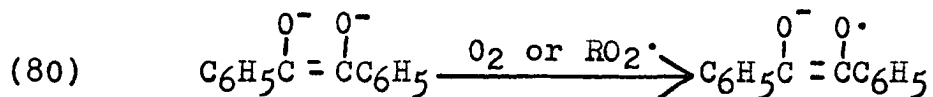
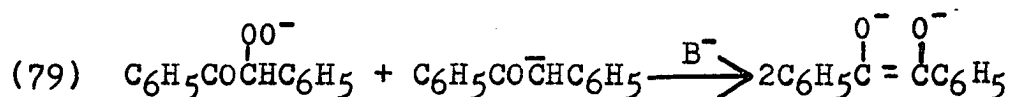


Figure 6. E.s.r. 1st. derivative spectrum of the radical-anion of benzil in DMSO(80%)-t-butyl alcohol(20%) prepared by the oxidation of benzoin

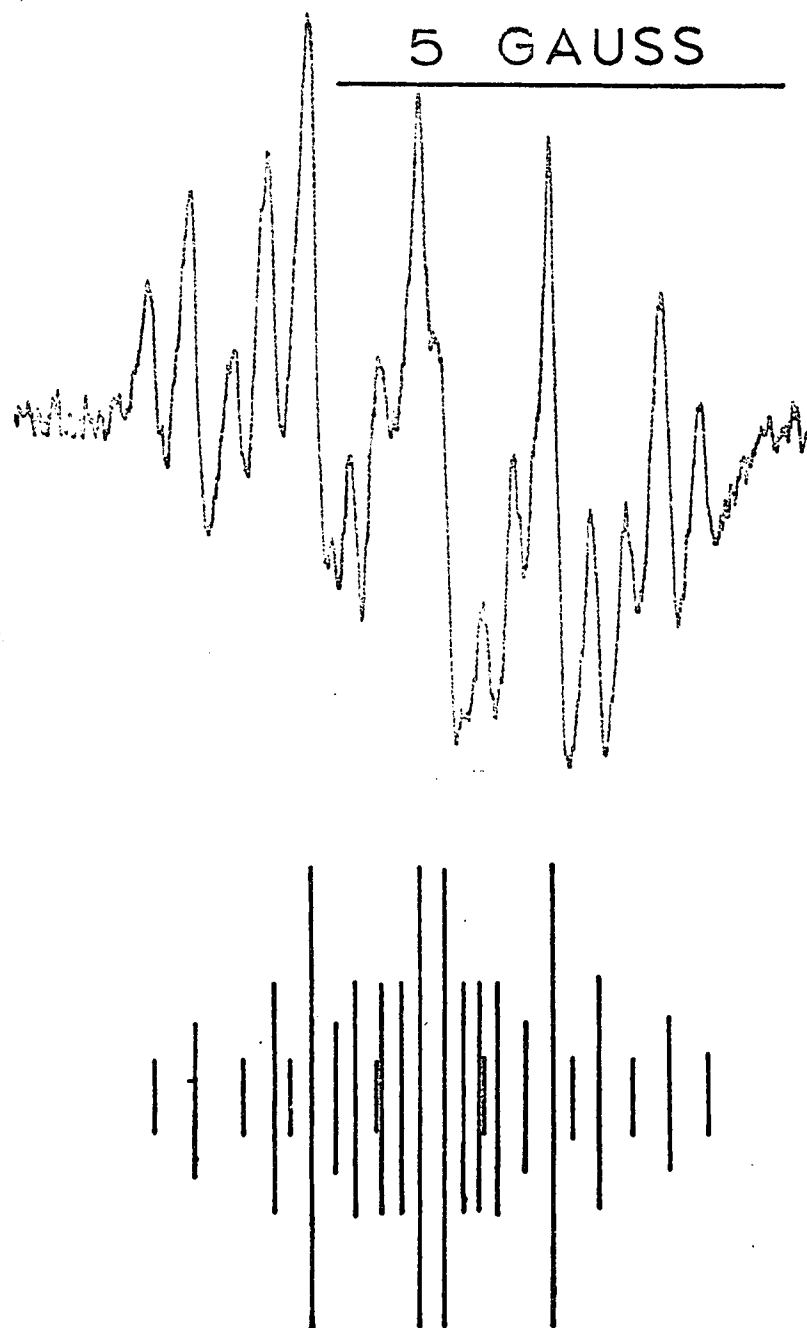




The e.s.r. spectrum of the radical-anion has also been reported in DMF (118). The formation of the benzil radical-anion also occurs readily by electron transfer between benzil and benzoin in ethanol containing alkali hydroxides (119, 120) or from benzoin and a trace of oxygen. In alcohol solutions containing alkoxide ions (but not hydroxide ion) benzoin in the absence of oxygen or added benzil gives appreciable concentrations of the benzil radical-anion.

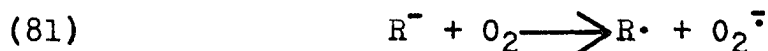
The oxidation in basic solution of acetophenone, propiophenone, or isobutyrophenone is known to produce benzoic acid as the main product (83, 121). Strong support for a radical or electron-transfer reaction mechanism in the oxidation of ketones and phenones is provided by the presence of semiquinone radical intermediates or by-products as detected by e.s.r. Thus semiquinones of the type $\text{R}-\overset{\text{O}^\cdot}{\underset{|}{\text{C}}}=\overset{\text{O}^-}{\underset{|}{\text{C}}}-\text{R}$ are observed in the oxidation of propiophenone (122), butyrophenone (122), isovalerophenone, steroidal ketones (123), and 2-decalones (123). Isovalerophenone produced the spectrum of Figure 5 upon exposure to oxygen in DMSO(80%)-*t*-butyl alcohol(20%) containing excess potassium *t*-butoxide. The calculated absorption spectrum of Figure 7 assumes $a_{\text{methine-H}} = 1.55$,

Figure 7. E.s.r. 1st. derivative spectrum ($\sim 9,500$ Mc./S.) of the radical-anion of 1-phenyl-3-methyl-1,2-butanedione in DMSO(80%)-t-butyl alcohol(20%) containing excess potassium t-butoxide; radical-anion prepared by the reaction of a trace of oxygen with isovalerophenone

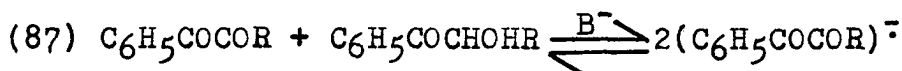
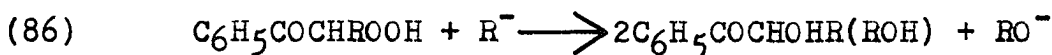
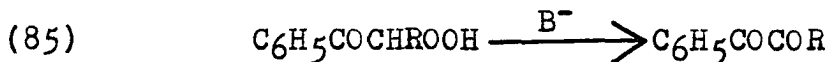
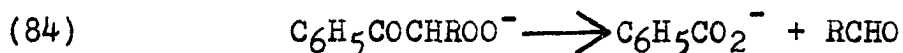
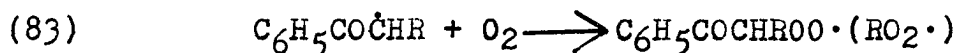
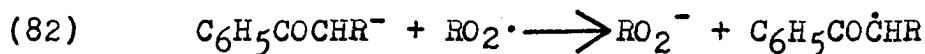


$a_{\underline{o},\underline{p}\text{-H}} = 1.30$, and $a_{\underline{m}\text{-H}} = 0.47$ gauss.

Since autocatalysis or inhibition periods are not observed in phenone oxidations, it appears that the reaction is initiated by a direct reaction between the carbanion and molecular oxygen.



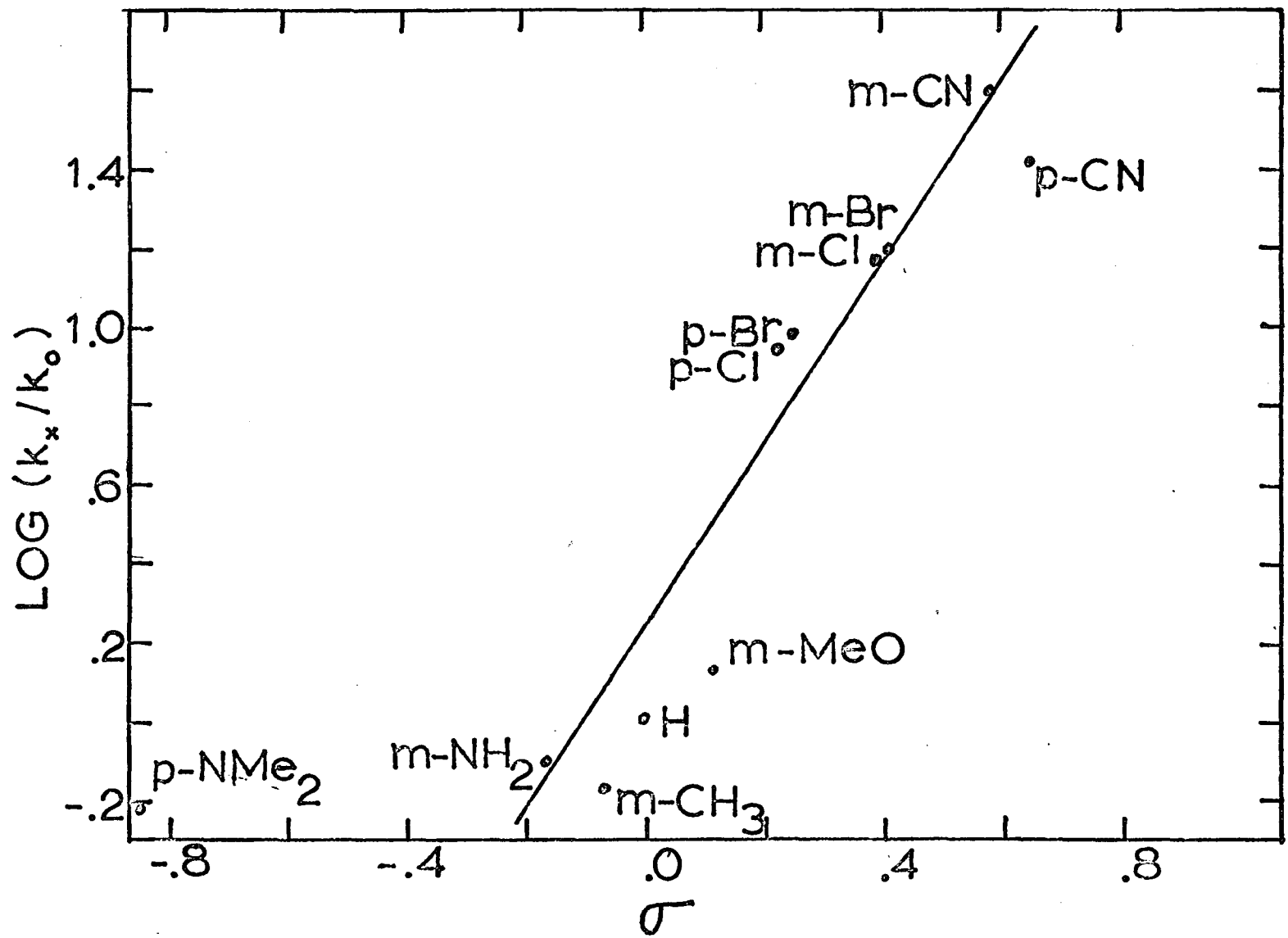
Among the possible routes to benzoic acid are the following reactions.



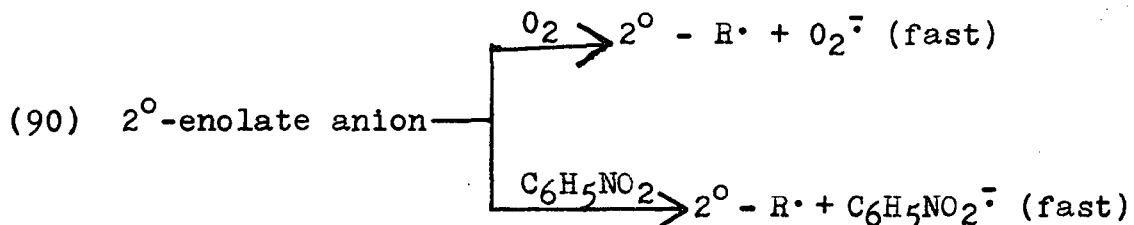
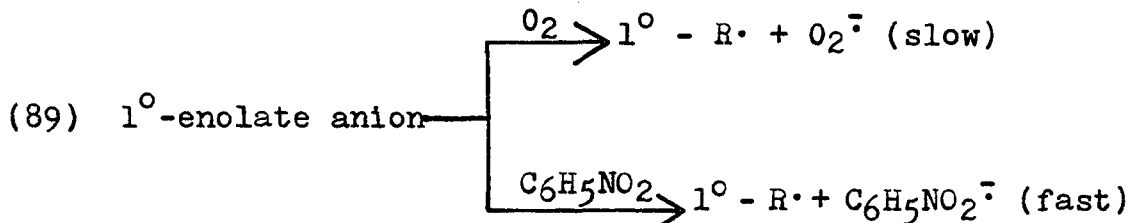
In cases where R contains an α -hydrogen atom the intermediate $\text{C}_6\text{H}_5\text{COCOR}$ can be ionized to an enolate anion and oxidized to intermediates which ultimately yield benzoic acid.

Further evidence for a free radical chain mechanism is provided by catalysis of phenone oxidations by nitroaromatics. In Figure 8 the catalytic effects of a series of substituted nitroaromatics on the oxidation of acetophenone are illustrated. The Hammett $\rho\sigma$ relationship is similar to that

Figure 8. Oxidation of 0.2 M. acetophenone in *t*-butyl alcohol containing 0.4 M. potassium *t*-butoxide and catalyzed by 0.1 M. nitrobenzenes; k_0 = rate catalyzed by nitrobenzene; k_x = rates catalyzed by substituted nitrobenzenes; $\rho = 2.3$



reported for the catalysis of the oxidation of fluorene.* In Table 9 the initial rates (by e.s.r.) of electron transfer between acetophenone and substituted nitrobenzenes are summarized together with the observed rates of the catalyzed oxidation of acetophenone. There is a good correlation between the catalytic effects in oxidation and the rates of electron transfer in the absence of oxygen. Table 10 lists the initial rates (by e.s.r.) of electron transfer between propiophenone and substituted nitrobenzenes. Nitroaromatics are, however, not as efficient as catalysts in the oxidation of propiophenone as they are for acetophenone. This probably reflects differences in the rates of oxidation of 1° and 2° enolate anions.



This is in accord with the work of Russell *et al.* who found

*Private communication from G. A. Russell and E. G. Janzen, Ames, Iowa. 1964.

Table 9. Rates of catalyzed oxidation and electron transfer of acetophenone and substituted nitroaromatics ($\text{RC}_6\text{H}_4\text{NO}_2$) in *t*-butyl alcohol^a

R	Oxidation rate, mole O_2 /mole acetophenone/min.	Electron transfer initial rate (moles/l.-min.)	Max. conc. of $\text{RC}_6\text{H}_5\text{NO}_2^-$ (moles/l.)
No catalyst	.006	.000037	.00002
<i>p</i> -(CH_3) ₂ N ^b	.012	.0013	.0016
<i>m</i> -CH ₃	.015	.0010	.0025
<i>m</i> -NH ₂	.016	.0030	.0016
H	.021		
<i>o</i> -I	.022		
<i>o</i> -Br	.025		
<i>o</i> -Cl	.026		
<i>m</i> -CH ₃ O	.029	.0055	.0061
<i>p</i> -Cl	.191	.038	.023
<i>p</i> -Br ^b	.197		
<i>m</i> -Cl	.308	.043	.023
<i>m</i> -Br	.323		
<i>p</i> -CN ^b	.454		
<i>m</i> -CN ^b	.837		

^a0.2 M. acetophenone, 0.4 M. potassium *t*-butoxide, and 0.1 M. $\text{RC}_6\text{H}_4\text{NO}_2$.

^bNot completely soluble under the reaction conditions.

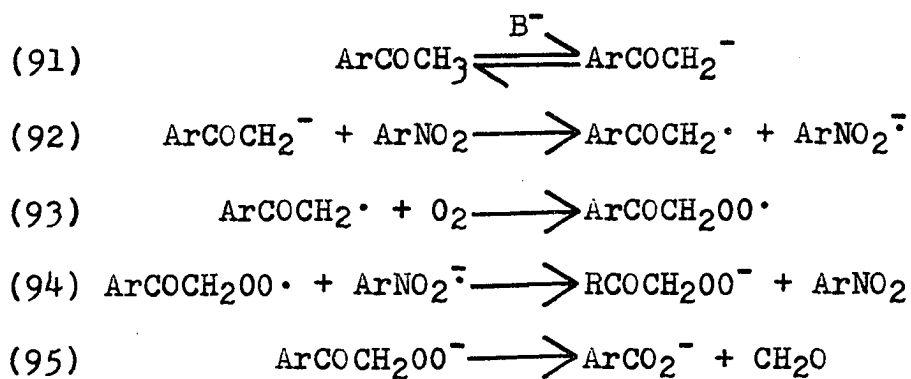
Table 10. Rates of electron transfer from propiophenone to substituted nitroaromatics ($\text{RC}_6\text{H}_4\text{NO}_2$) in DMSO(80%)-t-butyl alcohol(20%)^a

R	Electron transfer initial rate (moles/l.-min.)	Max. conc. of $\text{RC}_6\text{H}_4\text{NO}_2^-$ (moles/l.)
<u>m</u> -CH ₃	.000015	.00008
<u>m</u> -NH ₂	.000003	
H	.000041	.00009
<u>m</u> -CH ₃ O ⁻	.000063	.00018
<u>p</u> -Cl	.000030	.00012
<u>p</u> -CN	very fast	radical unstable

^a0.1 M. propiophenone, 0.2 M. potassium t-butoxide, and 0.005 M. $\text{RC}_6\text{H}_4\text{NO}_2^-$.

that the reactivity of a large number of carbanions to oxygen is $3^\circ > 2^\circ > 1^\circ$ (124).

An approximate estimate of kinetic chain length can be obtained from the data of Table 9. Thus, 0.1 M. nitrobenzene increased the initial rate of oxidation of acetophenone from 0.0012 to 0.004 moles oxygen absorbed/l.-min.; $R_{\text{O}_2} = 0.0028$. Under the reaction conditions the rate of electron transfer to nitrobenzene in the absence of oxygen was measured as 0.003 moles/l.-min. Thus, one electron transfer reaction resulted in the consumption of only one mole of oxygen. In the presence of nitrobenzene the initial oxidation appears to be best described by the following reactions.

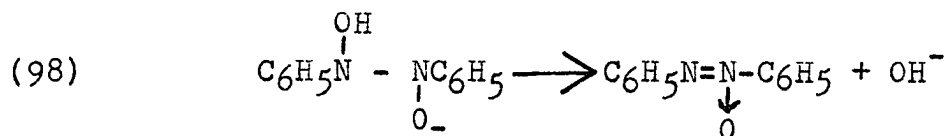
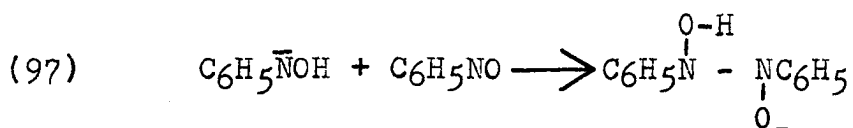
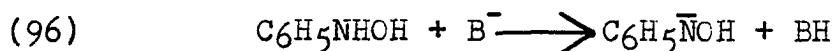


Catalysis by nitroaromatics has also been observed by Wallace et al. in the oxidation of mercaptide ions (125) and by Gersmann and Bickel in the oxidation of 2,4,6-trisubstituted phenols in basic solution (126).

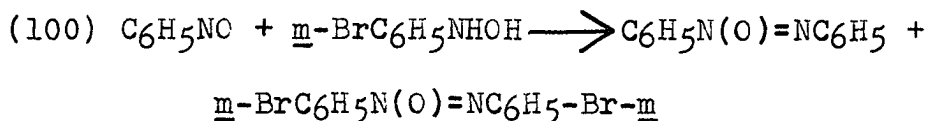
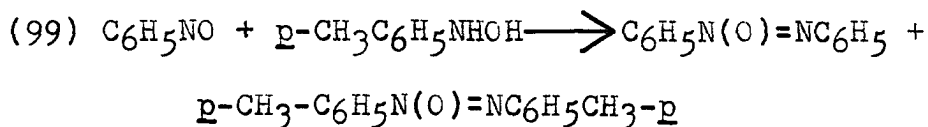
PART II. THE CONDENSATION OF NITROSOBENZENE
AND PHENYLHYDROXYLAMINE

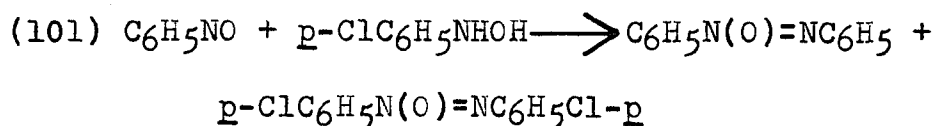
HISTORICAL

The condensation of nitrosobenzene and phenylhydroxylamine in the presence of a basic catalyst to give azoxybenzene in quantitative yield is an old well-known reaction. The mechanism previously assumed for this reaction involves anionic intermediates (117).

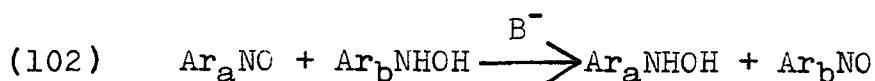


Conflicting evidence regarding the validity of this type of mechanism has existed ever since the reaction was discovered. As early as 1897 Bamberger and Renauld (127) found that reaction of nitrosobenzene with a number of substituted phenylhydroxylamines did not produce the expected condensation product but instead yielded mixtures of azoxybenzene and disubstituted azoxybenzenes.





These results were confirmed more recently (128, 129) and not only disubstituted azoxybenzenes were found but also both possible mono-substituted isomers were isolated. In the reaction of m-carboxyphenylhydroxylamine with o-nitrosotoluene all four possible products were found (128). The conclusion was made that interconversion of nitrosobenzene and phenylhydroxylamine took place prior to the condensation reaction (130).



An intermediate such as $\text{C}_6\text{H}_5\overset{\text{OH}}{\underset{|}{\text{N}}} - \overset{\text{OH}}{\underset{|}{\text{N}}}\text{C}_6\text{H}_5$ was proposed as the result of two different isotopic labeling experiments. In the first (131) nitrosobenzene was reacted with phenylhydroxylamine containing 0.56 atom % of excess O^{18} . In ethanol containing a trace of potassium hydroxide the azoxybenzene produced contained only 0.28 atom % excess O^{18} . In the second experiment (132) phenylhydroxylamine and nitrosobenzene (containing 37.2% N^{15}) were reacted for 2 minutes in ethanol containing a trace of potassium hydroxide. Upon addition of dilute sulfuric acid azoxybenzene was recovered in 92% yield. Analysis showed that one N atom contained 18.2% N^{15} and the other 19.1% N^{15} . Thus, the N^{15} originally present

in the nitrosobenzene was distributed equally between the two positions in the product.

The discovery during the course of this research of the presence of nitrosobenzene radical-anion ($C_6H_5NO^{\cdot-}$) and phenylnitroxide ($C_6H_5NHO\cdot$) in this condensation serves to explain the formation of all possible isomers of the products of crossed reactions (133). This will be discussed at greater length later in this section.

Phenylnitroxide was prepared by Buchachenko (134) by the oxidation of phenylhydroxylamine with lead dioxide. This was then converted by further oxidation to a second radical erroneously described by Baird and Thomas (135) as phenylnitroxide. Nitrosobenzene radical-anion and phenylnitroxide were also prepared by reduction of nitrosobenzene with sodium dithionate and titanous ion respectively (136). The reduction of nitrobenzene or nitrosobenzene by lithium aluminum hydride gives a mixture of phenylnitroxide and diphenylnitroxide (137).

Nitrosobenzene radical-anion and phenylnitroxide are probably intermediates in the reduction of nitrobenzene to azoxybenzene by reagents such as calcium hydride (138), or benzoin, anisoin, or furoin in alcoholic solution containing a trace of base (139), by concentrated sodium methoxide in methanol (140), by thallium metal (141), and by electrolytic reduction (142). The presence of one or both of these

radicals in reductions of nitrosobenzene to give azoxybenzene is quite probable. Nitrosobenzene can be reduced electrolytically (142, 143, 144), by potassium ethoxide in ether (145), and by potassium hydroxide in methanol or ethanol (146).

Radicals such as nitroxides or nitroso radical-anions may also be intermediates in the reduction of nitrosotri-fluoromethane to the aliphatic azoxy compound in the presence of alkaline hypophosphite (147).

Nitrosobenzene radical-anion is suggested as an intermediate in the sodium bisulfite reduction of nitrosobenzene to phenylhydroxylamine-N-sulfonic acid (148).

Aryl nitroxides were known as early as 1914 when diphenylnitroxide ($\text{Ar}_2\text{NO}\cdot$) was obtained by the oxidation of diphenylhydroxylamine with silver oxide (149). Diphenylnitroxide was prepared by reaction of diphenylhydroxylamine with di-t-butyl peroxide (150) and its e.s.r. spectrum has been carefully analyzed (150, 151).

Di-t-butylnitroxide was prepared recently (152, 153) and found to be a stable free radical existing as a red oil. This led to the preparation of other nitroxides such as phenyl-t-butylnitroxide (154). The nitroxides from 2,2,5,5-tetramethylpyrrolidines (155) and 2,2,6,6-tetramethylpiperidines (156, 157, 158) were prepared and found to be very stable. These nitroxides could undergo reactions at other positions

on the molecule without destroying the radical site (157, 158).

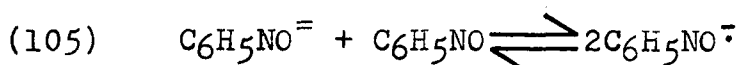
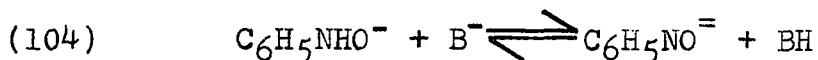
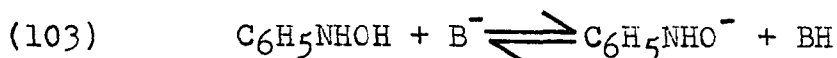
A nitroxide radical was observed by Tench and Coppens in the irradiation of o-nitrobenzaldehyde (159). On the basis of the e.s.r. spectrum they assigned the radical the structure $\underline{o}\text{-CO}_2^-\text{C}_6\text{H}_4\text{NHO}\cdot$. A very similar radical was observed in the electrolytic reduction of o-nitrobenzoic acid (160).

Radicals having a great deal of similarity to nitroxides are iminoxy radicals produced by mild oxidation of aldoximes and ketoximes (161). The iminoxy radicals exist in both syn and anti forms and e.s.r. hyperfine splitting by interaction through space was observed in iminoxy radicals such as those derived from the ketoximes of fluorenone, benzophenone, and benzil (162).

RESULTS AND DISCUSSION

The detection of free radicals derived from nitrosobenzene involved the use of two different sets of apparatus. For fast reactions the flow system illustrated in Figure 9 was employed and for the formation of radicals which were fairly stable under the reaction conditions the H-cell shown in Figure 10 was used.

Reaction of nitrosobenzene (0.005 M.) and phenylhydroxylamine (0.005 M.) in the presence of 0.05 M. potassium t-butoxide in deoxygenated DMSO (80%)-t-butyl alcohol (20%) solution at $23 \pm 1^\circ$ produces essentially a quantitative yield of nitrosobenzene radical-anions in less than 0.5 seconds. The radical-anion is probably produced by the following reactions.



Under these conditions the radical-anion decays slowly over a period of days.

In ethanol containing sodium hydroxide, nitrosobenzene and phenylhydroxylamine rapidly react to yield up to 96% of azoxybenzene. Nitrosobenzene radical-anions can be detected and identified under flow conditions but rapidly decay when the flow is stopped. Figure 11 illustrates a stopped flow

Figure 9. Flow system used for in cavity generation of short-lived radicals

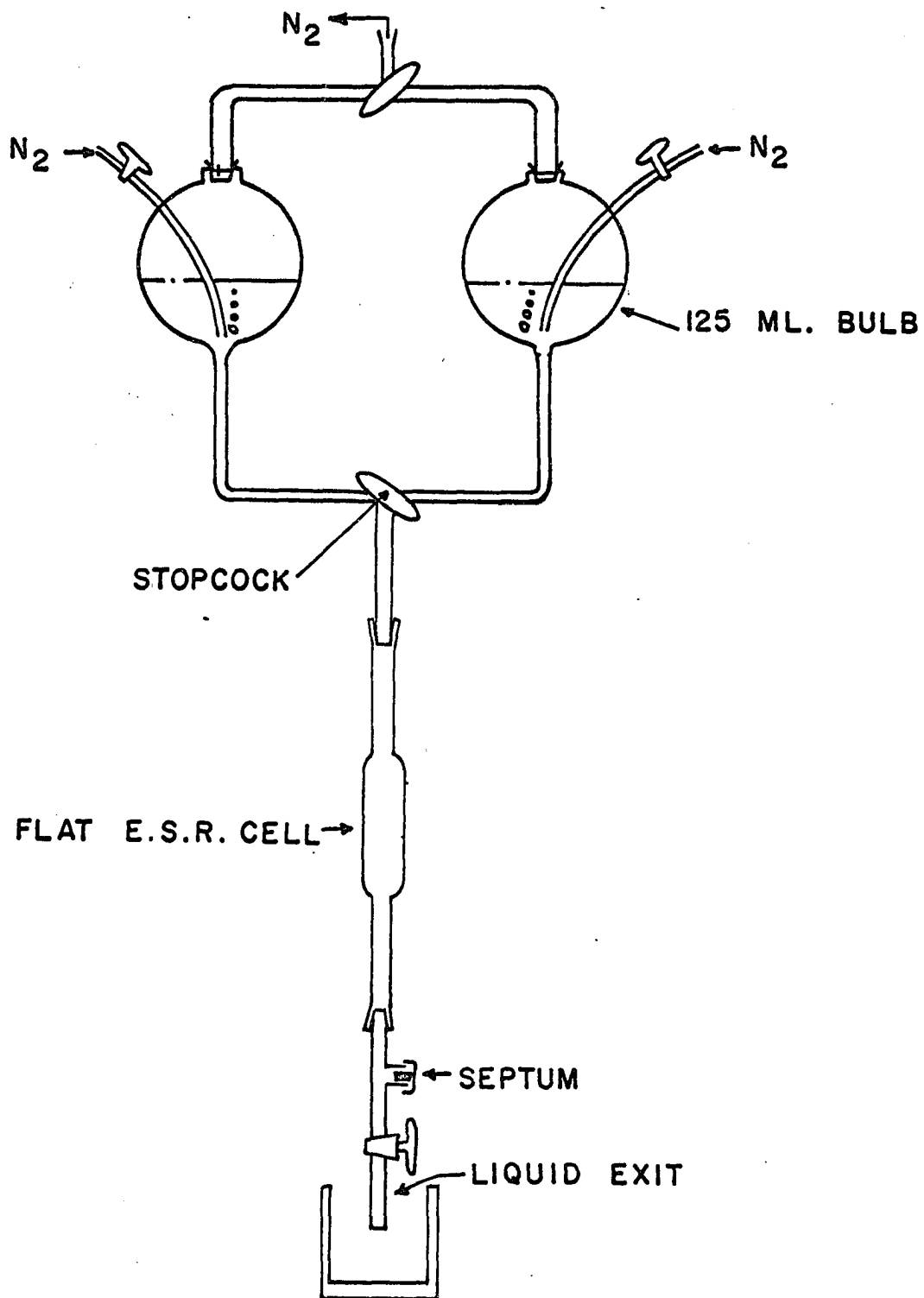


Figure 10. H-cell used for deoxygenating solutions prior to mixing and insertion into the cavity of the e.s.r. spectrometer

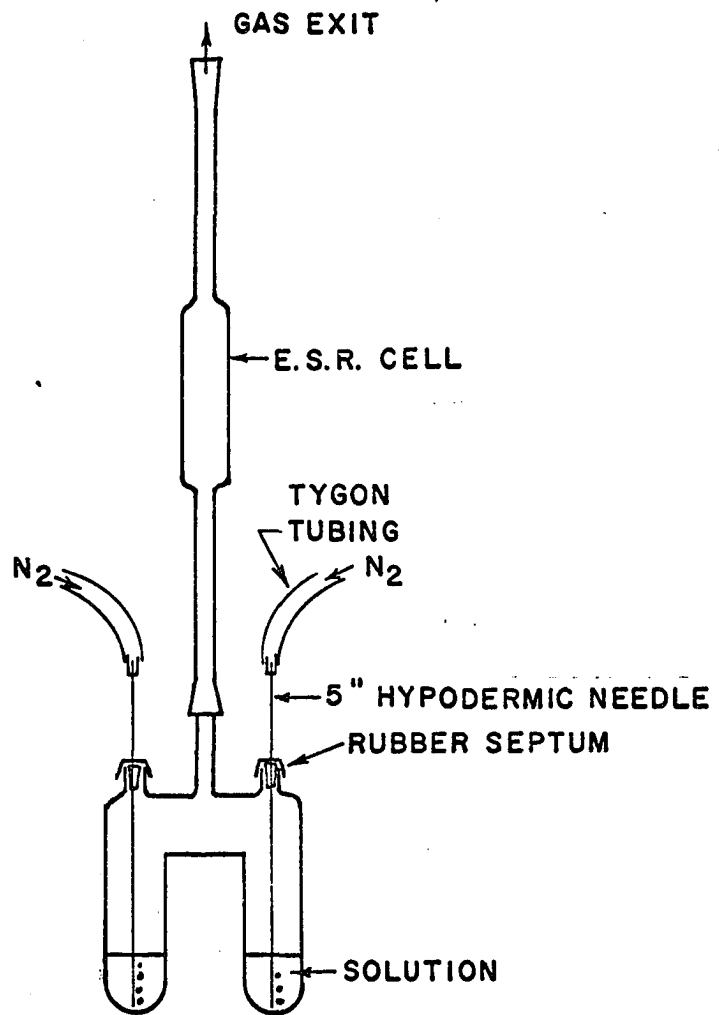
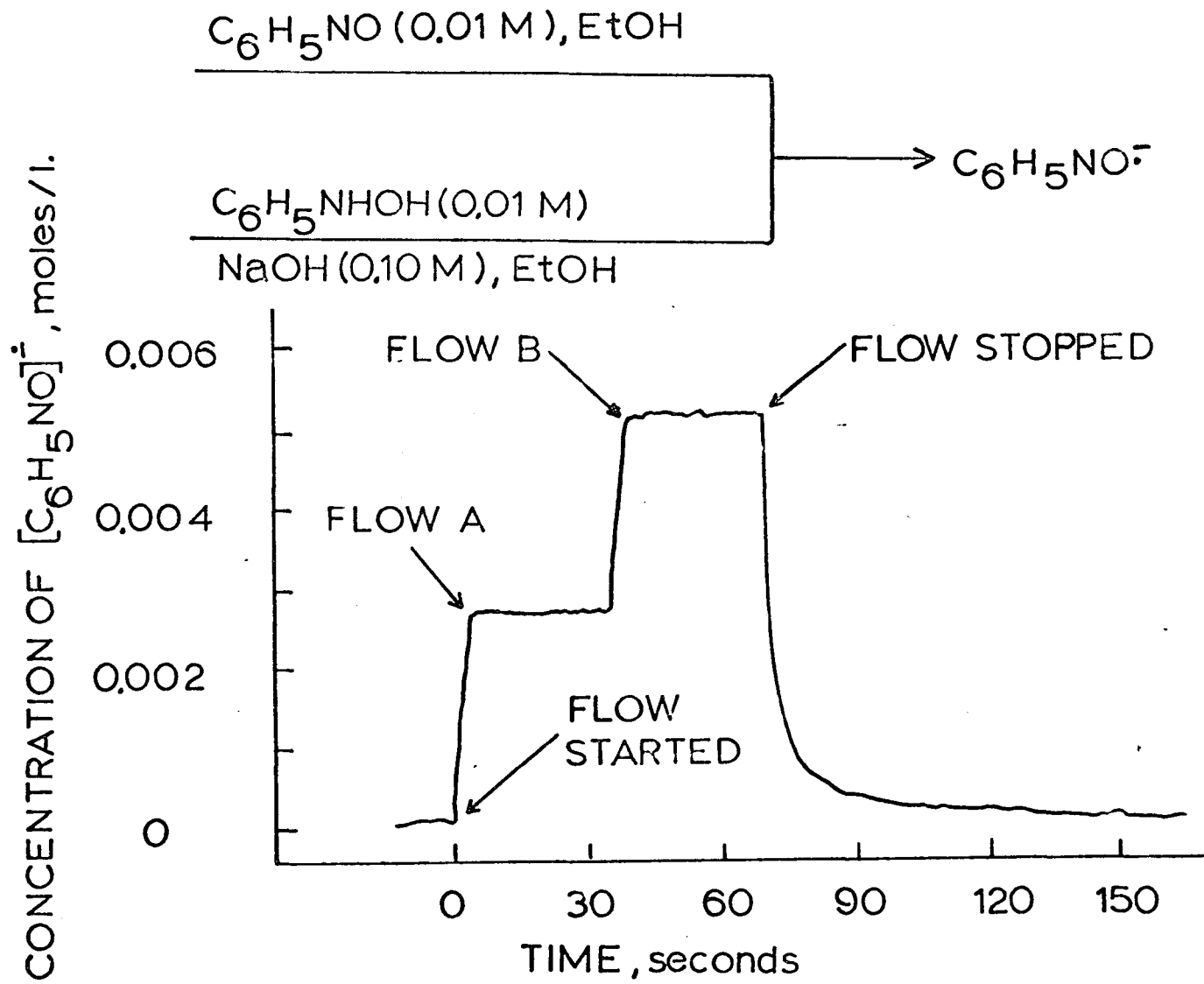
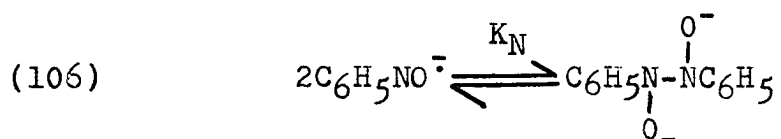


Figure 11. Intermediate detected by e.s.r. in ethanol at $23 \pm 1^\circ$ from the reaction of a solution initially 0.010 M. in nitrosobenzene with a solution initially 0.010 M. in phenylhydroxylamine and 0.10 M. in sodium hydroxide; Flow A, radical-anion detected 3 sec. after mixing; Flow B, radical-anion detected 0.5 sec. after mixing



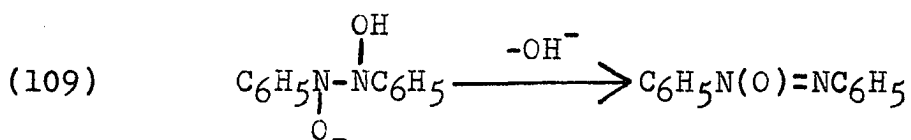
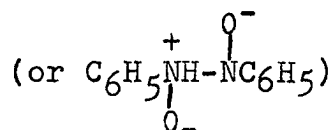
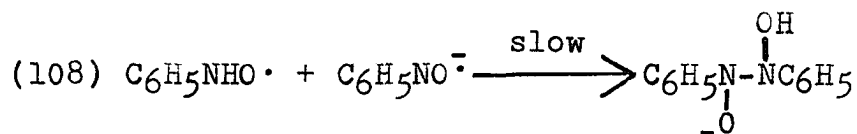
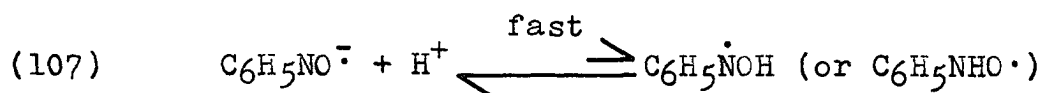
experiment of a solution 0.005 M. in nitrosobenzene, 0.005 M. in phenylhydroxylamine, and 0.05 M. in sodium hydroxide after mixing. The maximum concentration of nitrosobenzene radical-anion detected (about 0.005 M.) occurred at the fastest flow rate which represented a flow time of 0.5 seconds between mixing and detection. Under flow conditions the mixed solution underwent a blue to green to yellow color transformation in a matter of seconds, the blue and yellow representing the colors of nitrosobenzene and azoxybenzene respectively.

The decay curve for nitrosobenzene radical-anions given in Figure 11 follows 2nd-order kinetics from a nitrosobenzene radical-anion concentration of 0.005 M. to 0.00025 M. with a rate constant of 1.40×10^2 l./mole-sec. The kinetic and e.s.r. results suggest the following rapid equilibrium in the condensation reaction occurring in basic solution.

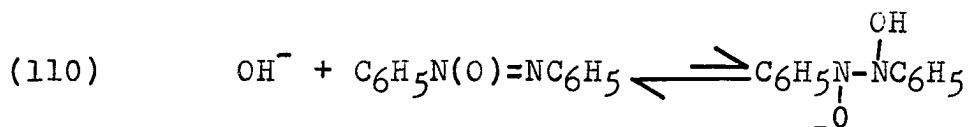


In ethanol or t-butyl alcohol the dianion apparently undergoes protonation followed by irreversible loss of hydroxide ion to yield azoxybenzene.

Another possible interpretation is that the nitrosobenzene radical-anion is protonated prior to condensation and elimination of hydroxide ion.



Apparently in DMSO (80%)-t-butyl alcohol (20%) containing potassium t-butoxide the low activity of protons and a value of K_N that greatly favors $\text{C}_6\text{H}_5\text{NO}^-$, prevents the last step of the condensation from occurring. Although no evidence could be found for the reversal of the condensation in DMSO (80%)-t-butyl alcohol (20%) at 23° , a solution of azoxybenzene (0.05 M.) in pure DMSO 50% saturated with potassium hydroxide slowly forms the nitrosobenzene radical-anion.



Exposure of such a solution to oxygen after a 3 hr. reaction period (1×10^{-3} M. nitrosobenzene radical-anion) destroyed the e.s.r. signal. After exposure to oxygen a new e.s.r. signal slowly developed which was recognized as that of nitrobenzene radical-anion.

Table 11 summarizes data regarding the formation of nitrosobenzene radical-anion under flow conditions from the reaction of nitrosobenzene and phenylhydroxylamine in various solvents containing base.

Table 11. Condensation of nitrosobenzene (0.005 M.) and phenylhydroxylamine (0.005 M.) under flow conditions in the presence of base (0.05 M.)

Solvent	Base	Radical concentration (M.)
Ethanol	NaOH	$5.0 \times 10^{-3}{}^a$
Ethanol	NaOH	$4.9 \times 10^{-3}{}^b$
<u>t</u> -Butanol	KOC(CH ₃) ₃	$10.0 \times 10^{-3}{}^c$
DMSO(80%)- <u>t</u> -butyl alcohol(20%)	KOC(CH ₃) ₃	$8.6 \times 10^{-3}{}^d$

^a0.38 seconds after mixing solutions.

^b0.48 seconds after mixing solutions.

^c0.50 seconds after mixing solutions.

^d0.60 seconds after mixing solutions.

The spectra obtained from nitrosobenzene radical-anion in DMSO (80%)-t-butyl alcohol (20%) and ethanol are illustrated by Figures 12 and 13 respectively. The analyses of these e.s.r. spectra as well as those of the radical-anions from p-deuterionitrosobenzene (Figure 14), p-chloronitrosobenzene (Figure 15), and 2,4,6-trideuterionitrosobenzene

Figure 12. 1st Derivative e.s.r. spectrum of nitrosobenzene radical-anion in DMSO(80%)-t-butyl alcohol(20%) at $23 \pm 1^\circ$; synthetic absorption spectrum based on hfsc given in Table 12; 1.60 gauss/cm.



Figure 13. 1st Derivative e.s.r. spectrum of nitrosobenzene radical-anion in ethanol at $23 \pm 1^\circ$; 2.46 gauss/cm.

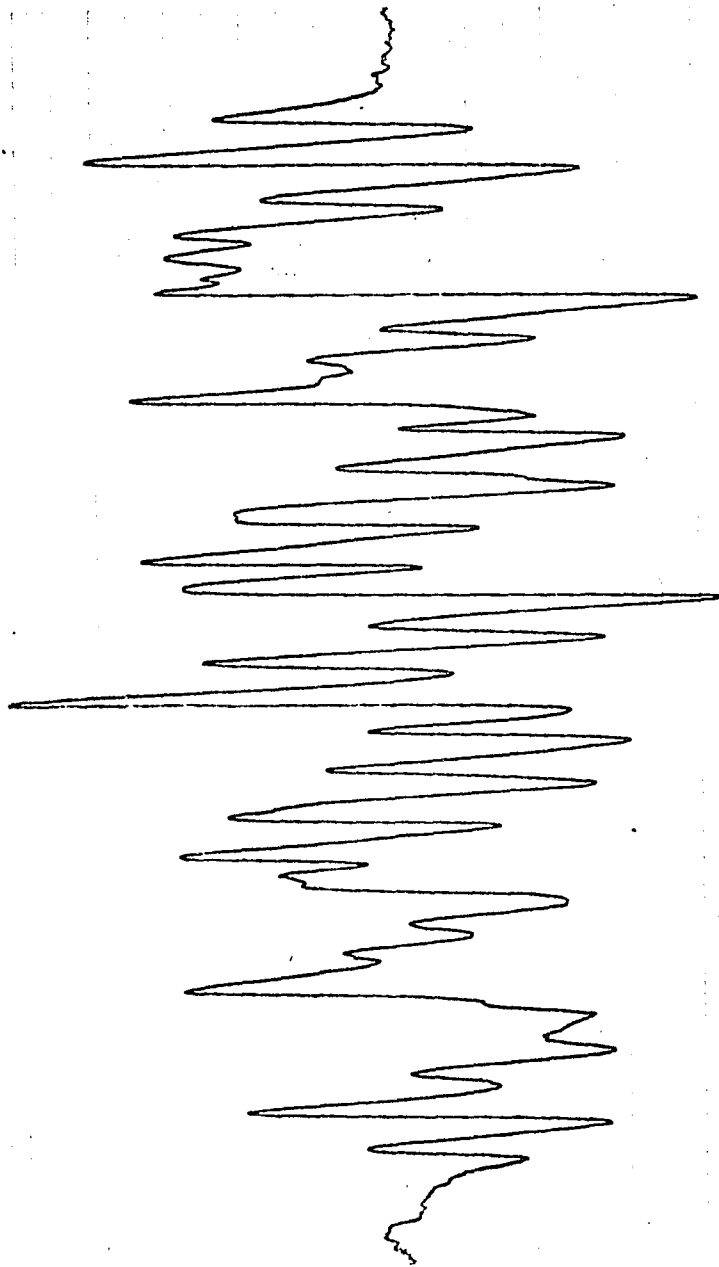


Figure 14. 1st Derivative e.s.r. spectrum of p-deuterionitrosobenzene radical-anion in DMSO(80%)-t-butyl alcohol(20%) at $23 \pm 1^\circ$; 1.31 gauss/cm.

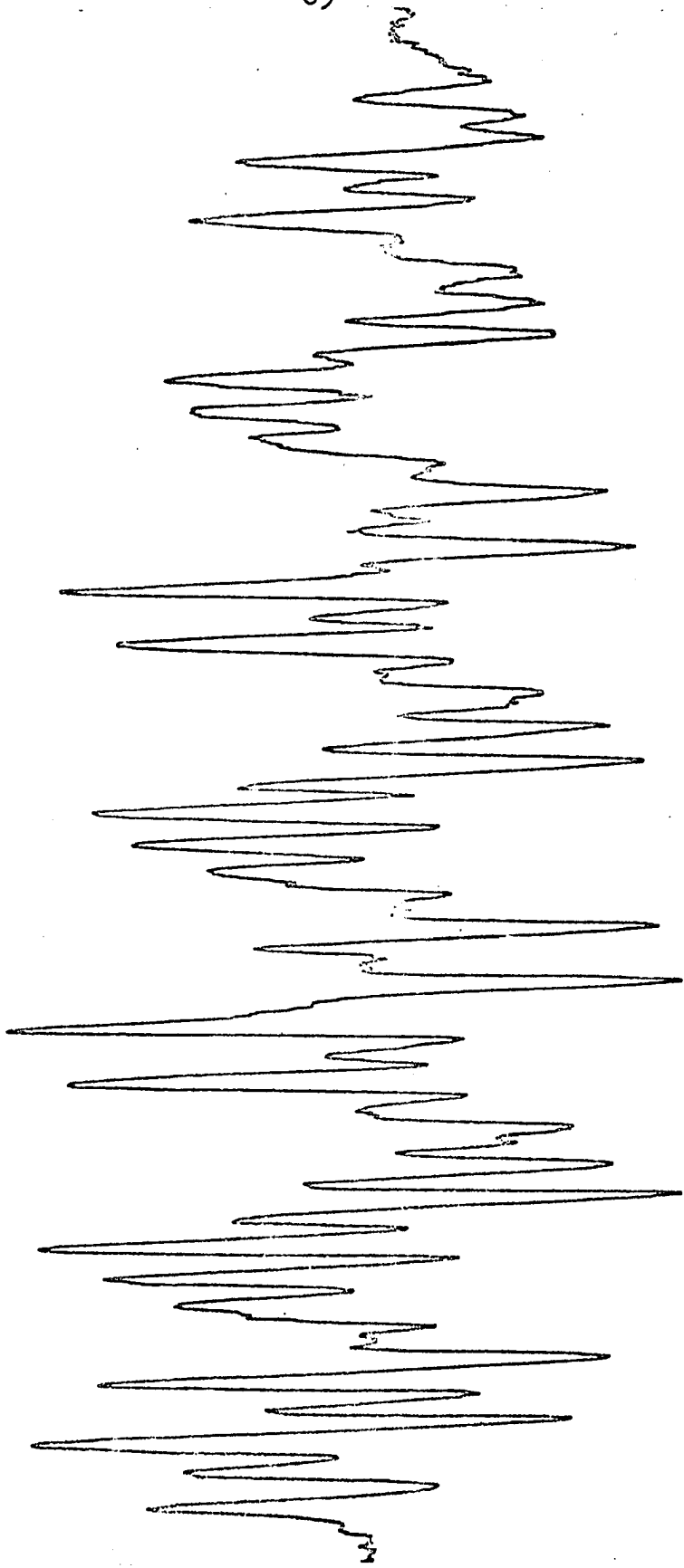


Figure 15. 1st Derivative e.s.r. spectrum of p-chloronitroso-benzene radical-anion in DMSO(80%)-t-butyl alcohol(20%) at $23 \pm 1^\circ$; synthetic absorption spectrum based on hfsc given in Table 12

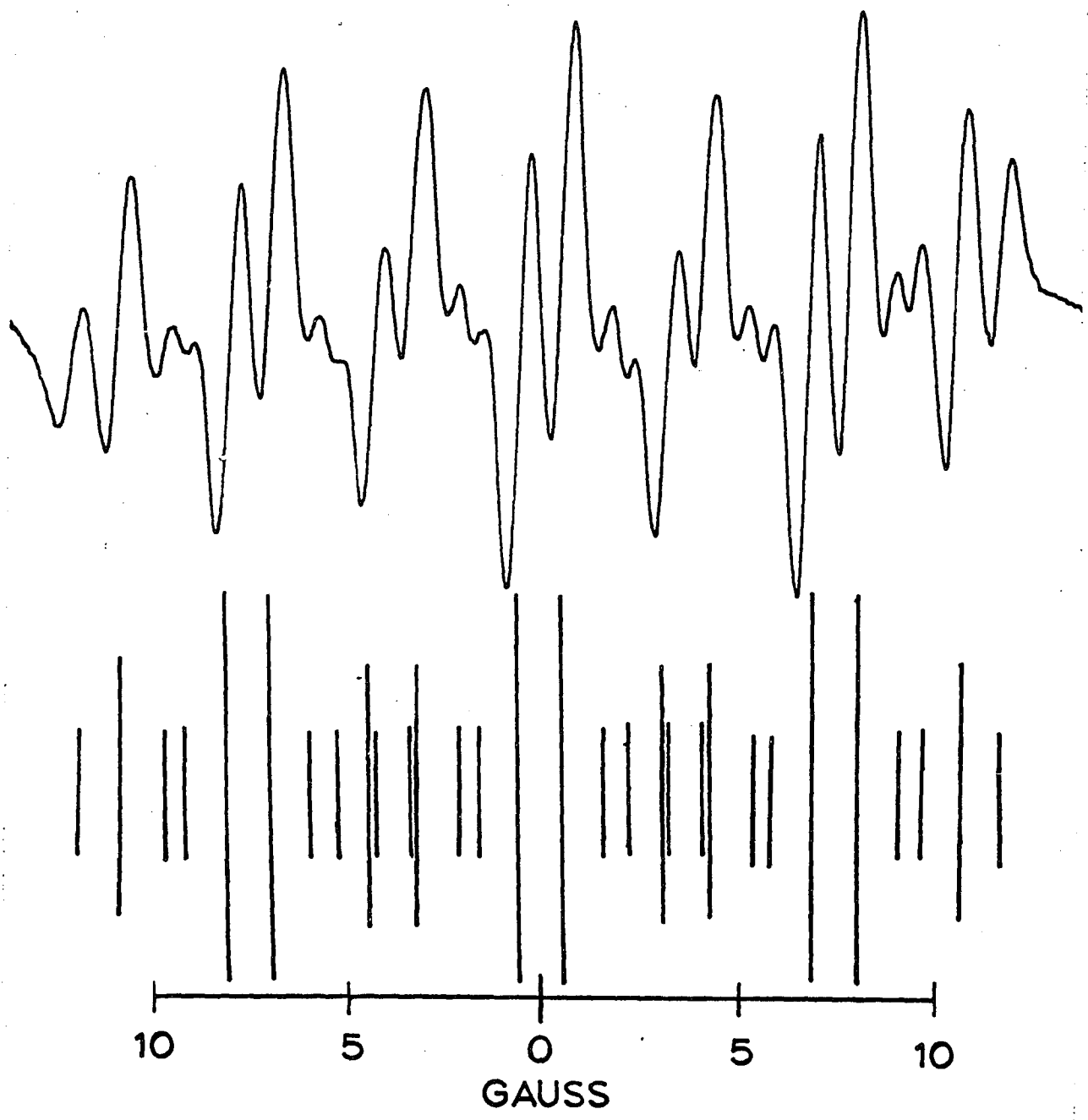
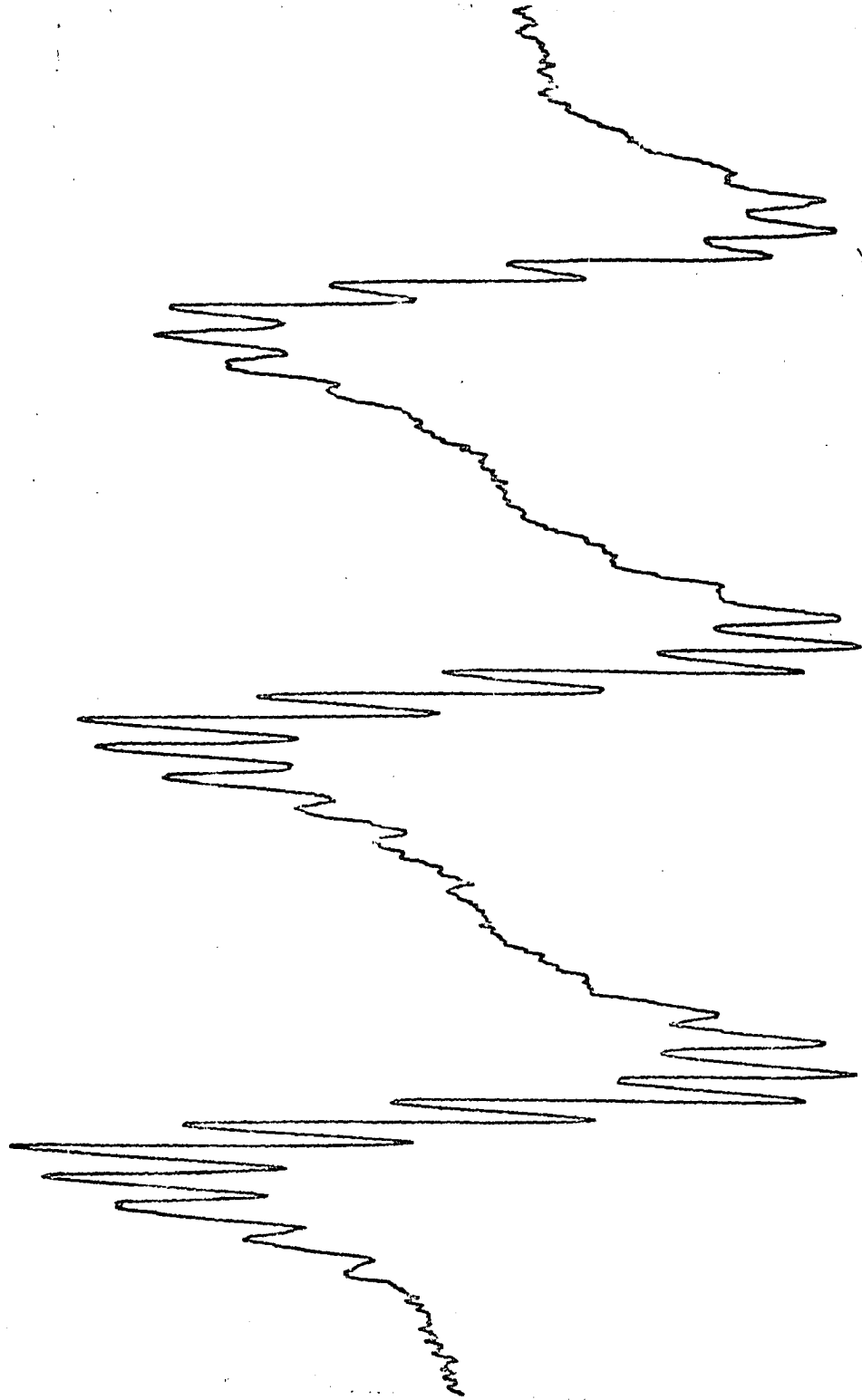
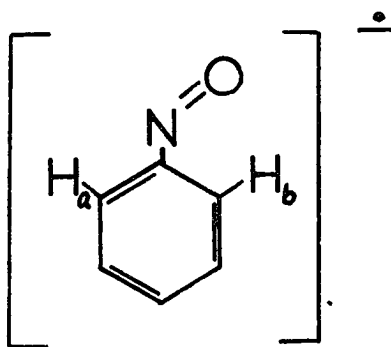


Figure 16. 1st Derivative e.s.r. spectrum of 2,4,6-trideuterionitrosobenzene radical-anion in DMSO(80%)-t-butyl alcohol(20%) at $23 \pm 1^\circ$; 1.31 gauss/cm



(Figure 16) demonstrated that the radical-anions are planar and have restricted rotation about the bonds between the aromatic rings and the nitrogen atoms. The planarity and restricted rotation causes the o-hydrogen atoms to be magnetically non-equivalent leading to different hyperfine splitting constants (hfsc) for each. The requirement of two hfsc for the o-hydrogen atoms demands a preferred planar conformational structure for the radical-anion that is stable in terms of the spectrometer frequency.



The spectrum of this radical-anion (Figure 12) in DMSO (80%)-t-butyl alcohol (20%) requires a weak hfs by 2 meta protons (1.01 G), a strong interaction with two equivalent protons (3.90 G), and a fairly strong interaction with a fifth proton (2.83 G). Other workers have assumed that the strong interaction (3.9 G) with magnetically equivalent protons must involve the ortho hydrogen atoms (52, 136). This is not the case since the spectra of p-deuteronitrosobenzene (Figure 14) and p-chloronitrosobenzene (Figure 15) radical-anions require

a strong interaction with two types of aromatic protons. The error arose because of the fortuitous magnetic equivalence of the p-hydrogen and one of the o-hydrogen atoms. It is likely that restricted rotation also occurs in the nitrobenzene radical-anion but the symmetry of the nitro group prevents experimental detection.

Restricted rotation about Ar-C or Ar-N bonds has been observed in radical-anions such as those derived from p-nitrobenzaldehyde (163), terephthaldehyde (164), p-nitroacetophenone (165), cis or trans-stilbene (166), 4,4'-dibenzoylazobenzene,* and azobenzene.*

Table 12 summarizes the hfsc of all the nitrosobenzene radical-anions mentioned above in DMSO (80%)-t-butyl alcohol, t-butyl alcohol, and ethanol.

In the absence of added base in DMSO, DMSO (80%)-t-butyl alcohol (20%), DMSO (50%)-H₂O (50%), t-butyl alcohol, ethanol, or benzene the reaction of nitrosobenzene (0.005 M.) and phenylhydroxylamine (0.005 M.) gives rise to low concentrations ($\sim 10^{-4}$ M.) of a radical whose e.s.r. spectrum in DMSO is shown in Figure 17. The concentration of radicals as measured by e.s.r. slowly decreases to zero over a period of hours and at this point an essentially quantitative yield of azoxybenzene can be isolated. The radical appears to be

*Private communication from G. A. Russell and R. Konaka, Ames, Iowa. 1964.

Table 12. Hyperfine splitting constants of substituted nitrosobenzene radical-anions in various solvents^{a,b,c} at 23±1°

Substituents	Splitting constants (gauss)				
	\underline{a}_N	\underline{a}_{H-o_1}	\underline{a}_{H-o_2}	\underline{a}_{H-p}	\underline{a}_{H-m}
H ^a	7.90	3.90	2.83	3.90	1.01
H ^b	9.30	4.00	3.45	4.00	1.25
H ^c	10.10	4.02	3.65	4.02	1.29
p-D ^a	8.00	3.90	2.90	-- ^d	1.00
p-D ^b	9.38	3.99	3.40	-- ^e	1.28
p-D ^c	10.02	4.04	3.52	-- ^f	1.23
p-Cl ^a	7.57	3.82	2.78		1.18
p-Cl ^b	9.28	3.90	3.48		1.22
p-Cl ^c	9.68	4.05	3.53		1.24
2,4,6-D ₃ ^a	7.90				
2,4,6-D ₃ ^b	9.38				
2,4,6-D ₃ ^c	10.10				

^aDMSO(80%)-t-butyl alcohol(20%).

^bt-Butyl alcohol.

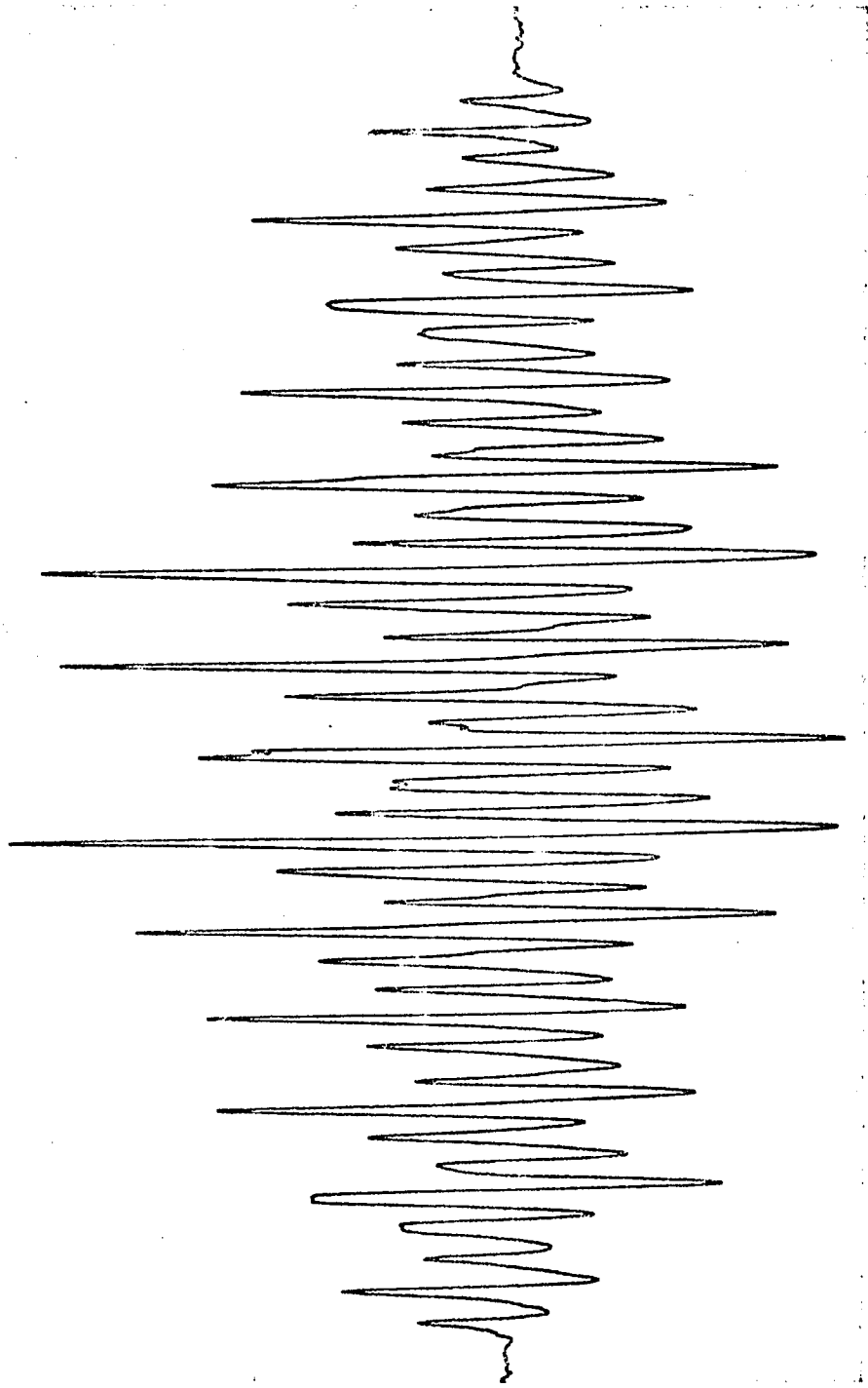
^cEthanol.

^d $\underline{a}_{D-p} = 0.59$ G.

^e $\underline{a}_{D-p} = 0.60$ G.

^f $\underline{a}_{D-p} = 0.61$ G.

Figure 17. 1st Derivative e.s.r. spectrum of phenylnitroxide in DMSO at $23 \pm 1^\circ$; 2.36 gauss/cm.



formed instantaneously as evidenced by rapid flow experiments and exists in a low steady-state concentration. The radical is apparently slowly destroyed to produce azoxybenzene as the final product. It is very stable as shown by its ready formation in protic and aprotic solvents both in the presence and absence of oxygen. Although the e.s.r. spectrum of this radical in non-deoxygenated solutions is recognizable, good resolution is impossible due to line broadening caused by electron exchange between the oxygen molecule and the unpaired electron (167).

Evidence in support of a phenylnitroxide structure ($C_6H_5NHO\cdot$) for this intermediate was obtained by use of deuterated phenylhydroxylamine (C_6H_5NDOD). Reaction of nitrosobenzene (0.005 M.) with deuterated phenylhydroxylamine in DMSO produced a new radical which gave rise to the e.s.r. spectrum in Figure 18. This clearly shows that the splitting due to the hydrogen on nitrogen in Figure 17 has been replaced by a much smaller splitting of deuterium and now the spectrum (Figure 18) is divided into the three main groups of lines due to the splitting by the nitrogen nucleus. This pattern is also found in DMSO (50%)- H_2O (50%) as solvent (Figures 19 and 20).

Changes in solvent seem to have some effect on the hfsc of the nitrogen atom and the hydrogen atom on nitrogen in the phenylnitroxide ($C_6H_5NHO\cdot$) radical. This results in a

Figure 18. 1st Derivative e.s.r. spectrum of phenylnitroxide- α -D
($C_6H_5NDO\cdot$) in DMSO at $23\pm 1^\circ$; 2.36 gauss/cm.

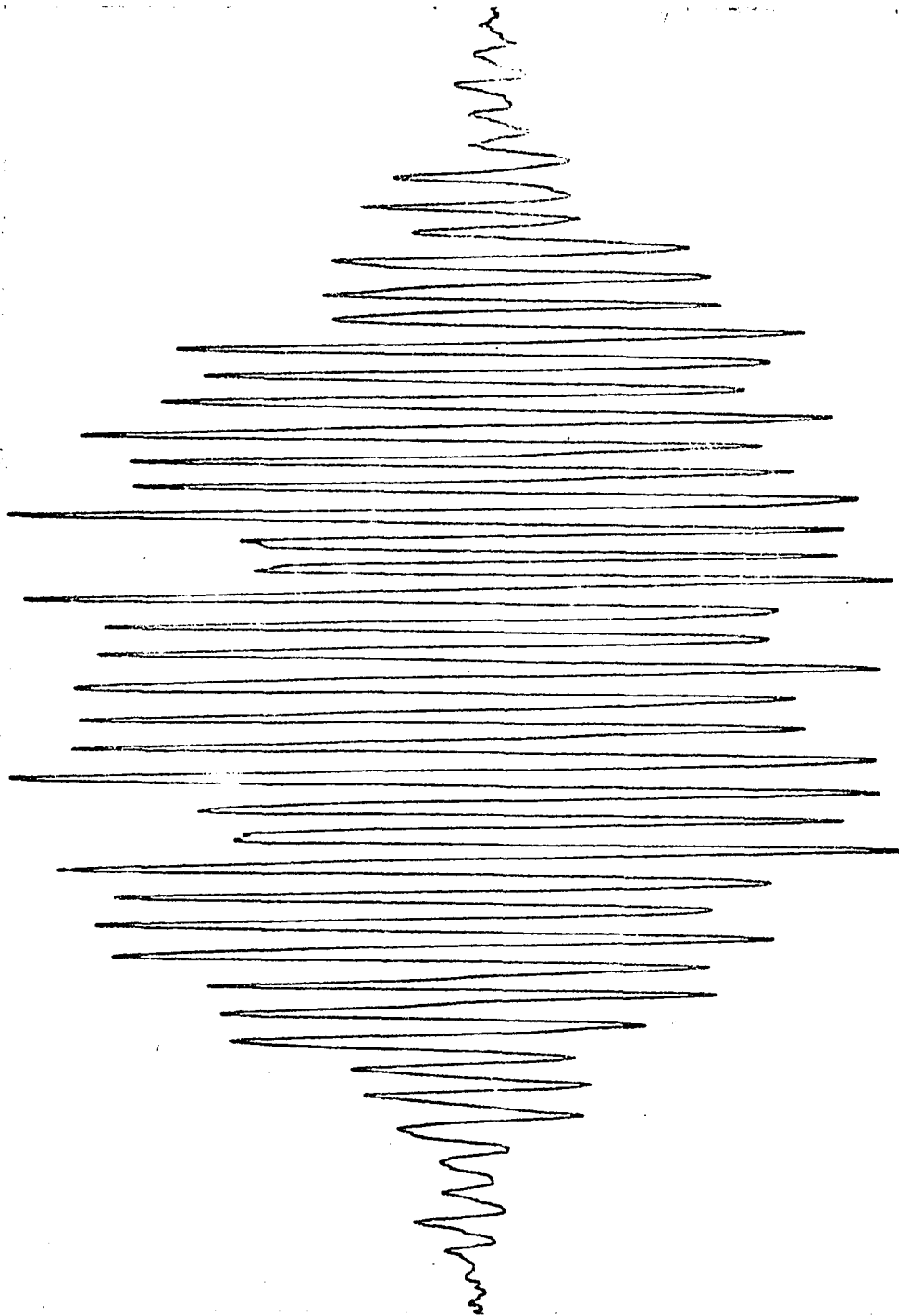


Figure 19. 1st Derivative e.s.r. spectrum of phenylnitroxide in DMSO(50%)-H₂O(50%) at 23±1°; synthetic absorption spectrum based on hfsc given in Table 13; 2.36 gauss/cm.

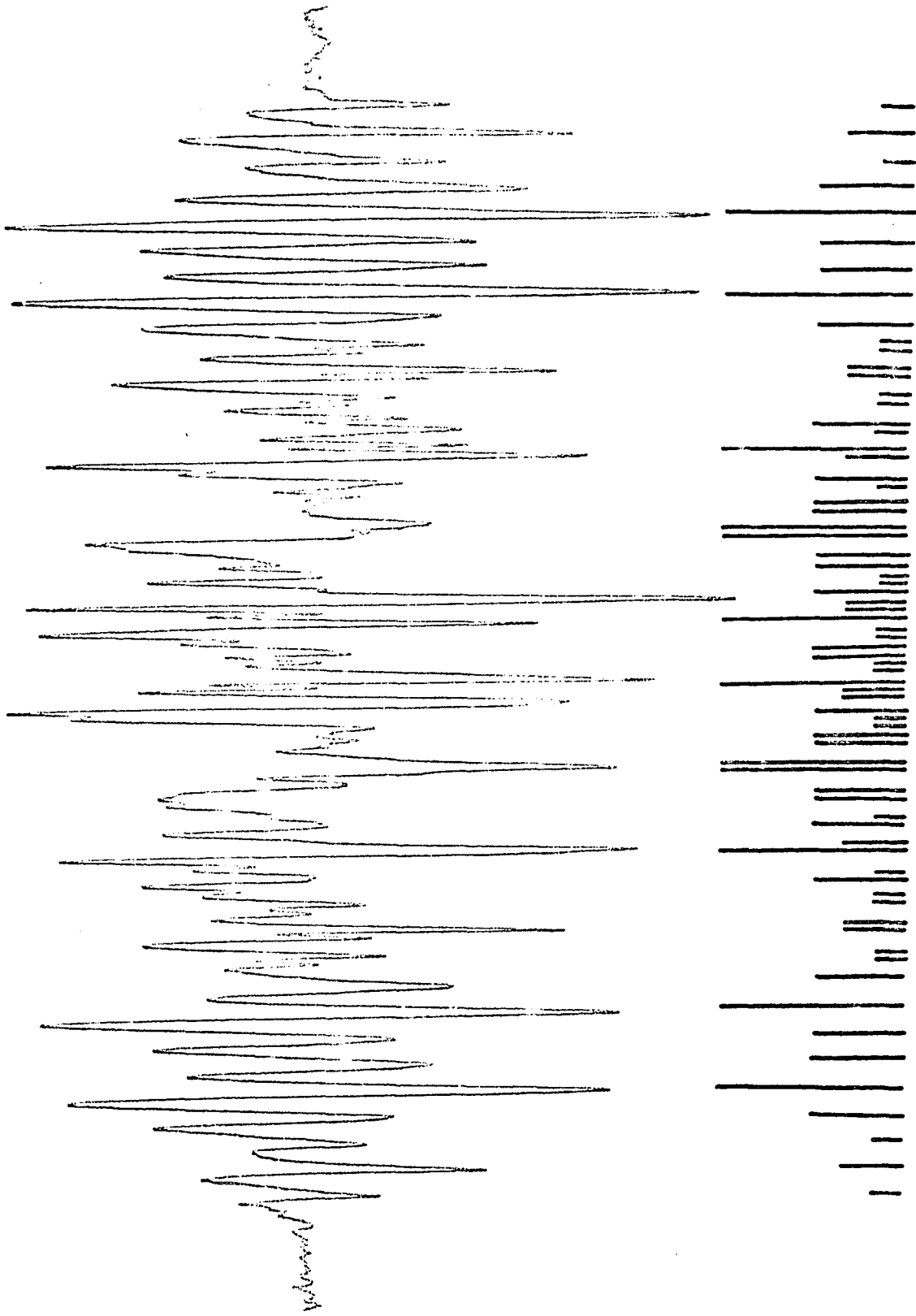
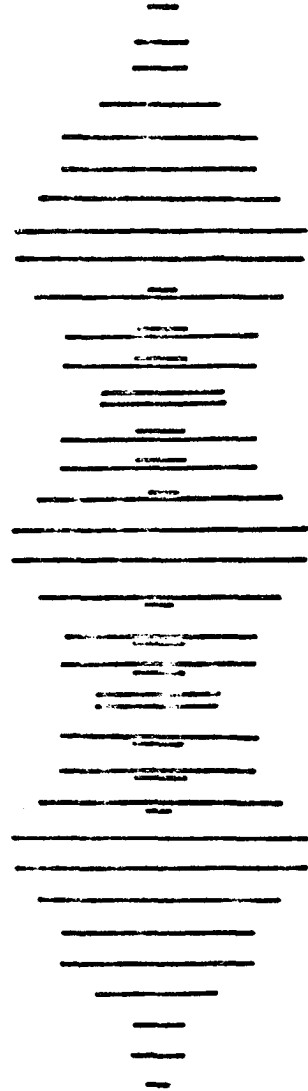
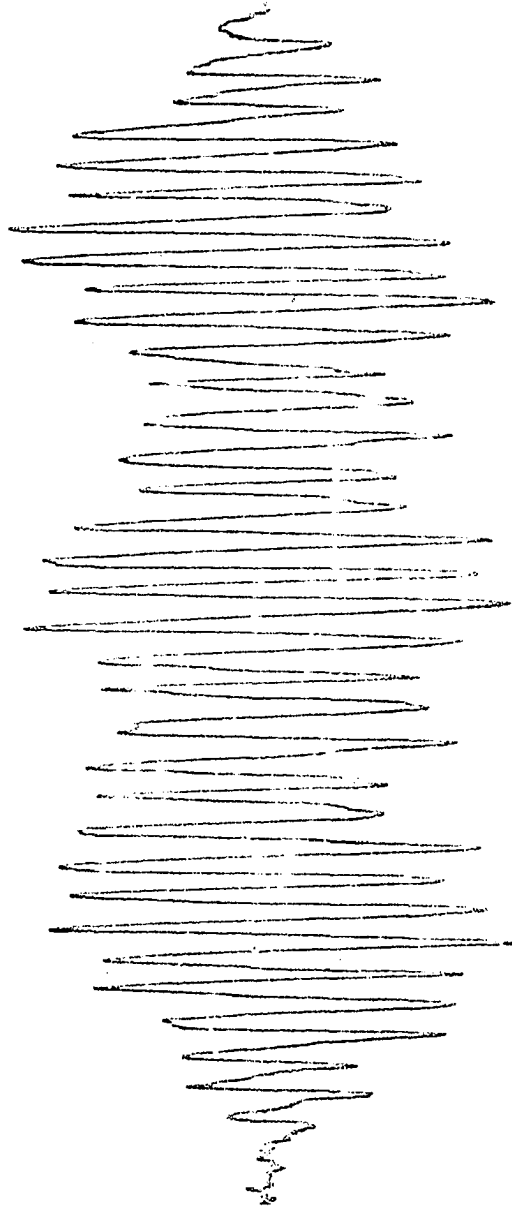
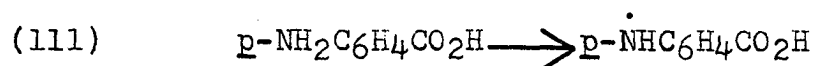


Figure 20. 1st Derivative e.s.r. spectrum of phenylnitroxide- α -D ($C_6H_5NDO\cdot$) in DMSO(50%)- H_2O (50%) at $23\pm 1^\circ$; synthetic absorption spectrum based on hfsc given in Table 13; 2.36 gauss/cm.



different spectrum in each solvent and is illustrated by the spectra of phenylnitroxide in DMSO (80%)-t-butyl alcohol (20%) (Figure 21), ethanol (Figure 22), and benzene (Figure 23). Reaction of 2,4,6-trideuteriophenylhydroxylamine with 2,4,6-trideuterionitrosobenzene in ethanol yields the nitroxide whose spectrum is shown in Figure 24. The six groups of lines represent the splitting of the three lines from the nitrogen isotropic interaction into six by the hydrogen nucleus bonded to nitrogen. The fine splitting is produced by the three deuterium and two meta hydrogen atoms. A large splitting constant for a hydrogen atom bonded to nitrogen was also found in the radical formed by the oxidation of p-amino-benzoic acid (168).



The hfsc for phenylnitroxide and substituted phenylnitroxides in a number of solvents are given in Table 13. The hfsc obtained from the spectrum of p-ClC₆H₅NHO· in DMSO (80%)-t-butyl alcohol (20%) (Figure 25) reveal that restricted rotation does not occur in the phenylnitroxides as it did in the case of the nitrosobenzene radical-anions.

A probable mechanism for the formation of phenylnitroxide and its subsequent reactions to produce azoxybenzene is illustrated by the following reactions.

Figure 21. 1st Derivative e.s.r. spectrum of phenylnitroxide in DMSO(80%)-t-butyl alcohol(20%) at $23 \pm 1^\circ$; synthetic absorption spectrum based on hfsc given in Table 13

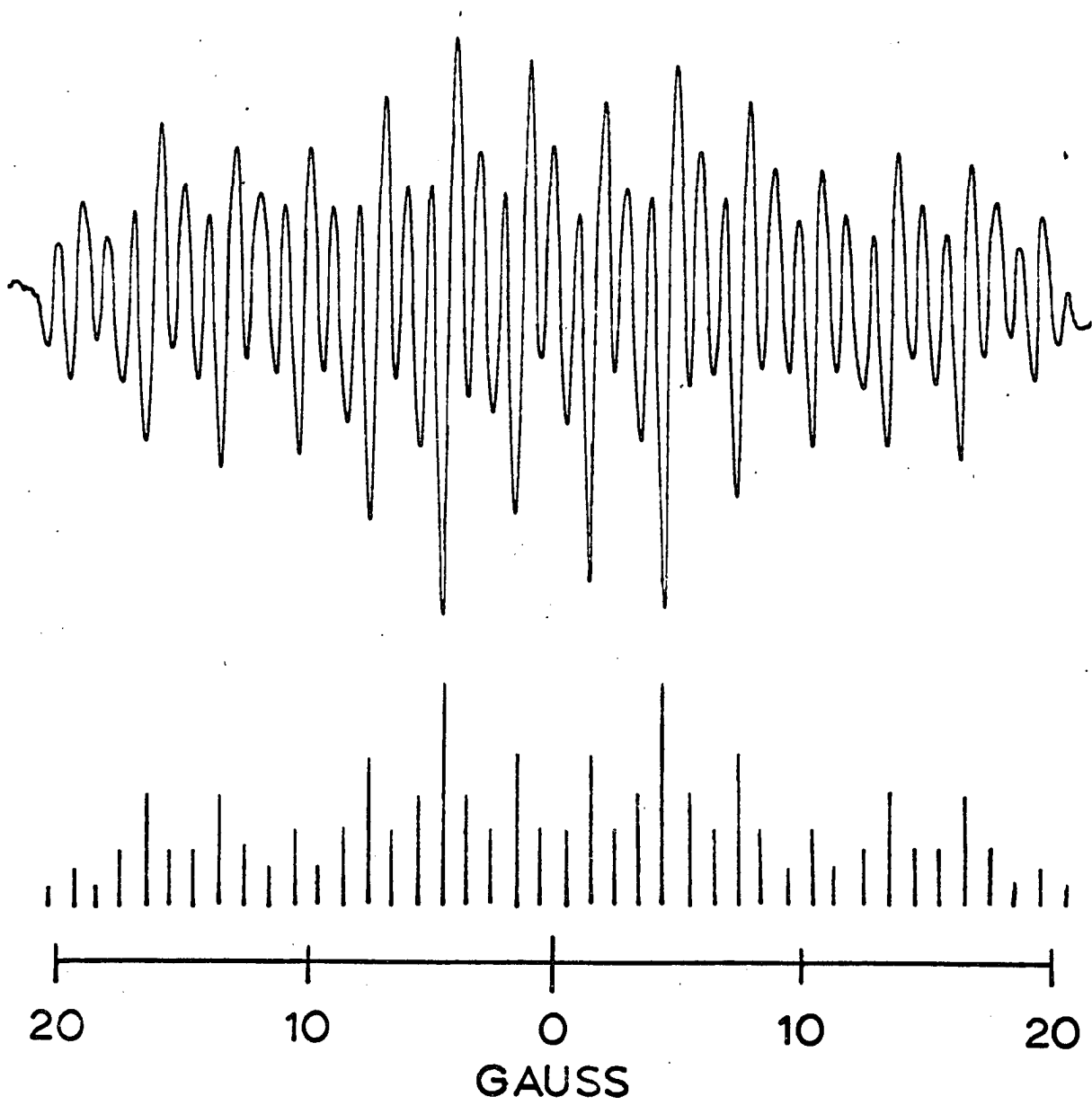


Figure 22. 1st Derivative e.s.r. spectrum of phenylnitroxide in ethanol at $23 \pm 1^\circ$; 2.40 gauss/cm.

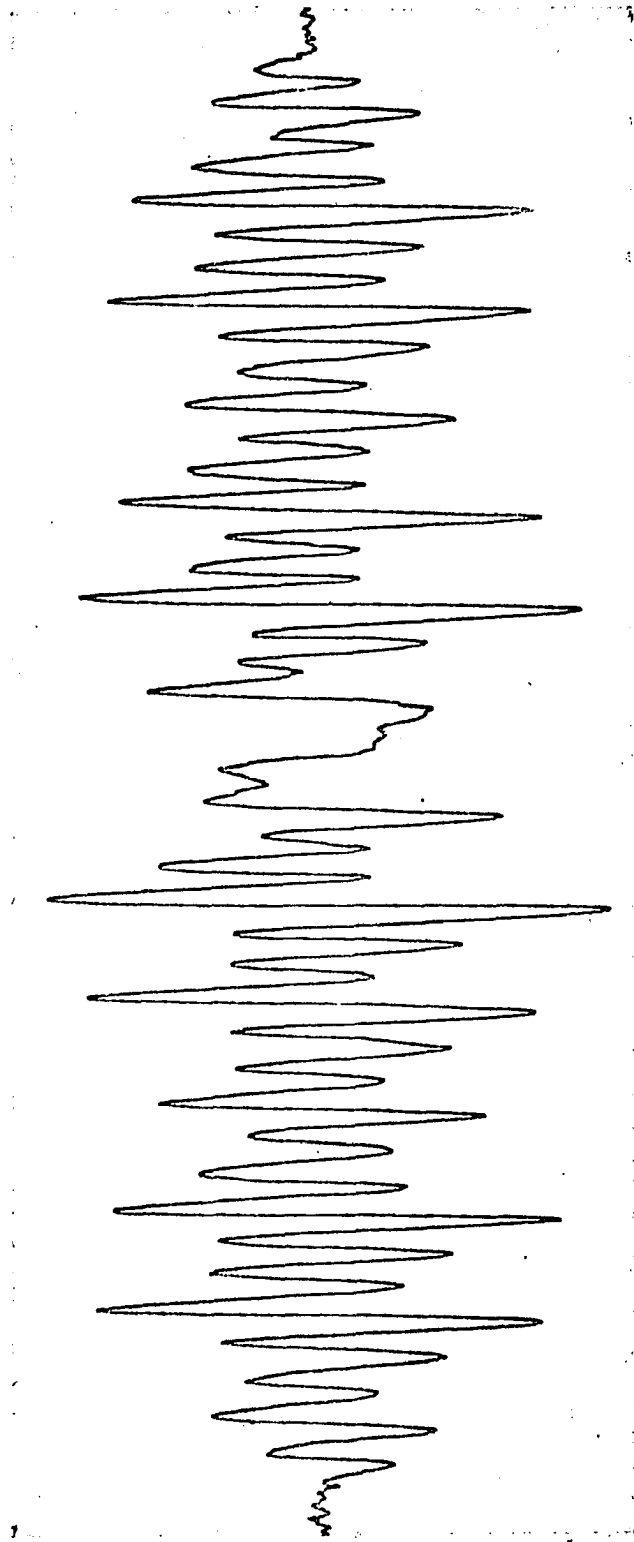


Figure 23. 1st Derivative e.s.r. spectrum of phenylnitroxide in benzene at $23 \pm 1^\circ$; 2.40 gauss/cm.

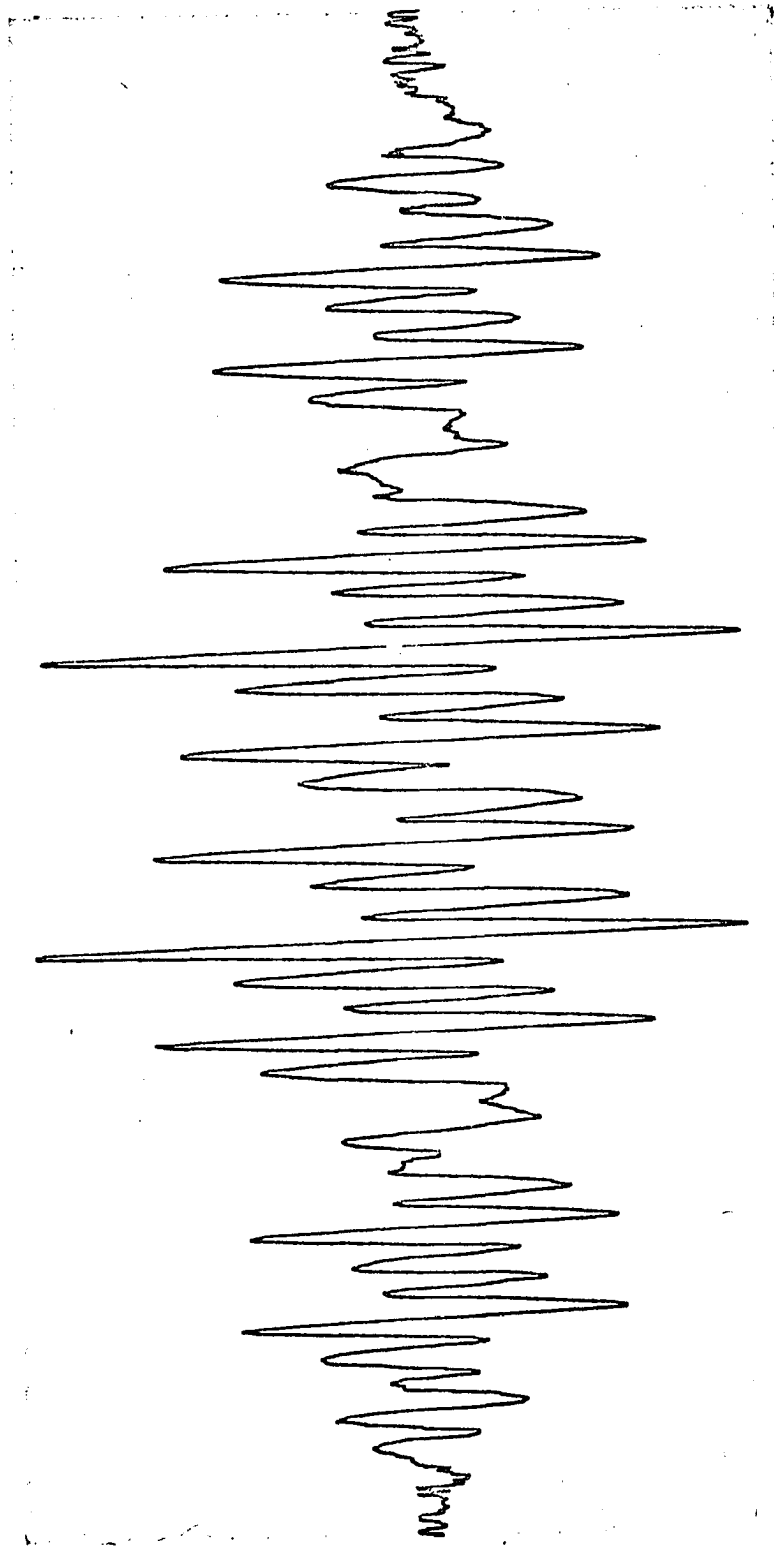


Figure 24. 1st Derivative e.s.r. spectrum of 2,4,6-trideuteriophenylnitroxide in ethanol at $23 \pm 1^\circ$; synthetic spectrum based on hfsc given in Table 13

10 GAUSS

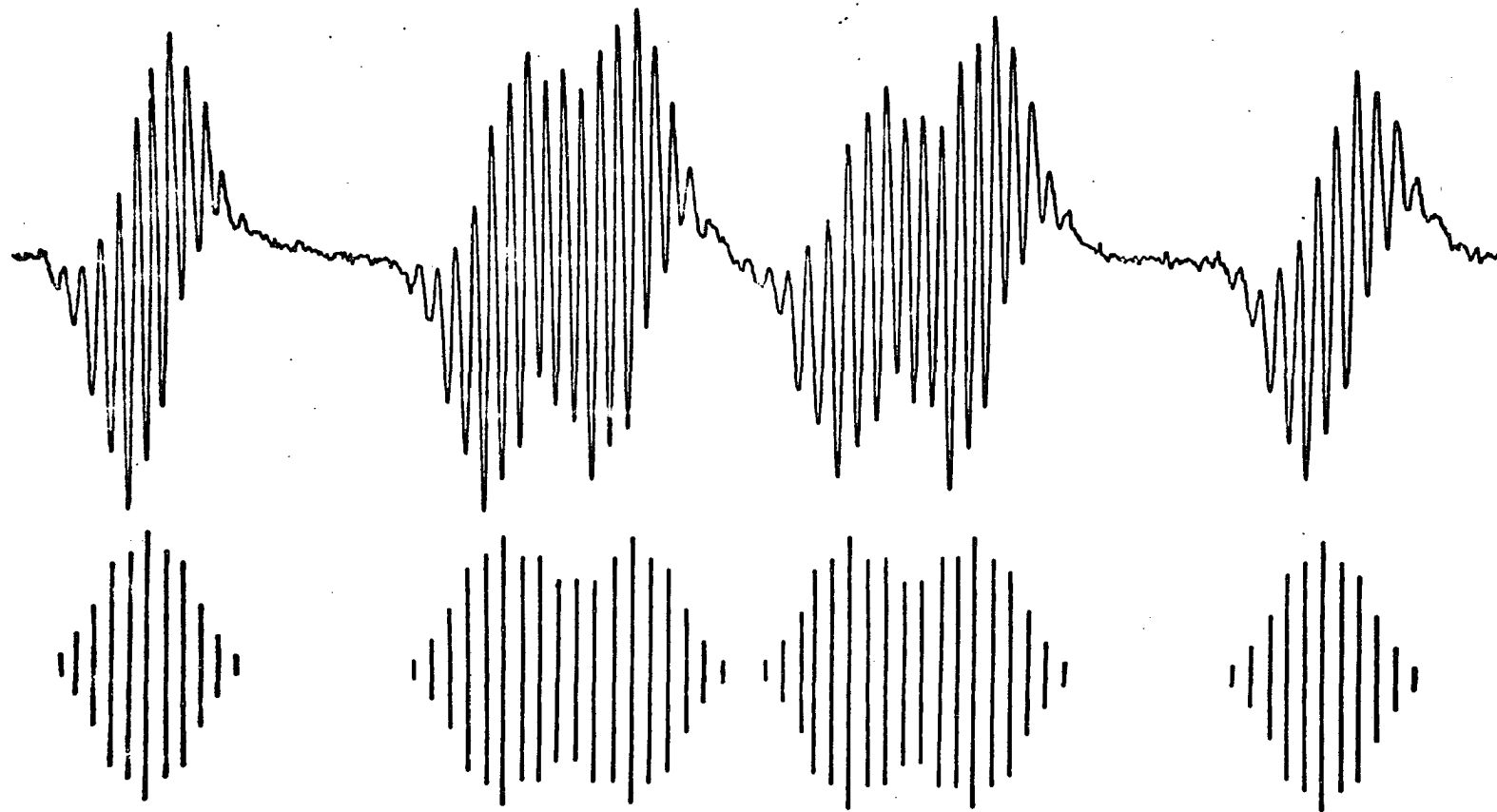


Table 13. Hyperfine splitting constants in gauss of substituted phenylnitroxides in various solvents at $23 \pm 1^\circ$

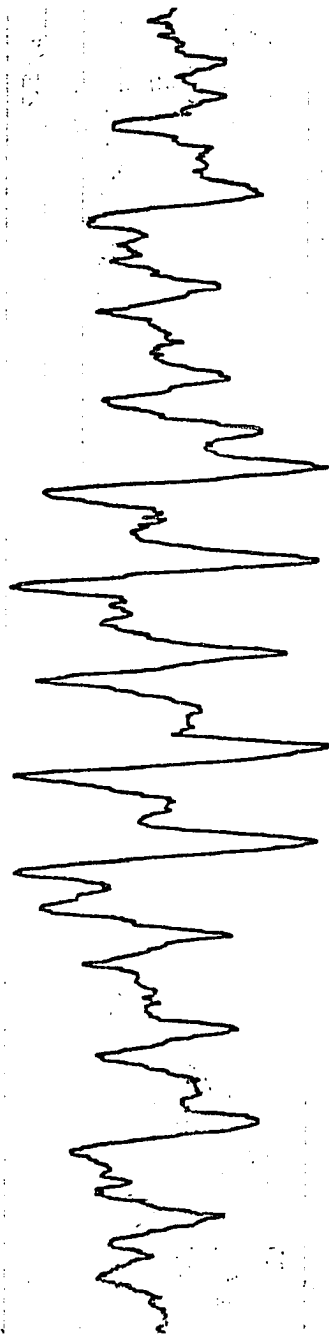
Substituent	Solvent	a_N	$a_{H-o} = a_{H-p}$	a_{H-m}	$a_{H(N)}$
H	DMSO	8.89	3.01	0.97	11.75
H	DMSO(80%)- <u>t</u> -BuOH(20%)	9.10	3.00	1.04	11.90
H	DMSO(50%)-H ₂ O(50%)	9.10	3.10	1.05	12.40
H	Benzene	9.02	2.88	1.00	11.87
H	<u>t</u> -BuOH	8.65	2.96	1.00	11.08
H	Ethanol	8.80	3.08	1.02	12.00
<u>p</u> -Cl	DMSO	8.90	2.98 ^a	1.00	11.70
<u>p</u> -Cl	DMSO(80%)- <u>t</u> -BuOH(20%)	8.95	3.00 ^a	1.00	11.75
2,4,6-D ₃	Ethanol	8.76	-- ^b	1.00	12.00
β -D	DMSO(50%)-H ₂ O(50%)	9.50	3.07	0.95	-- ^c

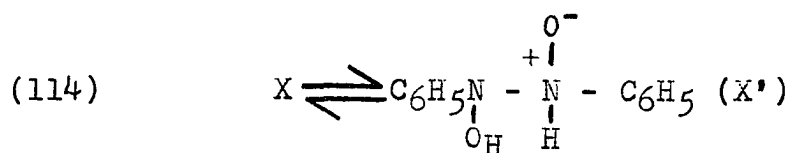
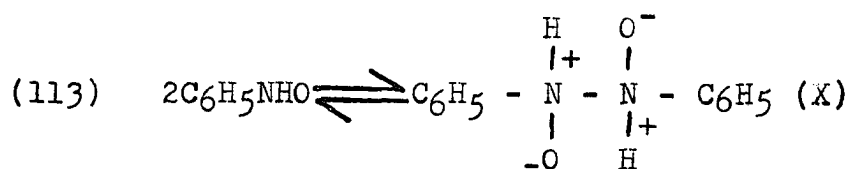
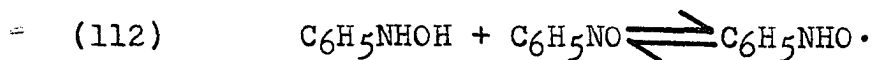
^aNo p-hydrogen atom present.

^b $a_{D-o} = a_{D-p} = 0.46$.

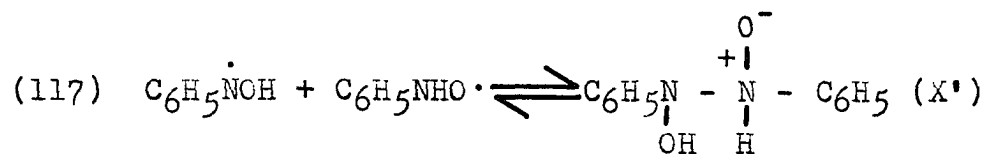
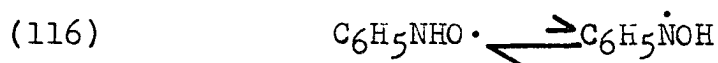
^c $a_{D(N)} = 1.84$.

Figure 25. 1st Derivative e.s.r. spectrum of p-chlorophenylnitroxide
in DMSO(80%)-t-butyl alcohol(20%) at $23 \pm 1^\circ$; 2.36 gauss/cm.

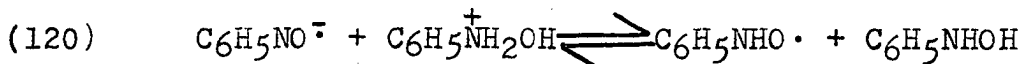
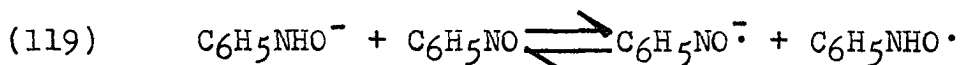
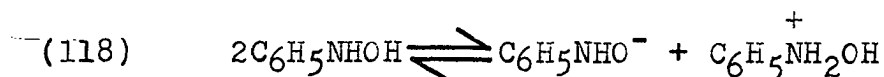




Alternately, a reactive isomeric radical ($\text{C}_6\text{H}_5\dot{\text{N}}\text{OH}$) can be postulated.



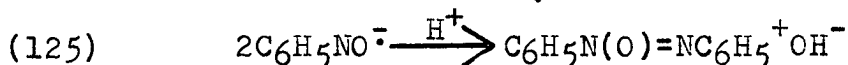
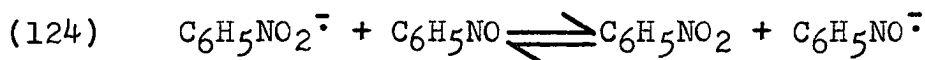
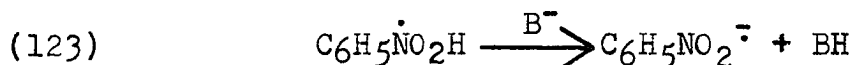
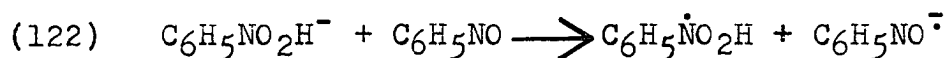
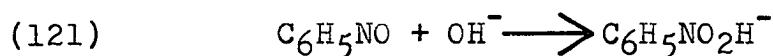
The low concentration of phenylnitroxide observed over a long period of time suggests that the nitroxide is slowly destroyed. This may reflect unfavorable equilibrium constants for reactions 112, 113, and 114 or for reactions 116 and 117. The details of reaction 112 are not clear. It may involve phenylhydroxylamine acting as a base.



The preferred explanation of the condensation reaction is

that an initial equilibrium is rapidly established via reaction 112 which lies far to the left. The formation of $C_6H_5\dot{N}OH$ from $C_6H_5NHO\cdot$ then occurs slowly. It is felt that the equilibrium reaction 118 greatly favors $C_6H_5NHO\cdot$. The formation of $C_6H_5\dot{N}OH$ must be followed by rapid reaction with the nitroxide. This is confirmed by the fact that the presence of $C_6H_5\dot{N}OH$ can not be detected by e.s.r. techniques. The final step involves attack by a base, probably unreacted phenylhydroxylamine with loss of hydroxide ion to form azoxybenzene.

The reaction of nitrosobenzene under a nitrogen atmosphere with base in DMSO (80%)-t-butyl alcohol (20%), t-butyl alcohol, or ethanol gives rise to azoxybenzene in yields of about 65-70%. The possibility was considered that nitrosobenzene could be reduced and oxidized simultaneously as shown in the reactions below. This would give as products 66% azoxybenzene and 33% nitrobenzene.

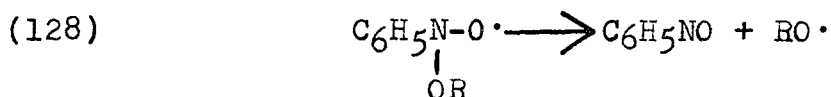
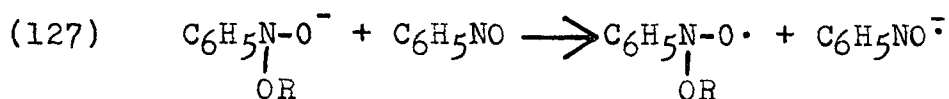
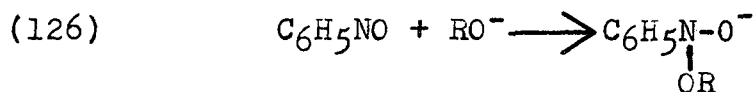


This mechanism breaks down however when the base used is potassium t-butoxide instead of hydroxide. In addition to

this, after reaction under nitrogen in the three solvents mentioned above no trace of either nitrobenzene or unreacted nitrosobenzene could be detected among the products. (Analysis by gas-liquid chromatography.)

Nitrosobenzene radical-anion can be detected by e.s.r. in basic solutions of nitrosobenzene in DMSO (80%)-t-butyl alcohol (20%), t-butyl alcohol, ethanol, and methanol. The concentration of the radical-anion in these solutions decreases to zero in ten to fifteen minutes with the exception of the DMSO (80%)-t-butyl alcohol (20%) solution in which the concentration did not change appreciably over a period of hours. The data summarizing the formation of the radical-anion is given in Table 14.

The radical-anion might be produced by electron transfer between an alkoxide-nitrosobenzene adduct to nitrosobenzene.



Electron transfer involving alkoxide ion has been observed in the reduction of *p*-benzoquinones to semiquinone radicals (169) and in the arylation of 1,3-indandiones (55) (see pages 9 and 10). These results can be explained by the

Table 14. Formation of nitrosobenzene in basic solutions of nitrosobenzene^{a, b}

Substrate (M.)	Solvent	Base	Conc. of base (M.)	Radical conc. (M.)
0.050	DMSO (80%)- <u>t</u> -BuOH (20%)	KOC(CH ₃) ₃	0.050	9.65x10 ⁻³ ^a
0.025	DMSO (80%)- <u>t</u> -BuOH (20%)	KOC(CH ₃) ₃	0.050	8.40x10 ⁻³ ^a
0.025	DMSO (80%)- <u>t</u> -BuOH (20%)	KOC(CH ₃) ₃	0.025	5.45x10 ⁻³ ^a
0.025	DMSO (80%)- <u>t</u> -BuOH (20%)	KOC(CH ₃) ₃	0.012	1.80x10 ⁻³ ^a
0.005	DMSO (80%)- <u>t</u> -BuOH (20%)	KOC(CH ₃) ₃	0.050	1.40x10 ⁻³ ^a
0.005	DMSO (80%)- <u>t</u> -BuOH (20%)	KOH	0.050	1.50x10 ⁻³ ^a
0.025	<u>t</u> -BuOH	KOC(CH ₃) ₃	0.025	4.10x10 ⁻³ ^{a, c}
0.005	<u>t</u> -BuOH	KOC(CH ₃) ₃	0.050	9.00x10 ⁻⁴ ^{a, c}
0.050	Ethanol	NaOH	0.250	6.63x10 ⁻⁴ ^{b, c}
0.050	Ethanol	NaOH	0.050	3.74x10 ⁻⁴ ^{b, c}
0.005	Ethanol	NaOH	0.050	1.03x10 ⁻⁴ ^{b, c}
0.005	Ethanol	NaOH	0.050	7.80x10 ⁻⁵ ^{a, c}
0.050	Ethanol	NaOCH ₂ CH ₃	0.050	2.30x10 ⁻⁴ ^a
0.005 ^d	DMSO (80%)- <u>t</u> -BuOH (20%)	KOC(CH ₃) ₃	0.050	2.50x10 ⁻³ ^a
0.005 ^d	Ethanol	NaOH	0.050	7.00x10 ⁻⁵ ^a
0.050	Methanol	NaOH	0.100	1.35x10 ⁻⁴ ^a

^aH-Cell was used in these experiments.

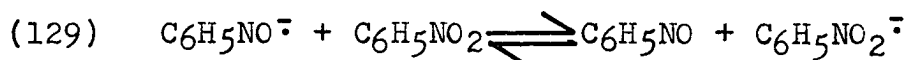
^bFlow system at maximum flow was used in these experiments.

^cRadical concentration decreases rapidly.

^dThe substrate was p-chloronitrosobenzene and the radical produced p-chloronitrosobenzene radical-anion.

use of reactions similar to reactions 126, 127 and 128.

The formation of the radical-anion from p-dimethylamino-nitrosobenzene is very slow even in DMSO (80%)-t-butyl alcohol (20%). Reaction of p-dimethylaminonitrosobenzene (0.050 M.) in DMSO (80%)-t-butyl alcohol (20%) containing potassium t-butoxide (0.05 M.) leads slowly to about 10^{-4} to 10^{-5} M. radical exhibiting the complex spectrum shown in Figure 26. Nitrosobenzene under these conditions forms nitrosobenzene radical-anion at a concentration of almost 10^{-2} M. in a few seconds. This indicates that nitrosobenzene is a much better electron acceptor than p-dimethylaminonitrosobenzene. Nitrosobenzene is also a better electron acceptor than nitrobenzene. Reaction of nitrosobenzene (0.005 M.) and nitrobenzene (0.05 M.) in ethanol containing sodium hydroxide (0.05 M.) leads only to nitrosobenzene radical-anion (5×10^{-5} M.). If the electron accepting ability of nitrobenzene was about the same as nitrosobenzene a ten-fold excess of nitrobenzene should favor the formation of nitrobenzene radical-anion in the equilibrium shown below.



However, reaction of phenylhydroxylamine (0.005 M.) with nitrobenzene (0.05 M.) in ethanol containing sodium hydroxide (0.05 M.) leads to the nitrobenzene radical-anion (3.4×10^{-4} M.) whose spectrum is shown in Figure 27. This radical-anion is probably formed according to the following reaction scheme.

Figure 26. 1st Derivative e.s.r. spectrum of p-dimethyaminonitrosobenzene radical-anion in DMSO(80%)-t-butyl alcohol(20%) at $23 \pm 1^\circ$; 1.58 gauss/cm.

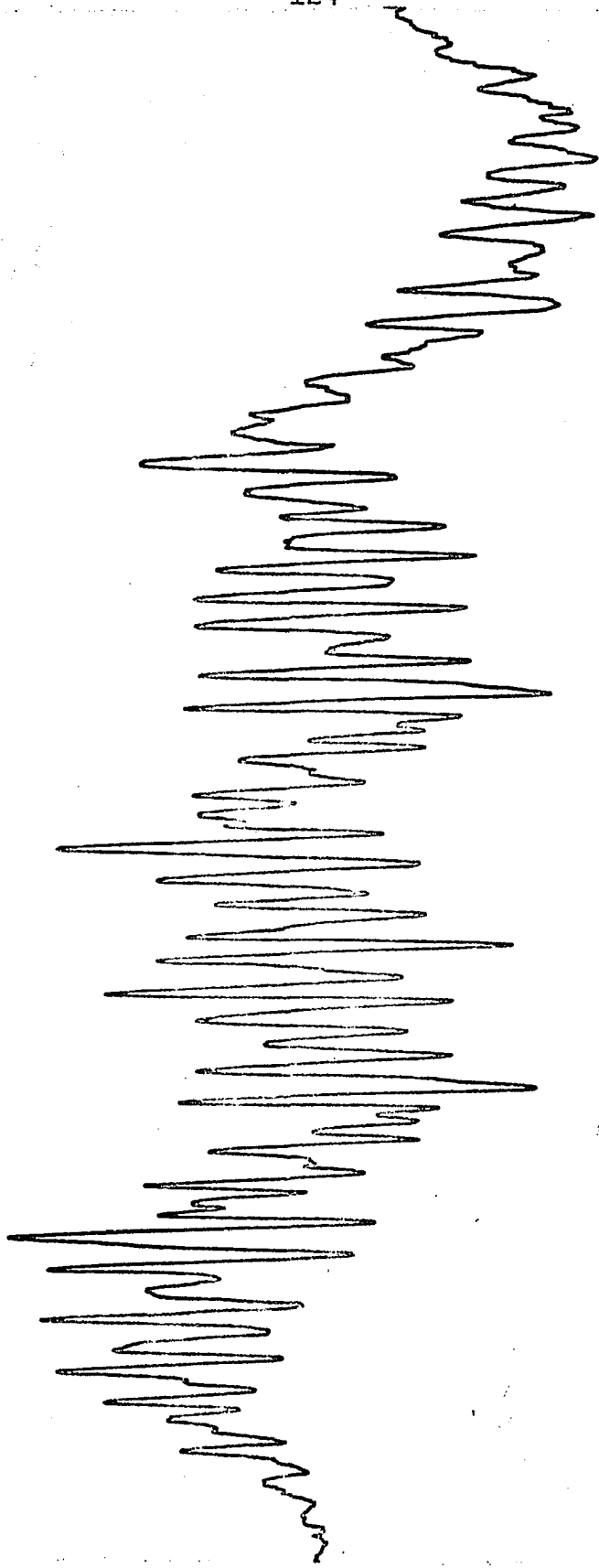
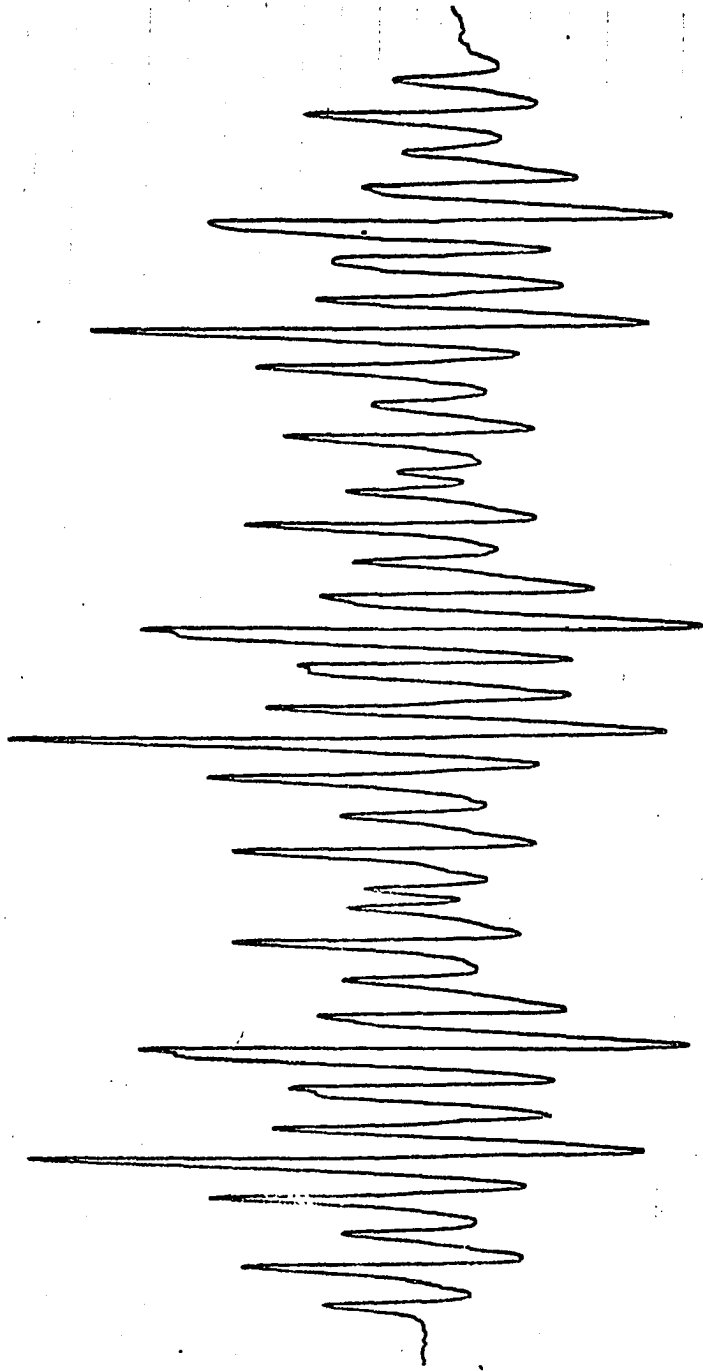
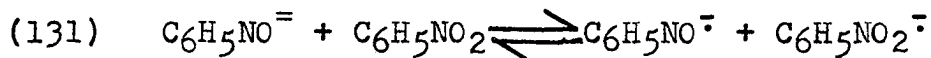
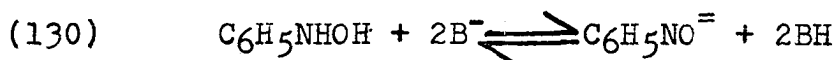


Figure 27. 1st Derivative e.s.r. spectrum of nitrobenzene radical-anion in ethanol at $23 \pm 1^\circ$; hfsc are $a_N = 13.1$, $a_{H-O} = 3.39$, $a_{H-p} = 3.53$, $a_{H-m} = 1.15$ gauss; 2.46 gauss/cm.



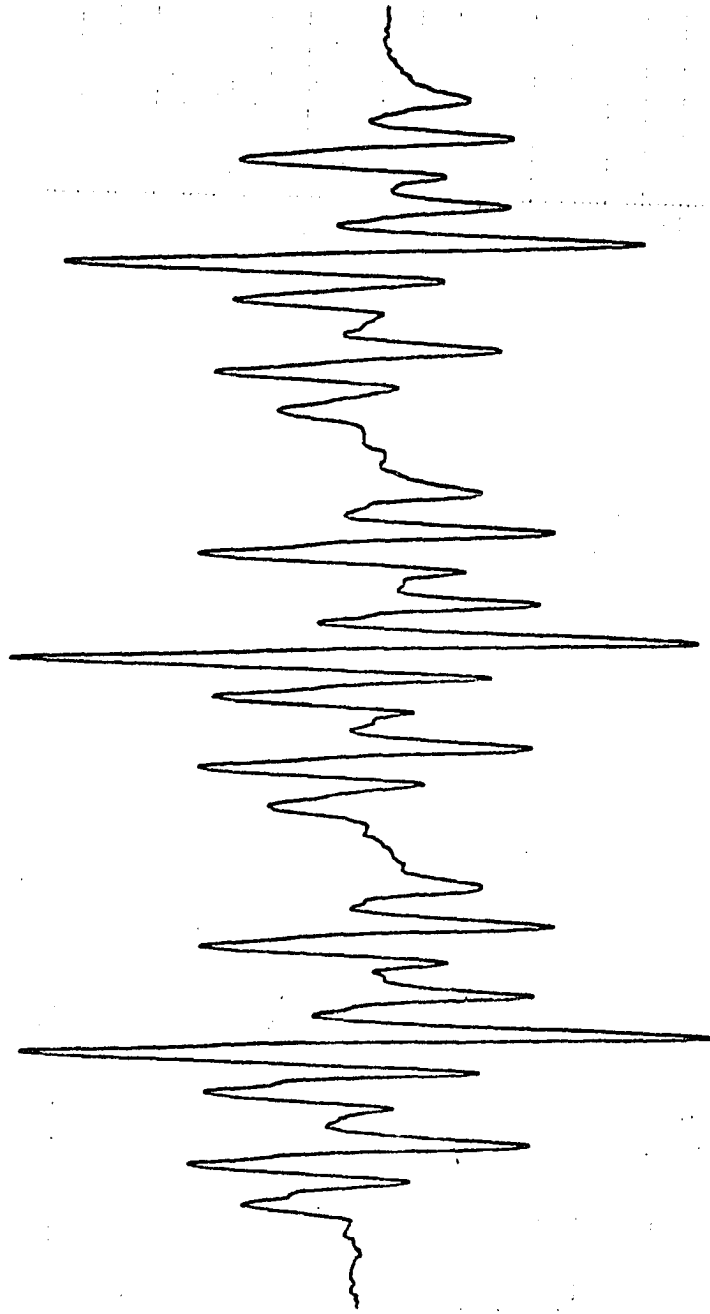


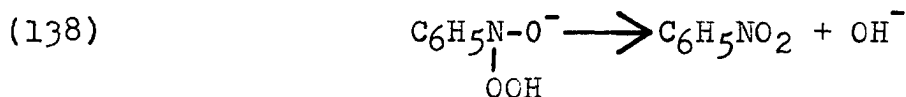
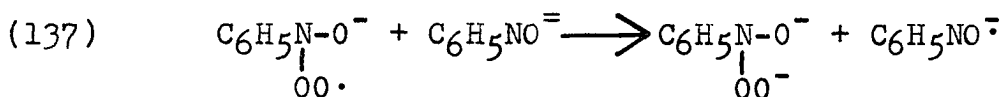
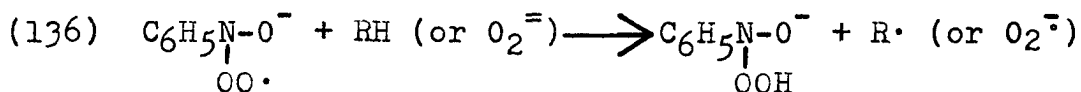
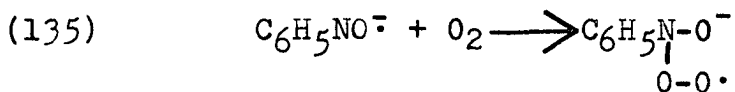
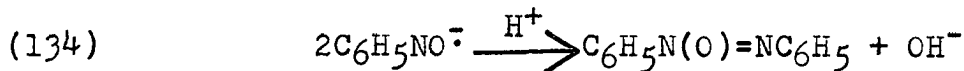
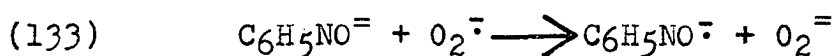
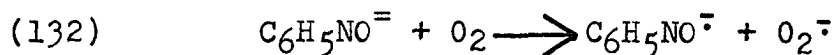
The nitrosobenzene radical-anion formed in reaction 131 would condense rapidly to yield azoxybenzene. Under the same reaction and concentration conditions as those given above, *p*-chloronitrobenzene yields the corresponding radical-anion (7.8×10^{-4} M.) whose e.s.r. spectrum is shown in Figure 28. Under the reaction conditions none of the reactants alone in basic ethanol gave rise to radical-anions.

The autoxidation of phenylhydroxylamine in methanol has been studied and found to give azoxybenzene as the only product (170). However, in *t*-butyl alcohol containing an excess of potassium *t*-butoxide, phenylhydroxylamine oxidizes very rapidly (Initial rate = 4.1 moles O₂/mole C₆H₅NHOH-min.) with the absorption of 0.92 moles of oxygen per mole of phenylhydroxylamine. Analysis of the oxidation product by gas-liquid chromatography revealed that 46.4% of the phenylhydroxylamine had been converted to nitrobenzene and the remainder to azoxybenzene. Oxidation of nitrosobenzene under these conditions proceeds with a much slower rate (Initial rate = 0.30 moles O₂/mole C₆H₅NO-min.), absorption of 0.88 moles of oxygen per mole of nitrosobenzene, and conversion to 62.9% of nitrobenzene with the remainder being azoxybenzene.

The oxidation of phenylhydroxylamine can be explained by the following sequence of reactions.

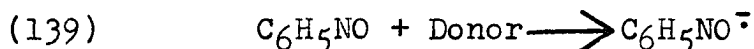
Figure 28. 1st Derivative e.s.r. spectrum of p-chloronitrobenzene radical-anion in ethanol at $23 \pm 1^\circ$; hfsc are $a_N = 12.46$, $a_{H-o} = 3.34$, $a_{H-m} = 1.20$ gauss; 2.46 gauss/cm.





The formation of less nitrobenzene from phenylhydroxylamine than from nitrosobenzene can be explained by assuming that reaction 132 proceeds more readily than reaction 135 and reduces the concentration of oxygen to a low level. Thus, most of the oxygen consumed produces a high concentration of radical-anion which forms azoxybenzene by reaction 134 rather than react with oxygen by reaction 135 to eventually give nitrobenzene.

In contrast to this is the oxidation of nitrosobenzene which is probably initiated by the formation of the nitrosobenzene radical-anion.



In this case the radical-anion reacts primarily with oxygen

present at a saturation level to produce nitrobenzene while the remainder condenses to yield azoxybenzene.

EXPERIMENTAL

All solvents used in this research were carefully purified. DMSO was fractionally distilled from calcium hydride at high vacuum and stored over Linde Type 4A Molecular Sieves. t-Butyl alcohol was distilled from sodium and from potassium before its use as a solvent or conversion into potassium t-butoxide. Absolute ethanol and analytical reagent grade methanol and benzene were used as supplied.

All organic solid substrates were carefully recrystallized to literature melting point and liquids were purified by fractional distillation.

1-Phenylpropanol and 2,2-dimethyl-1-phenylpropanol were prepared by reaction of benzaldehyde with the Grignard reagents from ethyl bromide and t-butyl chloride respectively. α -Deuteriobenzhydrol and α -deuteriofluorenol were prepared by reduction of the corresponding ketones with lithium aluminum deuteride.

Phenylhydroxylamine, p-chlorophenylhydroxylamine, and 2,4,6-trideuteriophenylhydroxylamine were prepared by reduction of the corresponding nitro-compounds with zinc dust in water containing ammonium chloride. The 2,4,6-trideuterio-nitrobenzene was prepared as follows. 2,4,6-Trideuterio-aniline was prepared by exchange of the hydrochloride with deuterium oxide in a sealed tube at 100°. This was then converted to the acetanilide with acetyl chloride and oxidized

to the nitrobenzene using 30% hydrogen peroxide in acetic acid. This gave a very low yield (5-10%) of 2,4,6-trideuterionitrobenzene.

p-Chloronitrosobenzene was prepared by oxidation of *p*-chlorophenylhydroxylamine with dichromate in aqueous solution. 2,4,6-Trideuterionitrosobenzene was prepared by Dr. R. Konaka by the oxidation of the corresponding aniline with neutralized Caro's acid.

The *p*-deuterionitrosobenzene was prepared as follows. *p*-Dibromobenzene was carefully purified and its mono-Grignard reagent treated with excess deuterium oxide to produce *p*-deuteriobromobenzene. The Grignard reagent from this was treated with chloramine to produce *p*-deuterioaniline in 10% yield. The *p*-deuterioaniline was then oxidized with neutralized Caro's acid to *p*-deuterionitrosobenzene.

The e.s.r. measurements were made with a Varian V-4500 spectrometer equipped with 100 kc./sec. field modulation. Flat fused silica cells (Varian V-4548 aqueous solution sample cell) were used for all experiments.

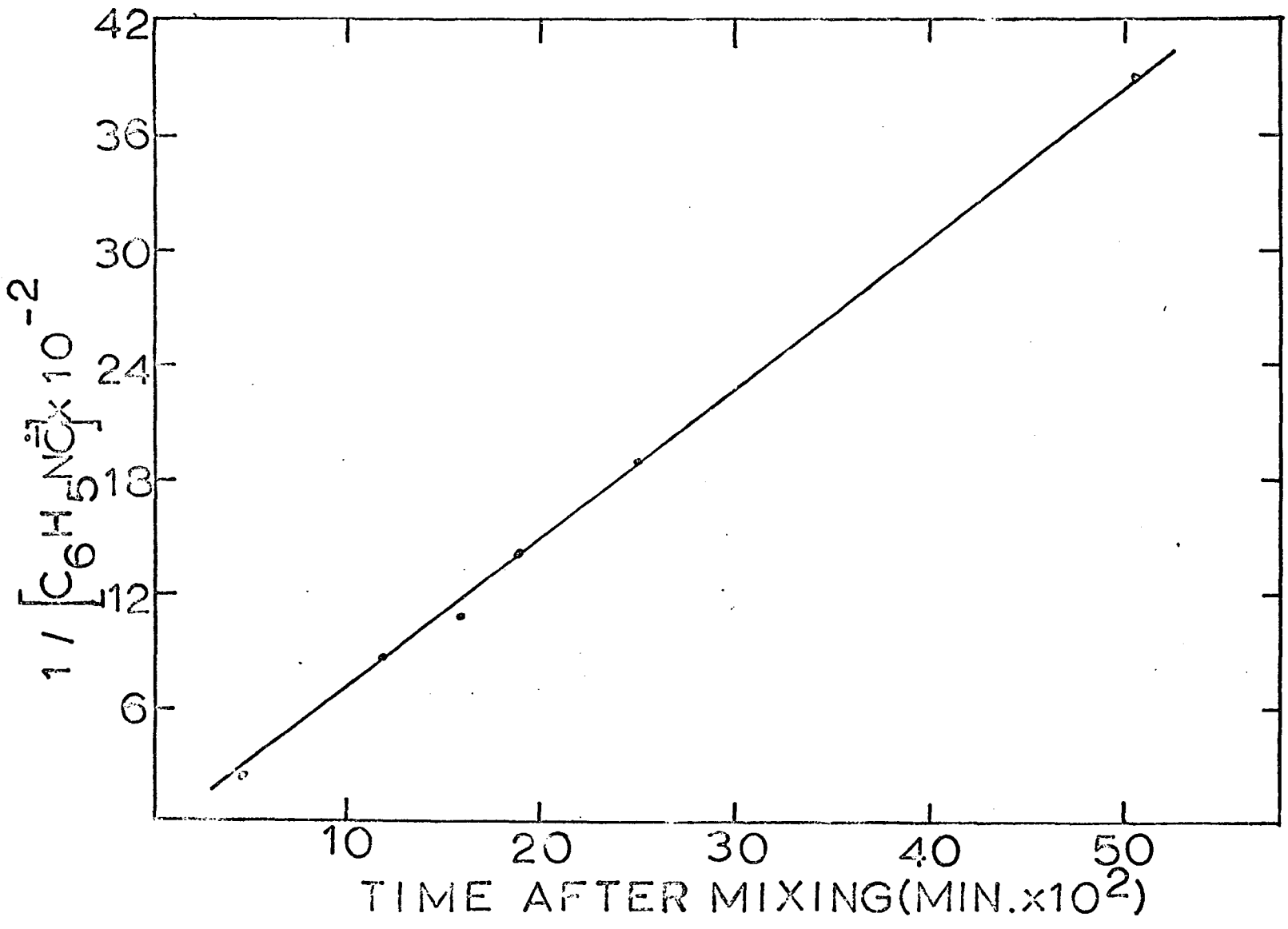
Radical concentrations were estimated by comparison of the height of an overmodulated 1st derivative curve with that obtained from a standard solution of diphenylpicrylhydrazyl radical in the same solvent.

Hyperfine splitting constants were obtained by using the *p*-benzosemiquinone radical as a standard for estimating the

change in magnetic field strength (gauss) with time. Then knowing accurately the speed of a strip chart recorder the change in magnetic field strength could be obtained directly in units of gauss per centimeter.

Determination of a 2nd-order rate constant for the disappearance of nitrosobenzene radical-anions (see Figure 11) was by obtaining the slope from a plot of $1/C_6H_5NO^{\cdot-}$ vs. Time as shown in Figure 29.

Figure 29. Plot of $1/C_6H_5NO^{\cdot-}$ vs. Time from a radical-anion concentration in ethanol of 0.005 M. to 0.00025 M.



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