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Oxidation of functionally substituted carbanions

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OXIDATION OF FUNCTIONALLY SUBSTITUTED
CARBANIONS.

Iowa State University of Science and Technology,
Ph.D., 1966
Chemistry, organic

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OXIDATION OF FUNCTIONALLY SUBSTITUTED CARBANIONS

by

Alan Greenway Bemis

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
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DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

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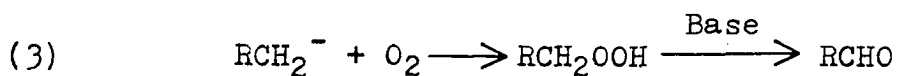
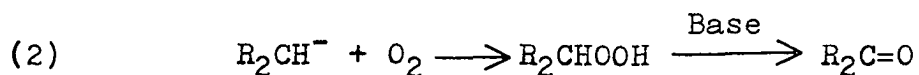
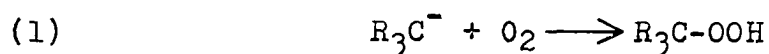
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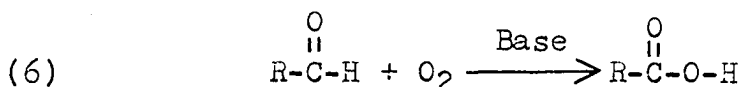
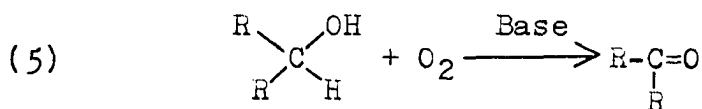
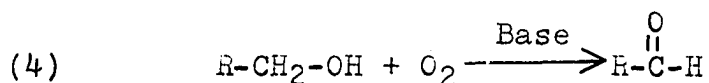
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I. INTRODUCTION

The reaction of carbanions with molecular oxygen is a synthetically useful method of oxygenating compounds having ionizable protons. The primary reaction product is a hydroperoxide. In most aprotic solvents, the hydroperoxide resulting from a tertiary carbanion (equation 1) is stable: the secondary (equation 2) and primary hydroperoxides (equation 3) undergo β -elimination to yield a ketone and aldehyde respectively.

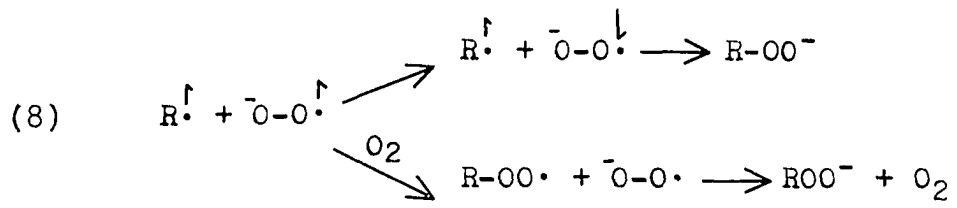
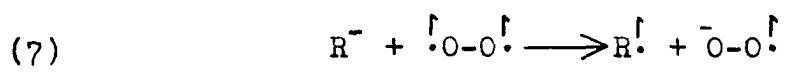


In dimethyl sulfoxide, the initial hydroperoxide is reduced to an alcohol, except for compounds which undergo β -elimination with exceptional ease. Primary and secondary alcohols and aldehydes will oxidize further forming respectively an aldehyde (equation 4), a ketone (equation 5), or an acid (equation 6).



This study is concerned with extending the scope of the reaction to compounds with less acidic hydrogens, and with an investigation of the mechanism of these base-catalyzed autoxidations. Toluene seems to be the least acidic compound which can be oxidized under the conditions employed. The discovery that the rate determining step of the oxidation is often the initial ionization of an activated carbon-hydrogen bond to give the carbanion is reported in this thesis. The subsequent electron-transfer of that carbanion with oxygen can be the rate determining step with rather acidic compounds.

The exact mechanism of the reaction of a carbanion with oxygen is controversial. A likely pathway involves initial electron-transfer to give the carbon radical and superoxide ion, followed by either spin inversion and recombination, equation 8, or interception of the radical by oxygen to give a peroxy radical, followed by rapid electron transfer between the peroxy radical and superoxide to give the hydroperoxide ion and to regenerate oxygen.

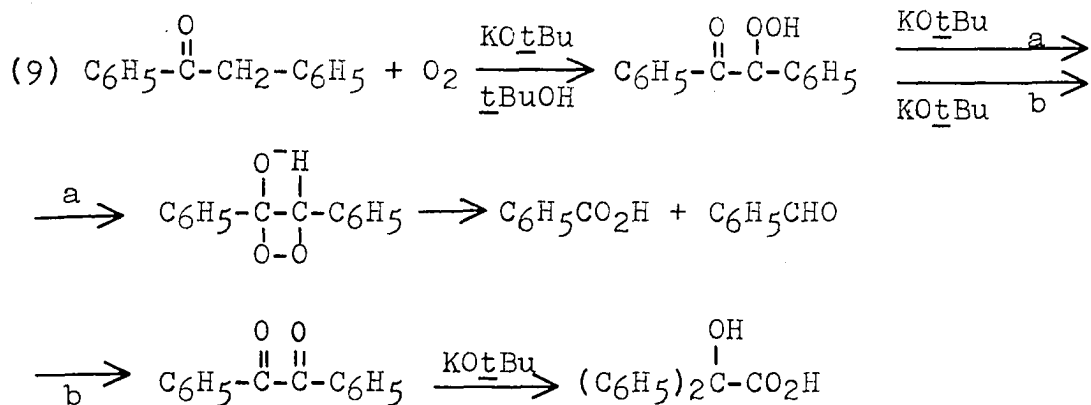


II. LITERATURE

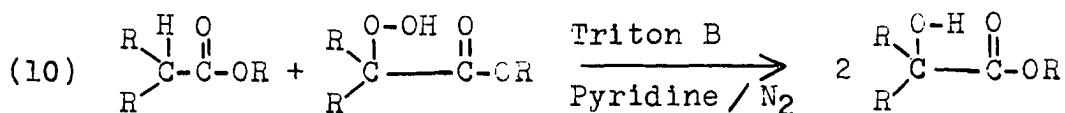
A. Reactions of Oxygen with Carbanions

Although base catalyzed autoxidations have been known for a long time (1-7), only a few detailed studies have been made. Moye (8) has reviewed the general field thoroughly and only work pertaining to mechanistic aspects, data on hydrocarbons, and recent publications will be covered.

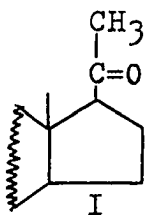
Ketones and esters have received considerable attention as autoxidizable substrates. Doering and Haines (9) oxidized acetophenone, propiophenone, and butyrophenone in t-butyl alcohol with potassium t-butoxide as the ionizing base and found the products to be benzoic acid in 60-70% yields. Camphor oxidized slowly to give 5-10% camphoric acid, while desoxybenzoin gave benzoic acid when shaken with oxygen but gave benzilic acid when oxygen was bubbled through the basic solution. Avramoff and Sprinzak (10, 11) oxidized esters



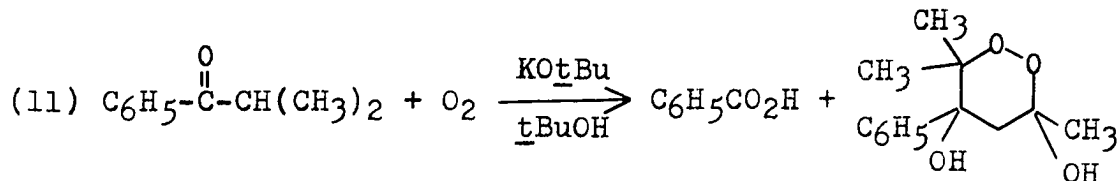
containing an α -tertiary hydrogen in pyridine with Triton B (benzyltrimethylammonium hydroxide) as base. At low temperatures (-30°C), the corresponding hydroperoxide could often be isolated. At room temperature, only the alcohols were isolable. This was shown to be due to reaction between the starting material and hydroperoxide to yield the alcohol, since it could be duplicated by mixing these two compounds in pyridine with Triton B present under nitrogen. Benzilic acid and benzophenone were isolated from the oxidation of methyl



diphenylacetate. Barton and co-workers (12-14) have oxidized ketones, mostly in the steroid field. They found that α -hydroperoxy ketones could often be prepared. The solvents used were tertiary alcohols, and the corresponding alkali metal tertiary alkoxide was used as the base. An interesting fact noted was that although sodium methoxide in methanol or sodium isopropoxide in isopropanol epimerized various progesterones, partial formula I, no oxidation occurred in the presence of oxygen. These compounds did oxidize in potassium t -butoxide in t -butanol. An explanation advanced was specific solvation by the less bulky primary and secondary alcohols, although the possibility of inhibition due to



abstraction from the alcohol of a reactive α -proton (not present in tertiary alcohols) was not eliminated (12). These workers (13) were also able to isolate a product derivable from an intermediate α -hydroperoxide in the case of isobutyrophenone. This peroxide apparently arises from the

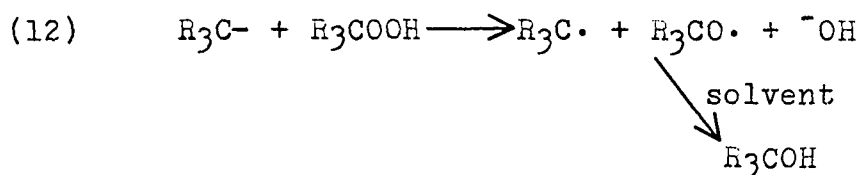


condensation of acetone, formed as a cleavage product from the intermediate hydroperoxide, and the hydroperoxide. Work on the oxidation of substituted maleic anhydrides resulted in the isolation of hydroperoxides or alcohols (14). Gersmann *et al.* (15, 16) have also oxidized aliphatic ketones and esters. They isolated α -hydroperoxides from oxidation of simple aliphatic ketones and esters (phenyl groups not needed) at -5°C to -25°C in mixtures of *t*-butyl alcohol and 1,2-dimethoxyethane (DME) using potassium *t*-butoxide as base. Avramoff and Sprinzak (11) had reported purely aliphatic esters as unreactive in pyridine. The reason for this difference is probably due to the kind of solvent effect found

by Pacifici et al. (17) in electron transfer experiments and also in agreement with conclusions drawn by Parker (18). Generally the rate of electron transfer from a "stable" carbanion is faster in nonpolar media than in the more polar solvents (19). Elkik (20) also oxidized ketones. His results were similar to those of Doering and Haines (9). Hanna and Ourisson (21) oxidized terpenoid and steroid ketones.

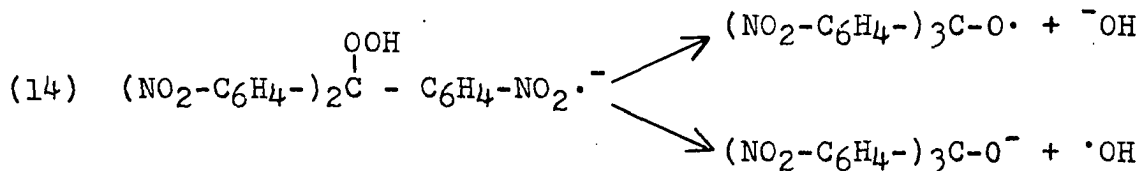
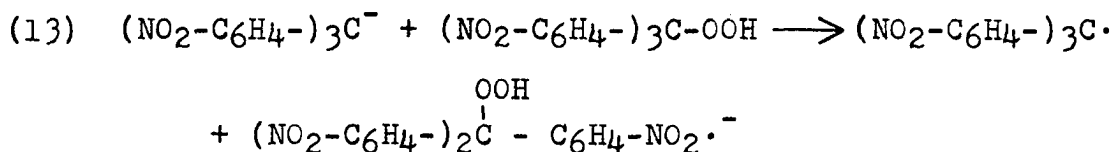
Russell (22) oxidized 2-nitropropane in aqueous solution, containing sodium hydroxide. Products are acetone and nitrite ion, plus small amounts of 2,3-dimethyl,2,3-dinitrobutane, nitrate ion, and organic acids. The oxidation is autocatalytic, and is strongly catalyzed by ferric chloride, ferrous chloride, chromic chloride, and sodium sulfide. Arsenic trioxide inhibits the oxidation strongly, and various oxidation states of manganese are good inhibitors also. The rate of reaction is affected by the concentration of base, the fastest rates being at intermediate base levels. In the oxidation of 2-nitropropane in alcoholic base, there is a much more dramatic effect of base concentration, for under these conditions there is no oxidation if there is no unionized nitro compound present. Hawthorne and Hammond (23) studied the reaction of oxygen and the carbanion from tris-(p-nitrophenyl)-methane. Hydroperoxide was isolated in 59% yield; the remainder of the reaction product being alcohol and a trace of p-nitrophenol. To explain why the reaction

did not give 100% hydroperoxide, they reacted the hydrocarbon and the tris(p-nitrophenyl)-methyl-hydroperoxide in ethanol with potassium hydroxide under nitrogen and observed the formation of the alcohol. A mechanism is written which entails electron transfer from the carbanion to the hydroperoxide to produce the tris(p-nitrophenyl)-methyl radical, the alcohol, and hydroxide ion. Evidence for this is the observation of the radical. This is an unusual system, since the hydro-



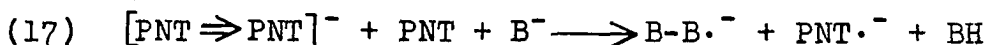
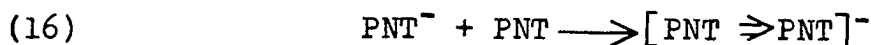
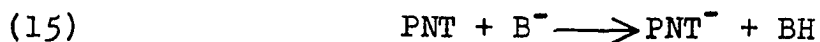
carbon is thought (23) to have a pK_a of 14 ± 2 , while most hydroperoxides are believed to be only slightly more acidic than alcohols, which have pK_a 's around 17. Thus the carbanion and the unionized hydroperoxide can exist together. It is also noted that the radical possesses a considerable stability towards oxygen (24). Interestingly enough, this trinitro compound did not oxidize in t-butyl alcohol with potassium t-butoxide (8). Whether this is due to a solvent effect on an electron transfer reaction is not open to question since it was observed that under conditions where less than a stoichiometric amount of base was present, the compound oxidized. This increase in rate in deficient base was noted in other solvents also (25). Catalysis by added nitro-

benzene was noted when excess base was present. It would seem that in the more weakly ionizing solvents, such as ethanol, the more rapid rate must be due to catalysis by unionized tris(p-nitrophenyl)-methane. The reaction between the carbanion and the hydroperoxide to produce the alcohol and the radical has been formulated as an electron transfer from the carbanion to the hydroperoxide (25), followed by the decomposition of the hydroperoxide radical anion to give either alkoxide ion or alkoxy radical. Russell and coworkers (26-



29) studied the autoxidations of carbanions derived from aliphatic or aromatic nitro compounds. In the most extensively studied case, p-nitrotoluene, the formation of major amounts of p,p'-dinitrobibenzyl and p-nitrobenzoic acid was observed in t-butanol/potassium t-butoxide. It was found that oxygen was not needed for the formation of the bibenzyl which was accompanied by the p-nitrotoluene radical anion in this spontaneous oxidation-reduction process. The following mechanism

was proposed to account for dimer formation.



PNT = *p*-nitrotoluene

$[\text{PNT} \Rightarrow \text{PNT}]^-$ = charge transfer complex

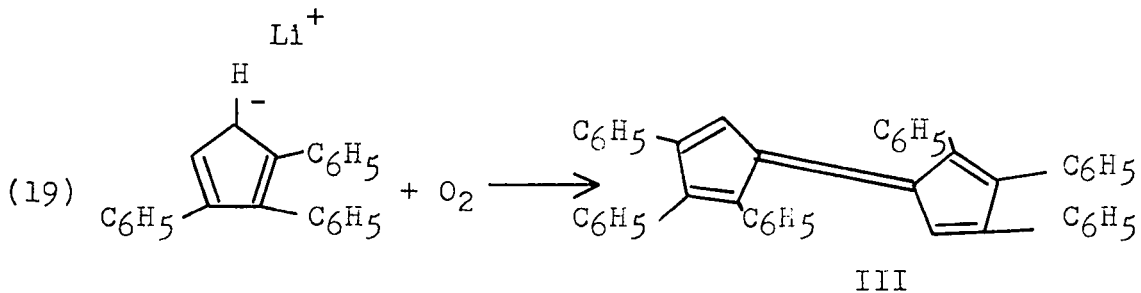
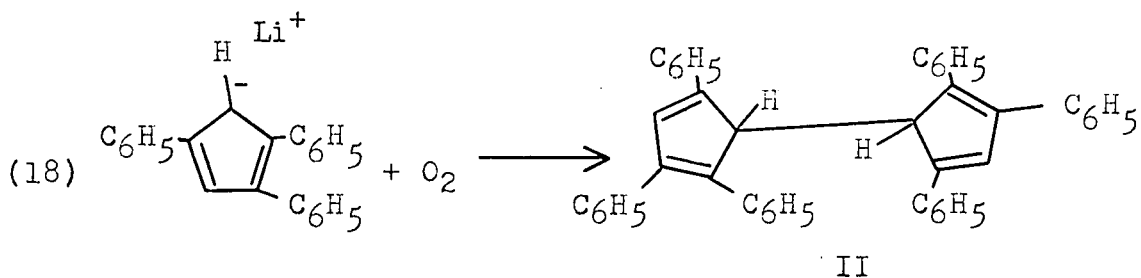
$\text{B-B}\cdot^-$ = *p,p'*-dinitrobibenzyl radical anion

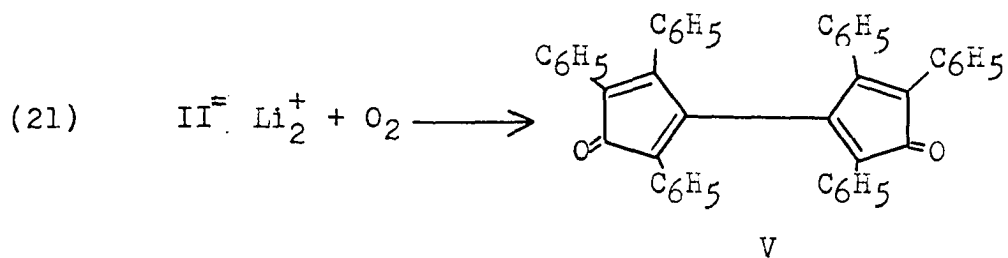
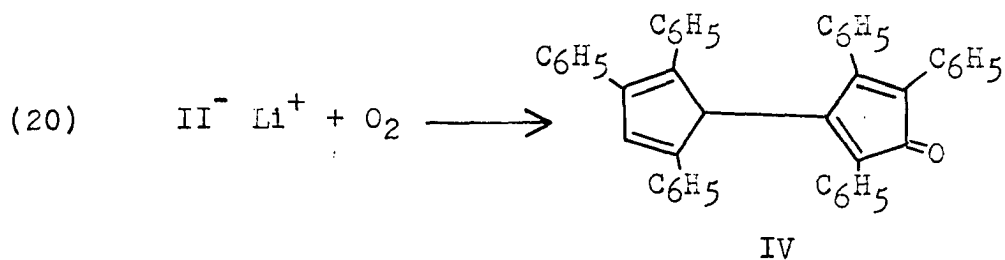
Under drastic conditions the bibenzyl is dehydrogenated by oxygen to yield *p,p'*-dinitrostilbene. The *p*-nitrobenzoic acid apparently arose from reaction of the *p*-nitrobenzyl carbanion with oxygen, although in dimethyl sulfoxide the stilbene is unstable and is oxidized to the acid.

The oxidation of fluorene and a number of 9-substituted fluorenes in pyridine with Triton B as base was studied by Sprinzak (30). He found a 1:1 stoichiometry of fluorene or 9-substituted fluorene with oxygen at -40°C and isolated the 9-hydroperoxyfluorene derivative except in the case of fluorene itself, where fluorenone was the product. No catalysis by ferric chloride or inhibition by arsenic trioxide was observed. The formation of fluorenone from fluorene was interpreted as the result of a β -elimination of water from the intermediate hydroperoxide, for which precedent exists (31). This is in accord with the observed 1:1 stoichiometry. To explain the isolation of alcohols instead of hydroperoxides when the reaction was performed at room temperature or 40°C ,

and the lowering of the oxygen stoichiometry to 1/2:1, Sprinzak (30) proposed a mechanism similar to that proposed by Russell (22) to explain similar stoichiometries. In this mechanism a carbanion displaces an alkoxide ion from an unionized hydroperoxide. In the case of 2-nitropropane, where this was first proposed (22), the solvent was water. The nitro compound was shown to be ionized, but there is a reasonable chance that most of the hydroperoxide molecules are not. In pyridine, with a stronger base present, it is hard to believe that any hydroperoxides remain unionized, for with pK_a 's of 17 or less, they are the most acidic substances present. It is difficult to rationalize the 1/2:1 oxygen to carbanion stoichiometry by other means however; perhaps sufficient hydroxylic protons are present (as water, etc.) so that the hydroperoxides are hydrogen-bonded, and proton transfer can occur simultaneously with nucleophilic displacement. Alternatively, and possibly more reasonably, the reaction proceeds through a small fraction of unionized hydroperoxides. One would not expect displacement by a negatively charged carbon species on a negatively charged oxygen to occur readily, since the charges repel each other. Sprinzak (30) also oxidized 2,3-diphenylindene. Equal amounts of 1,2-diphenyl 1-hydroperoxyindene and 2,3-diphenylindene-1-one were formed. Pratt and Trapasso (32) studied the oxidation of fluorene and analogous compounds on alumina impregnated with sodium meth-

oxide. Although fluorenone and other oxygenated products were formed in analogy with the base catalyzed autoxidations in solution, the nature of this reaction is unclear as sometimes oxygenated products were obtained with unimpregnated alumina. The autoxidation of substituted cyclopentadienyl lithium compounds was reported by Pauson and Williams (33). The monolithium salt of 1,2,3,4-tetraphenylcyclopentadiene gave tetraphenylcyclopentadienone when reacted with oxygen. The 1,2,4-triphenylcyclopentadienyl lithium compound gave a "saturated" dimer II, and the 1,2,3-triphenyl analog an unsaturated dimer III (see below). The monolithium salt of dimer A reacted with oxygen to form a ketone IV, while the dilithium salt gave a diketone V. The formation of dimer II seemingly arises via radical coupling.





Russell and coworkers (26, 27) have studied the autoxidation of a wide variety of hydrocarbons. By using a better ionizing solvent, dimethylsulfoxide (DMSO) (18), the oxidation of less acidic hydrocarbons was accomplished. In DMSO (80%)-*t*-butyl alcohol (20%) (so-called 80-20 DMSO) with potassium *t*-butoxide, triphenylmethane was found to oxidize rapidly when vigorously shaken with oxygen. The product was triphenylmethanol. Similarly diphenylmethane gave the DMSO addition product of benzophenone, 1,1-diphenyl-1-hydroxy-2-(methylsulfinyl)-ethane. It was shown that this addition product probably arose from benzophenone. Fluorene gave the DMSO addition product of fluorenone, xanthene gave xanthone, and 9,10-dihydroanthracene gave anthracene and the DMSO addition product of anthraquinone. The oxidation of diphenylmethane was unusual since more than 1 mole of oxygen per mole

reactant was required. This was shown to be due to the presence of benzhydrol as an isolable intermediate. Benzhydrol, benzyl alcohol, and other primary or secondary alcohols with α -aromatic groups have been shown to oxidize to the corresponding ketones or acids (34-37). In contrast, fluorene absorbed only one mole of oxygen per mole. Since no ESR signal could be detected when the oxidation was interrupted, but an ESR signal could be detected if the oxidation of 9-fluoreno \dot{l} was interrupted, the alcohol is not an intermediate which reaches an appreciable concentration during the oxidation of fluorene in t-butyl alcohol (29). The ESR spectrum of fluorenone ketyl could be detected in an interrupted oxidation of fluorene in 80/20 DMSO. This does not however prove that 9-fluoreno \dot{l} is an intermediate since the fluorenyl anion reacts with fluorenone to produce the ketyl of fluorenone in 80/20 DMSC (29). This is explainable as due to a fast β -elimination of the 9-hydroperoxyfluorene to give 9-fluorenone. Even in 80/20 DMSO, the hydroperoxide apparently eliminates very fast to give the ketone.

Janzen (25) studied the effect of nature of base and solvent on the autoxidations of hydrocarbons. The effect of solvent on the oxidation of fluorene using potassium t-butoxide as base is shown in Table 1. The general trend is polar solvents accelerate the uptake of oxygen as compared to nonpolar ones with the exception of t-butyl alcohol, which is

Table 1. Solvent effect on the oxidation of fluorene

| Solvent | Relative rate |
|----------------------------------|---------------|
| t-Butanol (100%) | 1 |
| Benzene (80%) t-butanol (20%) | 2.5 |
| Dioxane (80%) t-butanol (20%) | 19 |
| Morpholine (80%) t-butanol (20%) | 41 |
| Piperidine (80%) t-butanol (20%) | 45 |
| Pyridine (80%) t-butanol (20%) | 90 |
| HMPA (80%) t-butanol (20%) | 160 |
| DMF (80%) t-butanol (20%) | 205 |
| DMSO (80%) t-butanol (20%) | 220 |
| DMSO (10%) t-butanol (90%) | 19 |

probably more polar than several of the faster solvents. This is probably due to strong hydrogen bonding in t-butyl alcohol. The ordering is in accord with that predicted if the rate determining step was the formation of the fluorenyl carbanion. In this thesis, it will be shown that in neither t-butyl alcohol nor 80/20 DMSO is the ionization of fluorene the slowest step, and that in both cases it is much faster than the rate of oxidation. The solvent effect is the opposite of the order predicted (18, 19) if electron transfer is the slow step, and the carbanion is considered to be "stable". Electron transfer is almost certainly the rate determining step, as data from catalyzed oxidations show (25). The effect of base on the oxidation of triphenylmethane in 80/20 DMSO was also studied (25) (Table 2). The order observed is

Table 2. Effect of base on the oxidation of triphenylmethane

| Base | Initial rate ^a |
|-------------------------------|---------------------------|
| Lithium- <u>t</u> -butoxide | 0.15 |
| Sodium- <u>t</u> -butoxide | 0.32 |
| Potassium- <u>t</u> -butoxide | 0.82 |
| Sodium methoxide | 0.20 |

^aMoles O₂/mole ϕ_3 CH-min.

in agreement with the order of dissociation of the alkali metal alkoxides $K > Na > Li$ (18). This supports an ionization rate-limited mechanism for triphenylmethane, and evidence for this will be presented in this thesis. The most base-strengthening solvent used was hexamethylphosphoric triamide (HMPA). The three isomeric picolines which oxidized slowly in 80/20 DMSO, oxidized rapidly in this solvent (25).

Russell et al. (26, 27, 29) also showed that toluenes substituted with strongly electron withdrawing groups oxidized in DMSO 80/20. Products from the oxidations of phenyl p-tolylsulfone and methyl p-toluate were mixtures of the corresponding carboxylic acid and stilbene. A wide variety of other compounds were oxidized, including ketones, sulfones, nitriles, esters, and alcohols.

The mechanism of dimerization of substituted toluenes was shown to involve the intermediate aldehydes by experiments involving the addition of 5% of radioactive p-phenyl-

sulfonylbenzaldehyde to an oxidation of phenyl *p*-tolyl sulfone.¹ The radioactive aldehyde was converted to *p*-phenylsulfonylbenzoic acid and *p,p'*-di(phenylsulfonyl)stilbene in the same ratio as in the oxidation of phenyl *p*-tolyl sulfone.

In some cases, oxidative dehydrogenation is observed (29) instead of oxygenation. Table 3 shows examples from autoxidations in 80/20 DMSO with potassium *t*-butoxide.

Table 3. Oxidative dehydrogenation in 80% dimethyl sulfoxide-20% *t*-butyl alcohol

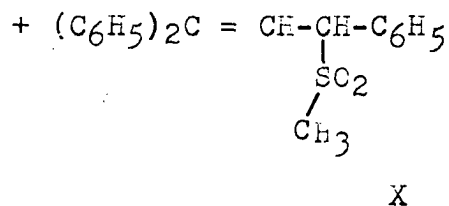
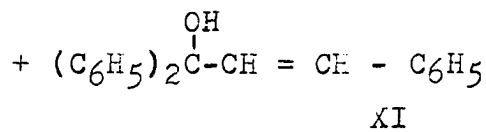
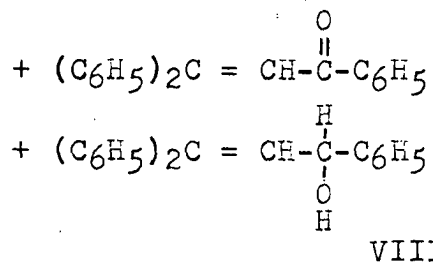
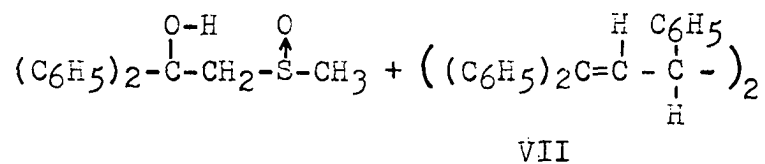
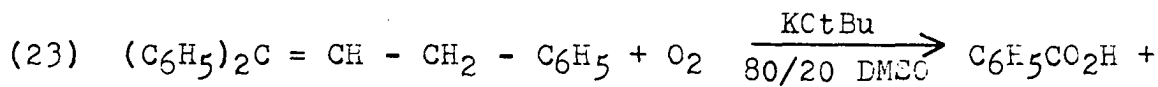
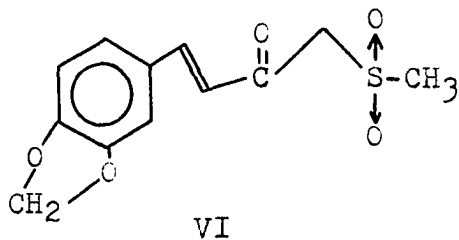
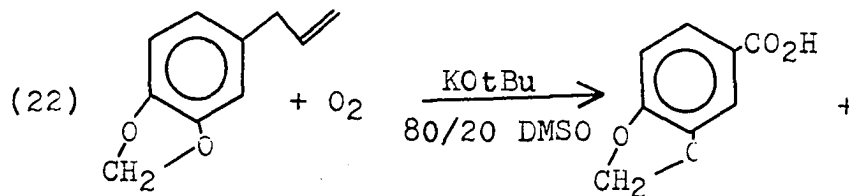
| Substrate | |
|-------------------------------|---------------------------------|
| <u>Sym</u> -tetraphenylethane | Tetraphenylethylene (96%) |
| Acenaphthylene | Napthalic anhydride (63%) |
| 9,10-Dihydrophenanthrene | Phenanthrene (88%) |
| 1,2-Dihydropyrene | Pyrene (90%) |
| 9,10-Dihydroanthracene | Anthracene (69%) |
| | Anthraquinone (11%) |
| | Anthraquinone-DMSO adduct (10%) |
| Acridan | Acridene (88%) |

Barton and Jones (38) recently oxidized several hydrocarbons in 80/20 DMSO using potassium *t*-butoxide as base. Safrole or isosafrole oxidized to give piperonylic acid in 42% yield. A sulfone was also formed, VI. 1,2-Dihydro-napthalene gave napthalene in 89% yield. 1,1,3-Triphenyl-

¹G. A. Russell and K. Y. Chang, Ames, Iowa. Mechanism of dimerization. Private communication. 1965.

prop-1-ene was oxidized to give a variety of products: benzoic acid, the DMSO addition product of benzophenone, a dimeric hydrocarbon VII, 1,1,3-triphenylprop-1-ene-3-one, two isomeric alcohols VIII and XI, and an unsaturated sulfone X. 9,10-Dihydroanthracene gave a mixture of anthracene and DMSO addition product of anthraquinone upon oxidation in 80/20 DMSO and potassium t-butoxide. 9-Hydroperoxyanthraquinone gave both anthracene and anthraquinone (and its addition product with DMSO) when treated with potassium t-butoxide in 80/20 DMSO under nitrogen. Apparently all of the anthracene in the oxidation did not arise from the hydroperoxide, as the ratio of the two products was different.

The oxidation of methyl groups on aromatic rings has been studied (39-42). Pyrrole was oxidized in t-butyl alcohol with potassium t-butoxide. Two moles oxygen were absorbed when 4:1 excess of base was used. The three isomeric picolines were oxidized in 80% dimethylformamide (DMF) 20% t-butyl alcohol, using potassium t-butoxide as base. In ten minutes, at 4 atmospheres of oxygen, the three isomeric picolines gave respectively yields of 59% 2-picolinic acid, 70% 3-picolinic acid, and 80% 4-picolinic acid (39). These authors found that the addition of lead (II) nitrate lowers the stoichiometry of the pyrrole oxidation from 2:1 to 7:4. The activation energy of the pyrrole oxidation was reported to be 4 kcal/mole at 25° to 55°C. Wallace et al. (40, 41)



were able to oxidize toluene in diphenyl sulfoxide at 100°C with potassium t-butoxide. The experimental data is given in Table 4. These authors plot moles oxygen absorbed to moles starting diphenylmethane versus time. From this graph,

Table 4. Oxidations in diphenyl sulfoxide

| Substrate | Base/ substrate | Product (yield) | Mole O ₂ / substrate | Time |
|-----------------|--------------------|--|------------------------------------|--------|
| Toluene | 3 | Benzoic acid (64%) | 1.06 | 21 hr. |
| o-Xylene | 3 | o-Toluic acid (54%) Phthalic acid (37.5%) | 1.07 | 21 hr. |
| p-Nitrotoluene | 1 | p-Nitrobenzoic acid (28%) | -- | 40 hr. |
| Diphenylmethane | 1.74 | Benzophenone (68%) | -- | 23 hr. |

diphenylmethane has absorbed about 0.6 moles oxygen per mole in one hour. The similar plot for toluene shows a region of autocatalysis after about one hour. At that point less than 0.10 mole oxygen per mole of toluene had been absorbed. These oxidations are obviously much different from those in 80/20 DMSO, 80/20 DMF, HMPA, or other polar aprotic solvents at room temperature, since in 80/20 DMSO for example, diphenylmethane picks up more than 1 mole of oxygen in 2 minutes and toluene is unoxidized. Although toluene is apparently ionized in

diphenyl sulfoxide at 100° at a rapid enough rate to account for the observed oxidations, from the rate of oxidation of diphenylmethane, and from the autocatalytic nature of the toluene absorption curve, one might suspect a radical chain mechanism, where the chain process involved hydrogen abstraction by peroxy radicals. The initiation processes might be via reaction of the appropriate carbanion with oxygen. At 100° long chain radical processes are favorable, if an initiation process is available. The actual chain length in these diphenyl sulfoxide oxidations may be a lot shorter than usually observed in initiated autoxidations, since an easy initiation process is available. Toluene was also oxidized in hexamethylphosphoramide (HMPA) with KOtBu (42). The results for toluene and substituted toluenes are shown in Table 5.

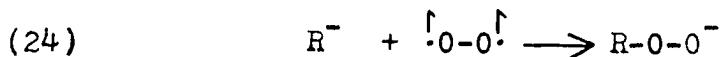
Table 5. Oxidation of substituted toluenes

| Substrate | Relative rate | Product | Yield |
|------------------|---------------|---------------------------------|--------|
| Toluene | 1.0 | Benzoic acid | 25-30% |
| <u>o</u> -Xylene | 3.1 | Phthalic acid | 35-40% |
| <u>m</u> -Xylene | 0.5 | Isophthalic acid | 50% |
| <u>p</u> -Xylene | 0.1 | Terephthalic acid | 15% |
| <u>p</u> -Cymene | 1.0 | <u>p</u> -Isopropylbenzoic acid | 10% |
| Tetralin | 1.0 | Phthalic acid | 46% |

These oxidations are very slow, 1/2 of maximum conversion of o-xylene taking one hour. To oxidize 10-15% of the starting toluene takes 3 hours, after which the rate decreases rapidly with time. The relative rates reported are in agreement with the reported rates of exchange (43).

B. Intermediacy of Radicals

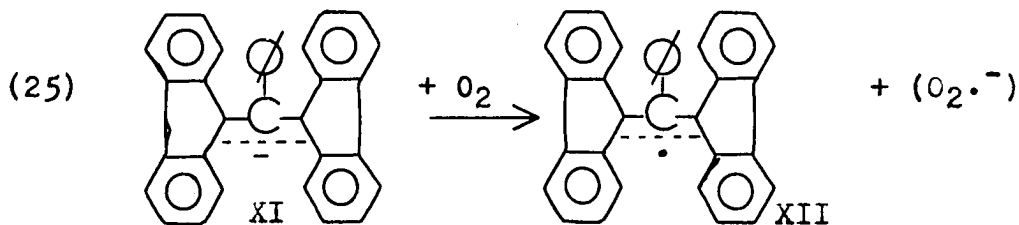
Considerable controversy exists over whether these base-catalyzed oxidations are radical chain processes, non-chain radical processes, or concerted direct additions of oxygen to carbanions. Direct oxygen addition is disfavored by the spin conservation rule (9, 22). Since oxygen is in a triplet state at room temperature (44), if it added to a carbanion



to produce a hydroperoxy ion, a change in the number of unpaired spins of electrons would be necessary. The spin conservation rule states that the total number of unpaired electron spins in a system does not change during the period when a bond is being made or broken. No exceptions are known to this rule (22). In addition about 24 kcal/mole are required to convert oxygen to its lowest excited singlet state, and about 38 kcal/mole to the next lowest one (44).

Evidence for the intermediacy of radicals in the reaction of carbanions with oxygen has been presented by Reid (45, 46) and Pacifici et al. (17). Reid found that peri-

perinaphthene when treated with oxygen and KOH in alcoholic ether gave rise to a radical, which slowly formed a "peroxide". The fate of the oxygen in the initial reaction was said to be potassium peroxide. Definitive proof of the structure of this radical was not presented; another possible structure for it whose ESR spectra might be similar is the ketyl of perinaphthenone. The perinaphthyl radical was proven to be produced from the reaction of perinaphthene with oxygen in *t*-butyl alcohol containing potassium *t*-butoxide.¹ Pacifici *et al.* presented evidence that treating the carbanion of 2-phenyl-bis(biphenylene)-propene (XI) with oxygen produced Koelsch's (XII) radical, which is known to be stable towards

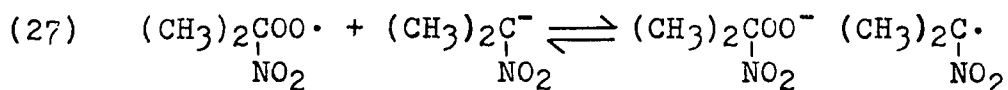
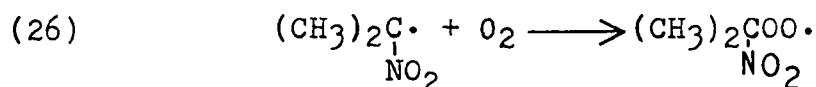


oxygen (47). They also found the rate of this electron transfer to be much faster in non-polar solvents such as ether or benzene than in DMSO, DMF, or pyridine. The reaction is first order in carbanion although the stoichiometry of the reaction is $2\text{R}^- \longrightarrow 1\text{R}\cdot + \text{X}$. It is interesting to note that a sample of Koelsch's radical kept in air for 23 years still contained a high degree of radical content (47).

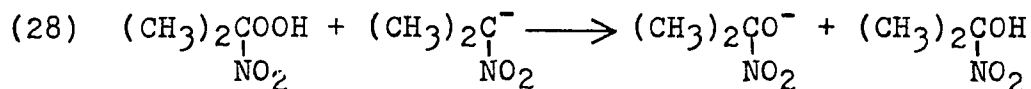
¹G. A. Russell and W. Danen, Ames, Iowa. Identity of radical from perinaphthene. Private communication. 1966.

Fluoradene apparently also gives rise to the corresponding radical in basic solution with oxygen, but dimerization is very fast even in the presence of oxygen, and the product observed is a 12,12'-difluoradenyl (48).

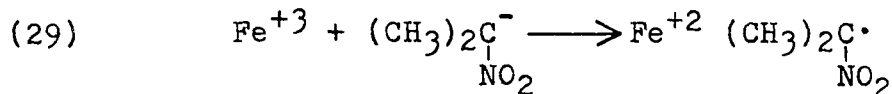
In the oxidation of 2-nitropropane, Russell (22) proposed a chain mechanism. During kinetic studies of this auto-oxidation in basic solution, catalysis by ferric ion and inhibition by arsenic trioxide was observed. Ferric ion is recognized to be a good electron acceptor, and arsenic trioxide is known to destroy hydroperoxides. The following propagation steps were written:



The observed products (acetone and nitrite ion), the stoichiometry of 1/2 mole oxygen to 1 mole 2-nitropropane and the effect of arsenic trioxide were explained by:

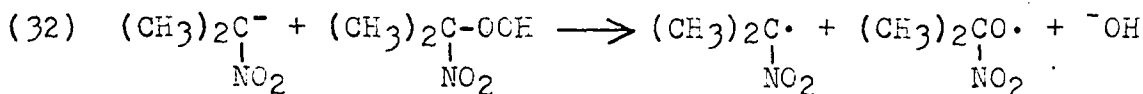
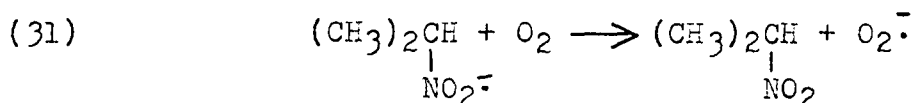
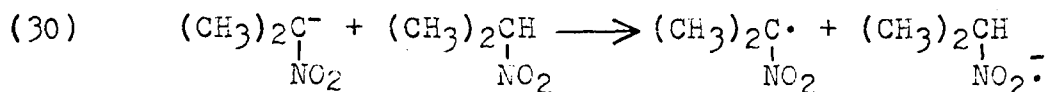


Catalysis and initiation presumably proceeds via:



More recently, Russell et al. (29) have revised this mechanism. The propagation steps remain unchanged, but another

initiation step is added to explain the fact that a deficiency of base accelerates the reaction. The details of the reaction of the carbanion with the hydroperoxide, which results in chain branching, and hence catalysis, have also been

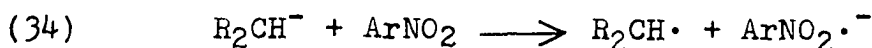
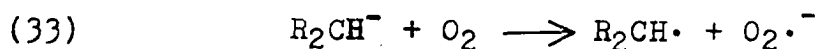


changed. A similar mechanism is proposed to explain inhibition of oxidation of tris(p-nitrophenyl)-methane in deficient base (29). Evidence for the reaction between carbanion and unionized nitro compound comes from ESR studies of electron transfer between many carbanions and many nitro compounds, including those of interest here (49). Further evidence is that nitrobenzene catalyzes the oxidation of 2-nitropropane in the presence of excess base. The reaction between the 2-nitropropane radical anion and oxygen to regenerate starting material and superoxide ion is reasonable in view of evidence presented in this thesis for nitrobenzene.

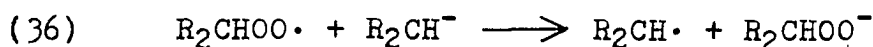
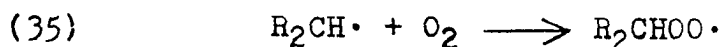
In t-butyl alcohol with potassium t-butoxide, the reaction of fluorene with oxygen was found to be strongly catalyzed by nitrobenzene or other nitroaromatics (26, 27). In

the absence of oxygen the ESR spectra of nitrobenzene radical anion could be readily detected, hence the oxidation was thought to be a radical process. The oxidation of fluorene, with various nitroaromatics as catalysts showed a correlation of log rate vs σ for the substituent on the nitrobenzene ring. The same slope (ρ) was obtained for ESR rate measurements of electron transfer from fluorenyl anion to these nitroaromatics (27, 28). These data are seen as evidence for the intermediacy of radicals in the base-catalyzed oxidation of fluorene and by extension, other hydrocarbons. A mechanism consistent with these observations is written as follows:

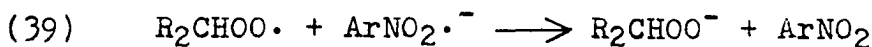
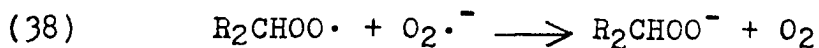
Initiation



Propagation



Termination



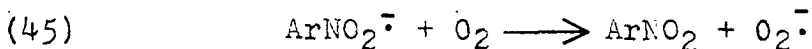
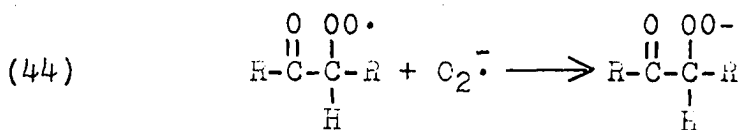
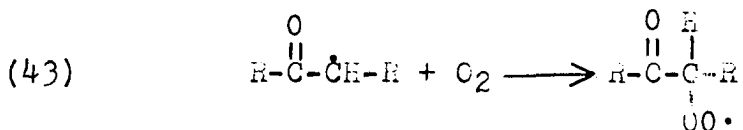
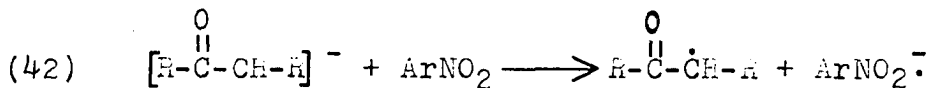
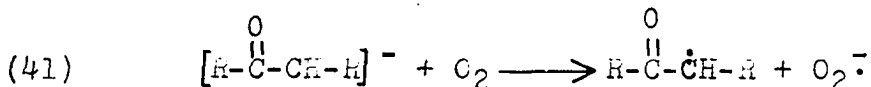
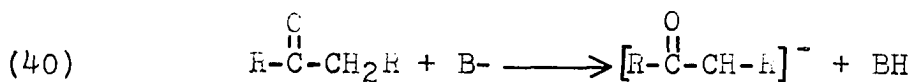
Russell *et al.* (29) have calculated the chain length of the fluorene oxidation in *t*-butyl alcohol to be 21 from the following data. The initial rate of oxidation of 0.1M fluorene

was 0.0015 moles O_2 /l min. In the presence of 0.0048M nitrobenzene the rate was increased to 0.0036 moles O_2 /l min. The increase in oxidation due to nitrobenzene was thus 0.0021 moles O_2 /l min. The rate of initiation found for the reaction of 0.1M fluorene with 0.0048M nitrobenzene was 0.0001 moles electron-transfer product/l min. (nitrobenzene radical-anion/l min.). Hence the formation of one fluorenyl radical leads to the consumption of approximately 21 molecules of fluorene, i.e., a chain length of 21.

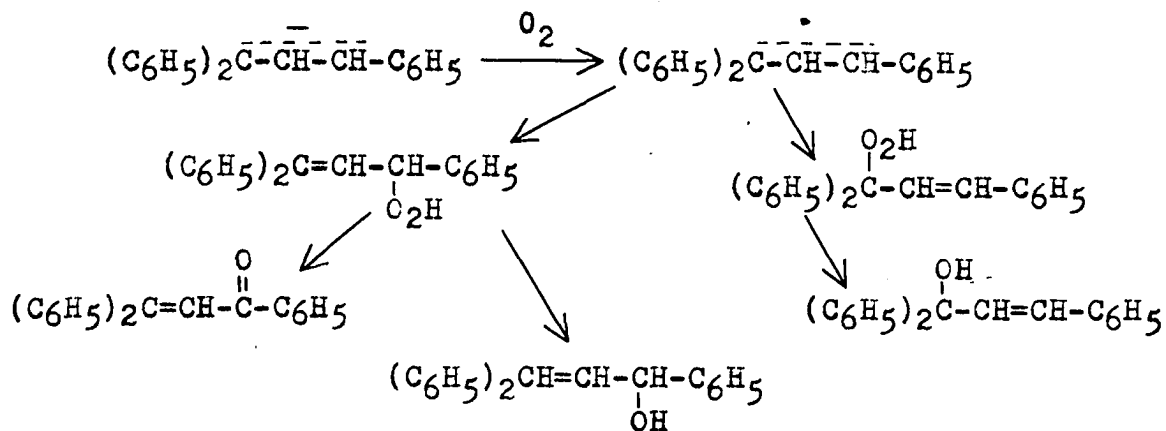
In the case of hydrocarbons which oxidize to dehydrogenated products, the ESR spectra of the corresponding radical-anion has sometimes been observed by reacting the hydrocarbons with base and a trace of oxygen. Examples where this was accomplished are acridan, 9,10-dihydroanthracene, and 9,10-dihydrophenanthrene (29). It is likely that the reaction involves attack of oxygen on the dianion of the dihydro compound.

Oxidizable ketones also give rise to radicals. The ESR spectra of the radical anions of 1,2-diketones has been found in interrupted ketone oxidations (29). The case of the base catalyzed autoxidation of acetophenone has been investigated thoroughly. The reaction is catalyzed by nitroaromatics. The same slope is gotten from plots of log oxidation rate vs σ and log electron transfer rate vs σ . In this case a calculation of chain length similar to that performed with

fluorene, yielded a chain length of one. Presumably the intermediate peroxy radical did not react with the enolate anion. A possible mechanism is written below:

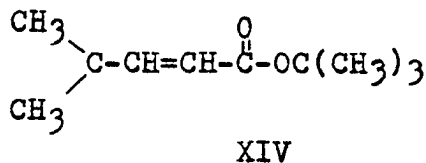
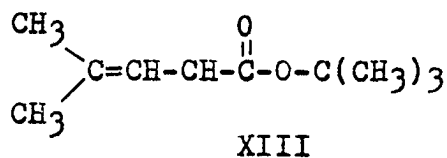


Earlier in this discussion, it was noted that Barton and Jones (38) had found a dimeric product in the oxidation of 1,1,3-triphenylprop-1-ene in 80/20 DMSC with $\text{K}\underline{\text{C}}\text{tBu}$. Barton and Jones (38) explained the dimer formation in terms of a radical intermediate, and drew the following schematic mechanism:



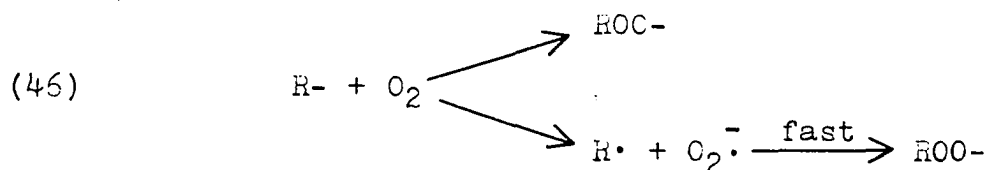
The formation of a sulfone was also rationalized by radical intermediates. Barton and Jones (38) also seemed to favor a radical intermediate in the oxidation of dihydroaromatics.

Gersmann *et al.* (15, 16) oxidized two isomeric unsaturated esters (XIII and XIV). They found that in an initiated

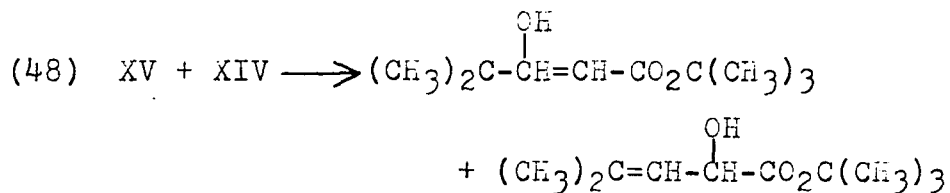
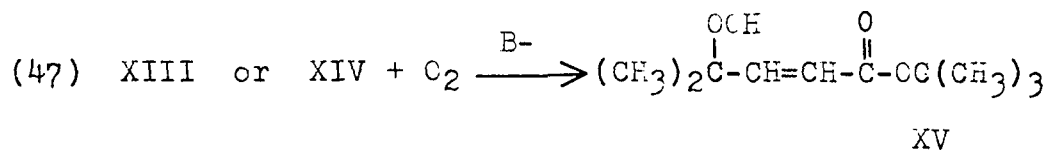


autoxidation, using azo-bis (2-methyl-2-propylnitrile) in benzene at 60°, only γ -oxidation products were found, starting from either A or B, while in a base catalyzed oxidation, using potassium t-butoxide in dimethoxyethane at -80°, at least 25% α -oxidation products were obtained. These authors

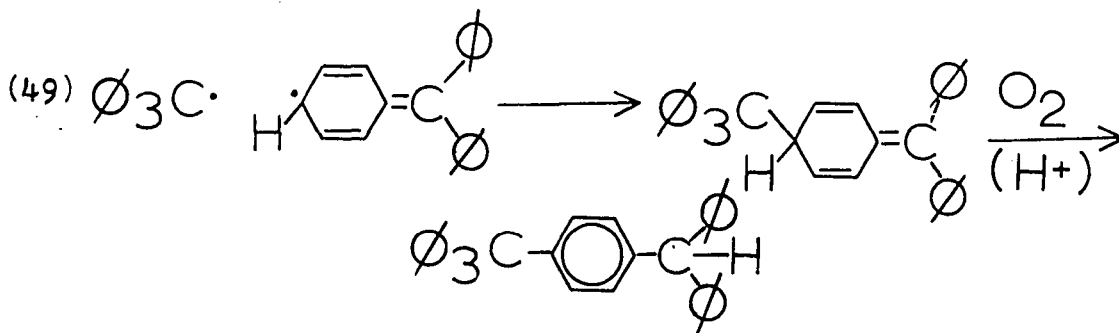
argued that in a free radical chain oxidation, only γ -products should be expected, as the intermediate radical would be best described as the tertiary radical. In a direct oxygen addition, a mixture would be anticipated as the negative charge would be localized on the secondary carbon, but tertiary carbanions are known to be more reactive towards oxygen than secondary. Gersmann et al. did not attempt to distinguish between a concerted addition and an electron transfer to oxygen followed by rapid combination of the carbon radical and superoxide ion,



With the great difference in reaction conditions between the two types of oxidation, these experiments can not constitute a proof that a radical chain process does not operate in base catalyzed autoxidations, but it is indicated that if free radicals are involved in a chain process in the oxygenation of carbanions, the radicals have different environments and/or lifetimes than those in the initiated process. Apparently the results can also be explained by the possible reaction:

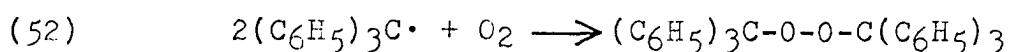
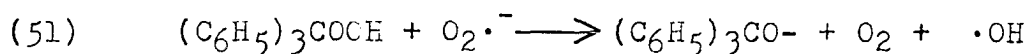
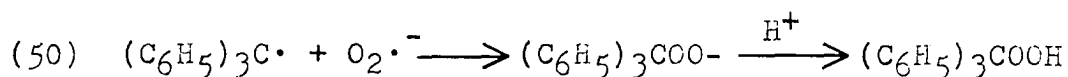


Some information about the postulated coupling of carbon radicals with superoxide ion has been obtained by Le Berre and Berguer (50). They reacted sodium superoxide with triphenylmethyl radicals in tetrahydrofuran. The products observed were triphenylmethanol, triphenylmethyl peroxide, and *p*-benzhydryltetraphenylmethane. This last substance arises from the "head" to "tail" dimerization of triphenylmethyl radicals, followed by the rearrangement of a proton by the base, in this case, superoxide ion. The other two products



are said to arise in secondary reactions from the initial product, triphenylmethyl hydroperoxide, which however, was not isolated. It was shown that triphenylmethyl hydroperoxide reacts with sodium superoxide in THF to produce the

sodium salt of trityl alcohol and oxygen. The presence of trityl peroxide in the trityl radical-superoxide ion reaction is then explained by the reaction of the oxygen produced from the hydroperoxide with the radicals.



Le Berre and Berguer (50) found that the function of the superoxide ion was not just to act as a base, for the treatment of trityl hydroperoxide with sodium t-butoxide (excess) did not decompose it. The observation by Kharasch et al.

(51) that the sodium salt of α -cumyl hydroperoxide reacted with the unionized hydroperoxide to give cumyl alcohol and oxygen does not seem to be important, as apparently all the trityl hydroperoxide is ionized. That this sort of decomposition can occur in the trityl hydroperoxide system, was however demonstrated by these authors (50).

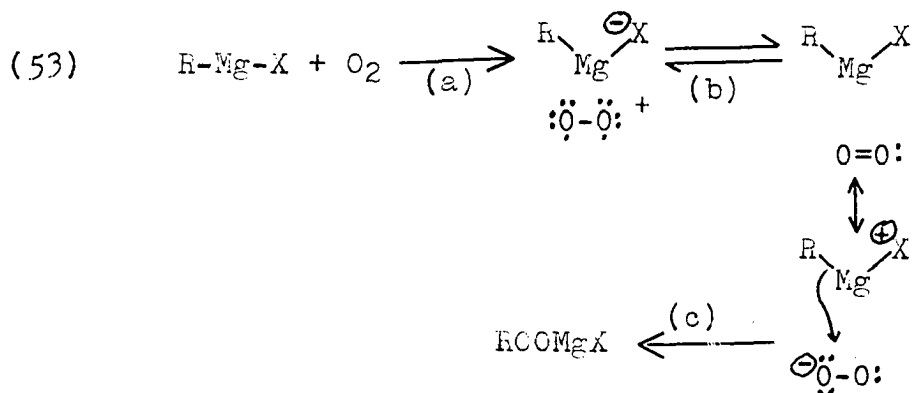
A number of reports of reaction of oxygen with organometallic compounds have been made. Schlenk and Marcus (3) reacted oxygen with triphenylmethylsodium in ether and observed the formation of trityl peroxide. Kraus and Rosen (2) repeated this work in liquid ammonia and found the same product, although the initial product which precipitated from

solution was said to be ether soluble, the insoluble peroxide precipitating from the ether after standing in air. The results in ether were questioned by Bachmann and Wiselogle (4) who found 67% triphenyl carbinol and only 4% trityl peroxide. Ziegler and Schnell (5) reported the formation of 1,1-diphenylethanol and 2,2,3,3-tetraphenylbutane from the reaction of 1,1-diphenylethylpotassium with oxygen. Wooster (6) claimed to find tetraphenylethylene from the reaction of oxygen and diphenylmethylsodium in liquid ammonia. The oxidation of Grignard reagents has been studied. Bodroux (52) found phenol from the reaction of phenylmagnesium bromide with air. Wuyts (53) found biphenyl, phenyl ether, *p*-terphenyl, and polymer as well as phenol. Schmidlin (54) reacted triphenylmethylmagnesium bromide with oxygen in ether, and found that trityl peroxide precipitated. Porter and Steel (7) repeated the phenyl Grignard oxidation and found all the previous products reported, as well as quinone and *p,p'*-dihydroxybiphenyl. They postulated the salt of phenyl hydroperoxide as an intermediate. Gilman and Wood also oxidized phenylmagnesium bromide (55). They found the previous products as reported by Porter and Steel (7) but also found a large amount of phenylmethyl carbinol. They attributed its formation to the reaction of phenyl Grignard and acetaldehyde, the latter substance being formed from the autoxidation of the ether. It could also come about via radical combination

processes (22). Kharasch et al. (56) confirmed the presence of the phenylmethyl carbinol as a product. Walling and Buckler (57, 58) investigated a variety of Grignard oxidations. Aliphatic Grignards in general reacted smoothly to give hydroperoxides when inverse addition was used, ensuring an excess of oxygen. Apparently when the Grignard reagent is in excess, the hydroperoxide salt reacts rapidly with a molecule of Grignard to produce two molecules of alcohol. The oxidation of aromatic Grignards produced the same products cited previously (7, 52-56). A free radical mechanism was disfavored since in the oxygenation of aliphatic Grignards, the addition of n-butyraldehyde had no effect (recovered; no acid formed), diphenylamine did not retard the reaction, and cumene was not consumed when added. The products can be explained by other than free radical mechanisms.

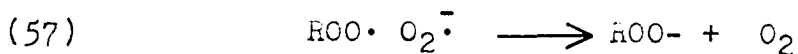
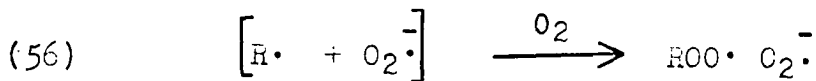
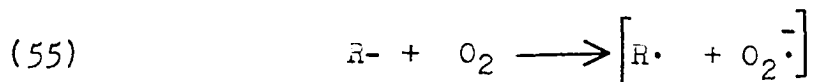
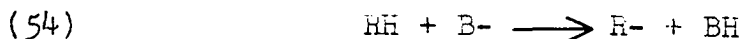
Walling and Buckler (57, 58) favor a concerted oxygen insertion in the carbon-metal bond after a prior complexing. The schematic mechanism thus proposed is shown below. Apparently the unpaired electrons on oxygen are paired in step (b) which is written as an equilibrium. It may be true that the mechanism of carbanion-oxygen reactions varies with the structure of the carbanion. In the case of Grignard reagents, the organic reactant looks very little like a free carbanion; the carbon-metal bond is thought to be quite covalent. Hence, Grignard reagents may react by a different

path than alkali metal salts of hydrocarbons.



The influence of solvent may also play a large part in determining the reaction pathway. As an example, in this thesis it will be shown that triphenylmethane gives the hydroperoxide on reacting with base and oxygen. Only in the case where pyridine was present as solvent was any trityl peroxide isolated.

A radical mechanism will be proposed in this thesis to explain the results to be presented. In outline form, it is given below.



C. Acidity of Hydrocarbons

The observation (59) that the rate of some base-catalyzed autoxidations was controlled by the ionization of a carbon-hydrogen bond is expanded in this thesis. Thus, in certain cases, the rate of oxidation is equal to the rate of ionization.

The abstraction of a proton from carbon is one of the most important reactions in chemistry. It is clearly useful to be able to measure the ease of abstraction of a proton bound to carbon, i.e., the acidity of the C-H bond. Either an equilibrium acidity, usually expressed as a pK_a ($-\log$ dissociation constant) or a kinetic acidity can be measured. The two types of measurements have been related, apparently successfully (60, 61).

Rates of ionization may well prove as useful theoretically as equilibrium acidities, but the theory of absolute rates is a very complex one, and accurate calculations have only so far been made for extremely simple molecules, such as diatomic ones (62).

To obtain pK_a 's of weak acids is difficult and there immediately arises two major problems. First, there are experimental difficulties. In general, C-H bonds are not ionized in aqueous solution (63). (There are, however, some exceptions, when a bond is sufficiently activated by electron

withdrawing groups.) Thus simple titration techniques are impossible, and even colorimetric or spectrophotometric techniques may fail if appropriate characteristic absorptions of unionized and ionized molecule can not be found. The experimental problems are not insurmountable. Streitwieser et al. (60) have recently reported equilibrium measurements in cyclohexylamine and Steiner and Gilbert (64) in DMSO. The second difficulty is more troublesome. How does one compare data from a polar, hydrogen bonding, protic solvent like water to solvents which are either much less polar, and less proton donating such as aliphatic amines, or to solvents like DMSO which apparently do not hydrogen bond anions at all or at best very weakly? In order to get a true pKa, the effect of quite different environment on the activity of the ions formed, and on the ion product of water would have to be known. There is apparently not a lot of data on activity coefficients of ions in organic solvents, except in mixtures with water, or for alcohols.

The equilibrium data which does exist for hydrocarbons is mostly from metallation reactions in ether (65, 66). By this technique, McEwen (65) developed an acidity scale (Table 6). For many years, this was the only scale of acidity for weakly acidic hydrocarbons.

Streitwieser et al. (60) have determined pKa's in cyclohexylamine with cesium or lithium cyclohexylamide by spectro-

Table 6. McEwen acidity scale

| Compound | pKa |
|------------------|------|
| Methanol | 16 |
| 9-Phenylfluorene | 21 |
| Indene | 21 |
| Fluorene | 25 |
| Xanthene | 29 |
| Triphenylmethane | 32.5 |
| Diphenylmethane | 35 |
| Cumene | 37 |

scopic measurement of relative amounts of anion formed for pairs of carbon acids. A portion of this scale is given in Table 7. Steiner and Gilbert (64) established a pKa scale in DMSO using dimethylpotassium as base (see Table 7). Similar values were obtained with 0.11% water in DMSO with KOH as

Table 7. Comparison of three acidity scales

| Compound | pKa ^a | pKa ^b | pKa ^c |
|----------------------------|------------------|------------------|------------------|
| 9-Phenylfluorene | | (18.5) | 21 |
| 4,5-Methylenepheneanthrene | <19.5 | 22.6 | |
| 2,3-Benzofluorene | <19.5 | 23.2 | |
| Fluorene | 20.5 | 22.9 | 25 |
| 9-Phenylxanthene | 24.3 | | |
| Triphenylmethane | 27.2 | 32.5 | 33 |
| Diphenylmethane | 28.6 | 34.1 | 35 |

^aResults of Steiner and Gilbert (64).

^bResults of Streitwieser et al. (60).

^cResults of McEwen (65).

base, and 0.02% methanol in DMSO with potassium methoxide. It is noted that Steiner and Gilbert's (64) scale is much more compressed than that of Streitwieser et al. (60), although both reflect the same overall trend. Both groups of authors essentially calculated pKa's on the basis of H₋ scales (66-69). H₋ is defined as follows:

$$(58) \quad H_- = -\log a_{H^+} \frac{\gamma_{I^-}}{\gamma_{IH}} = pK_{IH} + \log \frac{\gamma_{I^-}}{\gamma_{IH}}$$

where a_{H^+} is the activity of hydrogen ion, γ_{I^-} is the activity coefficient of indicator anion, and γ_{IH} is the activity coefficient of unionized indicator. It is assumed that $\frac{\gamma_{I^-}}{\gamma_{IH}}$ is a property of the solvent only. This is probably valid, and pKa's calculated for a given medium or media closely resembling each other are consistent. However, the activity coefficient ratio may change drastically as one goes from an aprotic polar solvent to a hydrogen-bonding polar solvent to an aprotic nonpolar solvent to a proton-donating nonpolar solvent. The H₋ method is internally consistent, and provides relevant qualitative measure of acidity. The pKa's, however, although usually referenced to aqueous solution at the lower (more acidic) end of the scale, may be compressed or expanded relative to an aqueous solution at the upper end. A good example of this is the pKa scales set up by Steiner and Gilbert (64) and Streitwieser et al. (60). The former authors utilized the H₋ technique directly in cal-

culating pKa's in DMSO, while the latter utilized equilibrium constants for pairs of indicators, but still made the assumption implicit in the H_- technique, namely that $\frac{\gamma_{I^-}}{\gamma_{HI}} = 1$ or that the activity coefficient ratio was a constant. Both groups assumed one pKa, at the low end of the scale, for a compound whose pKa had been independently measured in aqueous solution. Not only were the scales quantitatively different, but in one case (2,3-benzofluorene vs fluorene) there was a qualitative disparity (see Table 7). The explanation of this lies with the assumption concerning the activity coefficient ratios. If both solvent systems interact with anion and hydrocarbon similarly, then the ratio will be reasonably constant, and the pKa's will be very similar. But in DMSO, salts are thought to be dissociated (18) and anions essentially unsolvated, while cations are often highly solvated. In cyclohexylamine, evidence has been presented (70-74) that lithium cyclohexylamide is not dissociated, and indeed that the ion-pair is the effective base in this solvent. Aggregation of ion-pairs is very important here, while not observed in DMSO. Cyclohexylamine is essentially a non-polar solvent. The difference in the pKa values is probably due primarily to the fact that in DMSO free anions are involved, while in cyclohexylamine, the ion pairs. Certainly $\frac{\gamma_{I^-}}{\gamma_{IH}}$ (free) would not be expected to be similar to $\frac{\gamma_{I^-M^+}}{\gamma_{IH}}$. Other differences in the two solvents may be important in the equilibria also. It

is important to note that neither of these scales may be similar to an aqueous scale, if such could be determined. Hydrogen-bonding alone, in water solution, should be much more important than in either DMSO or cyclohexylamine, and would be expected to affect the activity coefficient ratios differently.

The theoretical solution to this problem is not obvious; the evaluation of the activity coefficients of ions as a function of solvent might be possible, but undoubtedly difficult. The scales are useful from a practical standpoint, but have to be known for each solvent of interest. Even changing a solvent slightly, as from pure DMSO to 80% DMSO-20% t-butyl alcohol, may change the properties greatly. In this thesis the discovery of a large isotope effect on the oxidation of triphenylmethane or diphenylmethane in 80/20 DMSO is presented. The oxidation rate is shown to be identical to the rate of exchange. Cram (75) found only a small isotope effect on exchange reactions in pure DMSO, and recently Hoffmann et al. (76) reported no isotope effect for exchange of toluene in pure DMSO. Presumably equilibrium acidities could also be different in 80/20 than in pure DMSO.

Other recent thermodynamic approaches have been made. Applequist and O'Brien (77) measured the equilibrium constants between alkyl and aryllithiums and the appropriate iodides in ether or ether-pentane. Salinger and Dessy (78)

and these are the best available equilibrium data for saturated, aliphatic compounds.

Various attempts have been made to calculate theoretical equilibrium acidities (79, 80). Streitwieser's calculated scale (80) differs widely from the experimental ones in being greatly expanded.

In view of the difficulties of getting pKa's of very slightly acidic compounds, rates of ionization are as useful for comparative purposes, and often much easier to obtain.

The general kinetic approach is to measure the rate of formation of the carbanion, by trapping techniques such as bromine (61, 81-83) or to measure the gain or loss of deuterium or tritium. The bromine trapping method has been used by Pearson and Mills (82) and Pearson and Dillon (61, 83) to measure rates of formation of carbanions from molecules with acidity constants in the range 10^{-4} to 10^{-20} . The success of the method is due to the rapid reaction of bromine with the carbanion. A reasonable correlation between rates of carbanion formation, measured in this way, with the acidity constant (established by equilibrium methods) exists (61). When $\log k$ (rate) is plotted vs pKa, a good straight line can be drawn, the only points which deviate greatly are the nitro compounds, which are explainable by the acinitro form (see Table 8).

The use of hydrogen isotopes as labels to measure rates

Table 8. A comparison of equilibrium and kinetic acidities

| Compound | K _a | k (min ⁻¹) |
|----------------------|-------------------------|------------------------|
| Nitromethane | 6.1 x 10 ⁻¹¹ | 2.6 x 10 ⁻⁶ |
| Nitroethane | 2.5 x 10 ⁻⁹ | 2.2 x 10 ⁻⁶ |
| Ethyl nitroacetate | 1.5 x 10 ⁻⁶ | 3.8 x 10 ⁻¹ |
| Dinitromethane | 2.7 x 10 ⁻⁴ | 50. |
| Acetone | 10 ⁻²⁰ | 2.8 x 10 ⁻⁸ |
| Chloroacetone | 3 x 10 ⁻¹⁷ | 3.3 x 10 ⁻⁶ |
| 1,1-Dichloroacetone | 10 ⁻¹⁵ | 4.4 x 10 ⁻⁵ |
| Ethyl acetoacetate | 2.1 x 10 ⁻¹¹ | 7.2 x 10 ⁻² |
| Acetoacetone | 1 x 10 ⁻⁹ | 1.0 |
| 3-Methylacetoacetone | 1 x 10 ⁻¹¹ | 5 x 10 ⁻³ |
| Acetonitrile | | 4 x 10 ⁻¹² |
| Malononitrile | 6.5 x 10 ⁻¹² | 9 x 10 ⁻¹ |
| Diethyl malonate | 5 x 10 ⁻¹⁴ | 1.5 x 10 ⁻³ |

of proton exchange has been extensively studied (70-74, 84-98). Shatenshtein (89, 90, 91) made an extensive survey of rates of proton exchange in hydrocarbons, in basic media. The method used was measurement of amount of deuterium incorporation in the hydrocarbon on allowing it to exchange with liquid ND₃ or KND₂ in liquid ND₃. A comparison of rates of exchange in ammonia and ethanol is shown in Table 9.

Table 9. Rates of exchange

| Hydrocarbon | 1st order rate constant (sec^{-1}) at 120°C | | |
|-----------------------------|--|---------------------|--------------------------|
| | ND_3 | EtOD | EtOD/EtOK |
| Fluorene | 2×10^{-2} | 1×10^{-7} | 6×10^{-4} (25') |
| Acetophenone | 4×10^{-3} | 2×10^{-7} | 4×10^{-5} (0') |
| Methyl-2-naphthyl ketone | 1.5×10^{-5} | $10^{-6} - 10^{-7}$ | |
| Triphenylmethane | 2×10^{-7} | | 3×10^{-5} |
| Diphenylmethane | 7×10^{-9} | | |
| 2-Methylquinoline | 8×10^{-8} | 2×10^{-6} | 2×10^{-3} |
| 2-Picoline | | 3×10^{-8} | 3×10^{-5} |
| Indene | 4×10^{-1} | $10^{-6} - 10^{-7}$ | 7×10^{-4} (0') |

Streitwieser and coworkers' approach was somewhat different (70-74, 85-88). They used lithium cyclohexamide in cyclohexylamine as solvent and base and exchanged specifically deuterated hydrocarbons. The amide ion was ruled out as the active catalyst by a consideration of kinetic order, and the active base was shown by a kinetic treatment to be the monomeric, undissociated lithium cyclohexamide. A large positive isotope effect was measured, $k_D/k_T = 2.8-3.2$, equivalent to about $k_H/k_D = 10-14$, and this supports a viewpoint that the transition state for exchange resembles a carbanion. The relative rates for toluene- α - d_1 , *m*-xylene- α - d_1 , and *p*-xylene- α - d_1 , when plotted vs Hammett's σ^- constant gave a straight

line, with $\rho = 3.2$. The large value of ρ may indicate considerable carbanion character in the transition state. Some data is summarized in Table 10.

Another method of obtaining rate constants for the ionization of very weak acids was that employed by Hofmann et al.

Table 10. Relative exchange rates for substituted toluenes^a

| X-C ₆ H ₄ -CH ₃ | o- | m- | p- |
|--|------|------|------|
| X = | | | |
| CH ₃ | 0.6 | 0.6 | 0.3 |
| CH(CH ₃) ₂ | 0.4 | 0.6 | 0.3 |
| F | 12.0 | 22.0 | 0.7 |
| CH ₃ O | | 2.1 | 0.09 |

(76). They reacted hydrocarbons in tritiated DMSO with potassium t-butoxide as base, then assayed the radioactivity of the hydrocarbon by a counting technique. Table 11 is a comparison of data from various sources.

Streitwieser et al. (99) report the rate of exchange of tritiated hydrocarbons in cyclohexylamine with lithium cyclohexylamine at 25°C as 1.2×10^{-5} for triphenylmethane-o-t₁ and 2.9×10^4 for diphenylmethane-o-t, values relative to benzene-t as 1.0.

Several attempts to make quantitative correlations of rates of ionization with acidity constants have been made

Table 11. Rates of exchange of substituted toluenes

| Compound | Relative rates | | |
|------------------|-------------------|------------------------------|--------------|
| | DMSO ^a | Cyclohexylamine ^b | ^c |
| Toluene | 1.0 | 1.0 | 1.0 |
| <i>o</i> -Xylene | 1.4 | 0.6 | |
| <i>m</i> -Xylene | 0.5 | 0.6 | |
| <i>p</i> -Xylene | 0.03 | 0.3 | |
| Ethylbenzene | 0.2 | 0.1 | 0.15 |
| Cumene | 0.02 | 0.008 | 0.03 |

^aHofmann et al. (76).

^bStreitwieser et al. (73).

^cShatenshtein (90).

(61, 86, 92). One relation expressing this correlation is the Bronsted catalysis law (100). $\log k = x \log K_a + C$

Another way to derive a relation is from the definition of K_a ; $K_a = k_f/k_r$ (k_f is the rate of the forward reaction, k_r the rate of the reverse). If k_r is large and constant, then K_a is proportional to k_f . Evidence for this has been found by Dessy et al. (92) in the reaction of $\text{CH}_3\text{C}=\text{C Li}$ in dioxane with a 3/2 mixture of $\text{H}_2\text{O}/\text{D}_2\text{O}$. Products with H and D in the ratio of 3/2 were obtained leading one to believe that the discharge of an anion which is the conjugate base of a weak acid is diffusion controlled. Streitwieser et al. (60) report a successful Bronsted law correlation of $\text{p}K_a$'s of substituted fluorenes determined in cyclohexylamine (presumably room tem-

perature) and rates of exchange in sodium methoxide/methanol at 44.9°C.

III. EXPERIMENTAL

A. Methods

The method of measuring the rate of oxidation was a variation of the volumetric constant-pressure technique previously described by Moye (8), Janzen (25), and Geels (101). The oxidations were performed in a 125 ml creased flask equipped with a 10 ml addition flask which could be rotated, and a bubbler. The apparatus is pictured in Figure 1. Normal oxidations were conducted in the following manner: The addition flask was filled with substrate solution, and placed in the normal (down) position. A solution containing the base was placed in the creased reaction flask. Occasionally, some substrates were too insoluble in solvents used to dissolve in 10 ml; then they were put in the creased flask with solvent and the base put in the addition flask. This was called inverse conditions. The total volume of solution in both flasks was 25 ml. The bubbler was then inserted in the reaction flask, and the whole apparatus attached to a mechanical shaker (Figure 2). All joints were lightly greased with high vacuum lubricant. A tygon tube was attached to the bubbler, and connected to a glass tube, which in turn had connected to it a mercury manometer, an oxygen inlet, and a buret equipped with a mercury leveling device. With this apparatus, the pressure could be maintained at a constant value by raising

Figure 1. Oxidation apparatus consisting of creased flask, addition flask, and bubbler

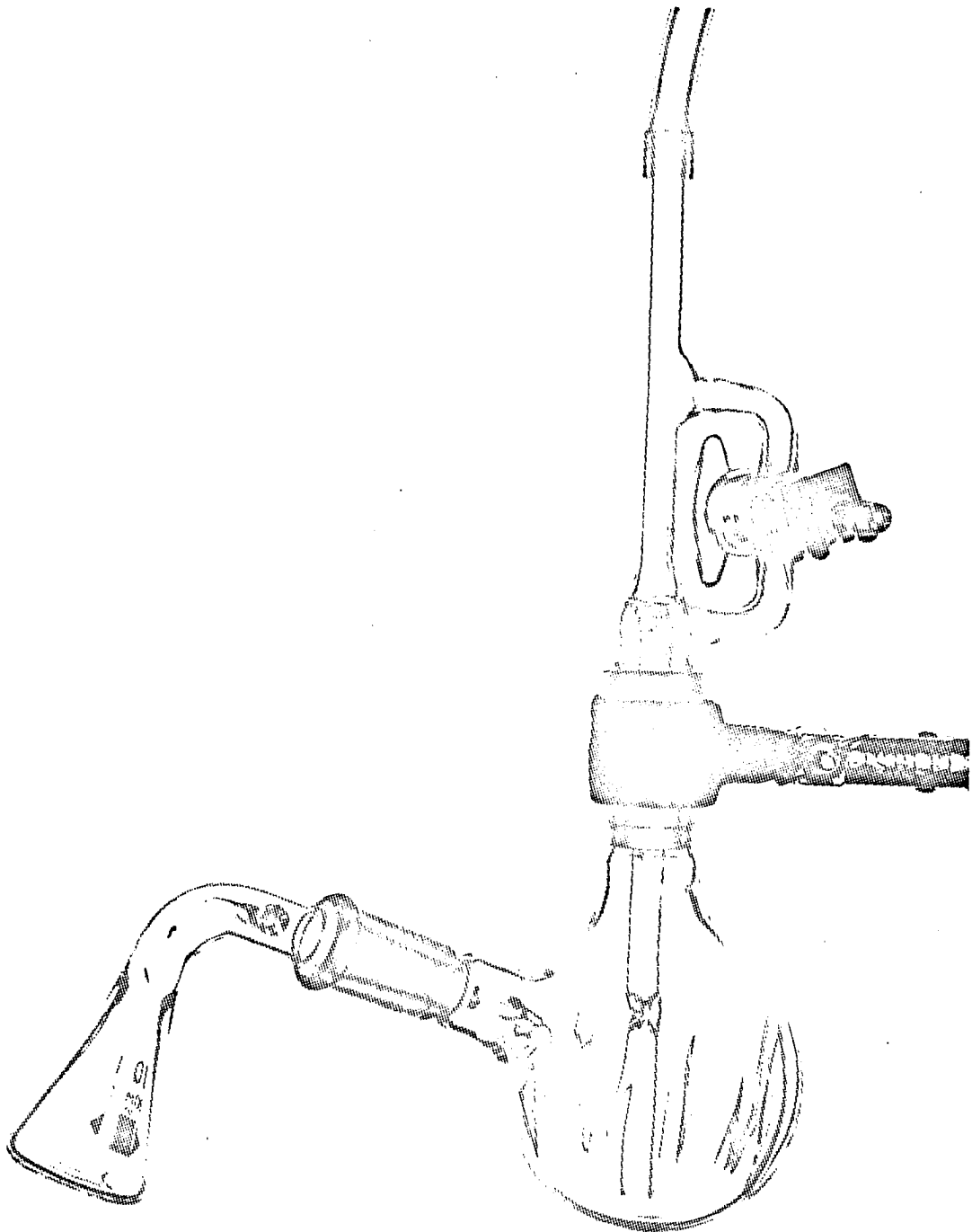
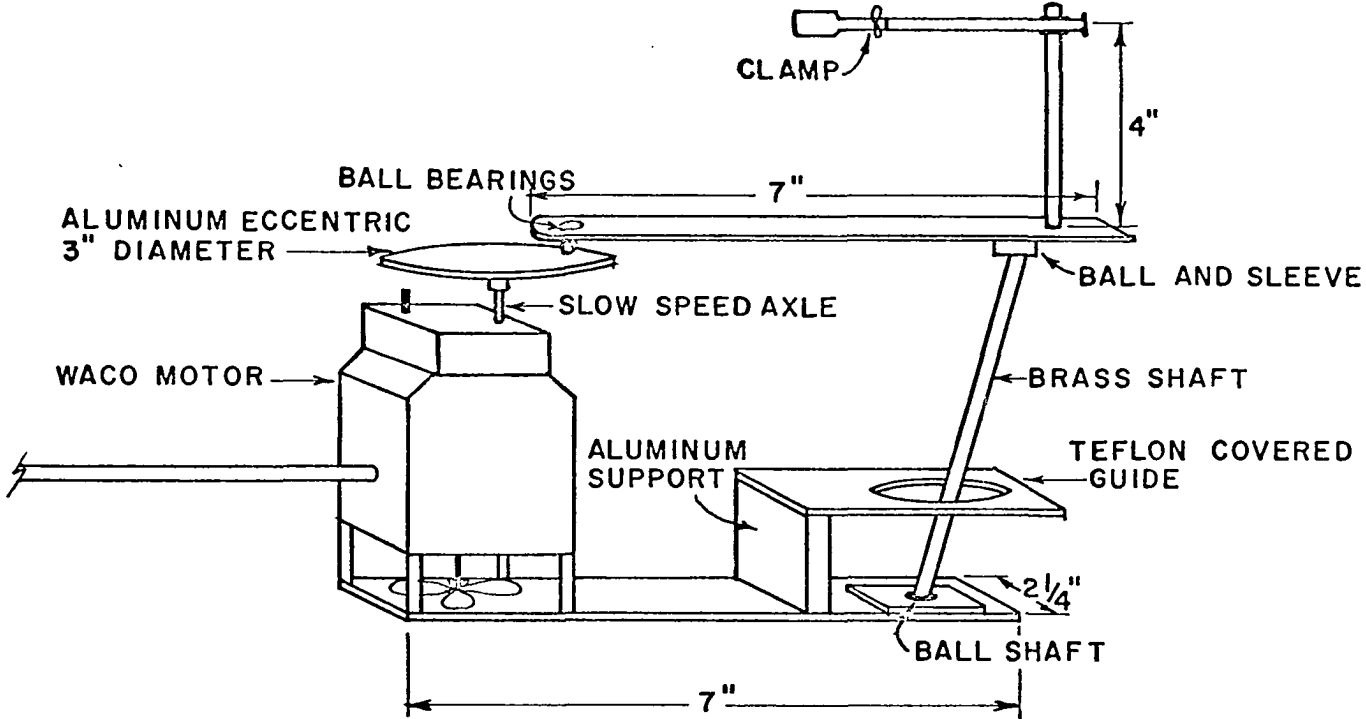


Figure 2. Mechanical shaker used to agitate solutions for oxidations

WRIST SHAKER



or lowering the mercury leveling bulb on the buret, and the change in volume measured. Volumes were read to the nearest 0.1 ml and were reproducible to 0.2 ml. Pressure could be kept to within 1.0 mm of the desired constant value. Prior to beginning an oxidation, oxygen was admitted to the system, the burets purged by raising and lowering the mercury leveling bulb several times, and the solution degassed via the bubbler. The bubbler was equipped with a three-way stopcock so that the solution containing the base could be purged. During the purging, or bubbling operation, oxygen travelled from the tygon tubing down the center glass tube of the bubbler to near the bottom of the creased flask, where it bubbled out through the base solution. The oxygen then flowed up around the outside of the center tube and into the stopcock where it exited via a hole bored in center of it out into the air. Just before starting an oxidation, the buret was filled with oxygen, the flow stopped and simultaneously the three-way stopcock on the bubbler apparatus turned to a position where the oxidation system was isolated from the air, but oxygen could readily flow into the reaction flask from either the center tube or via the outside tube and stopcock, hence preventing any pressure difference in the system. The addition flask was fitted with rubber bands or springs so that when released, it would turn up and remain in that position.

At time zero, the addition flask was released, hence the substrate solution entered the reaction flask and mixed with the base, the timer was started, and the mechanical wrist-shaker started. This could easily be done within 2 seconds.

The rate of oxidation was then followed by raising the mercury leveling bulb to a point where the pressure equalled the initial pressure, and then recording the time and volume. By this technique, base and oxygen stable solvents gave no volume change in the absence of substrate, but in the presence of base. If bubbling was not done, an initial oxygen uptake was noted, due probably to dissolution of oxygen in the solvent. Reproducible blanks were obtained in the case of solvents which slowly absorbed oxygen in the presence of base.

For some kinetic runs, the reaction apparatus (addition flask, creased flask, and bubbler) was assembled as usual, but just before starting the oxidation, was immersed in a constant-temperature oil bath for 15 minutes. The oil bath could be maintained at $\pm 0.1^{\circ}\text{C}$ of the desired temperature. Experiments showed for oil bath temperatures between 20° - 35°C , and the reaction apparatus initially at room temperature (which varied between about 23° and 33°) that 15 minutes was sufficient time for the contents of the flask to come to the oil bath temperature. After thermostating, the reaction apparatus was quickly moved to the shaker, and the oxidation

begun. In this way, initial temperatures (at $t = 0$) of $\pm 0.1^\circ$ of the desired value could be achieved. This crude thermostating technique was effective; reproducibility improved, and rates were consistent within 1%. In some oxidations, the temperature was found to rise 5° - 10° during the course of the reaction. This was usually in fast oxidations. Using a mechanical shaker, the oxidations could not be done in an oil bath, and for fast reactions the temperature could not be held constant in any case. Rates measured after circa 20-40 seconds are believed to be valid for the initial temperature. For triphenylmethane, diphenylmethane, and fluorene oxidations in particular, there was no significant temperature change in most solvents. For these cases, the excellent kinetic results seem to show temperature change not to be an important factor.

Products from oxidations were generally treated according to the following general scheme. The reaction mixture from an oxidation was added to 300-400 ml of water. In many cases a precipitate formed, which was filtered, dried, and recrystallized from an appropriate solvent. Where a precipitate did not form, the basic solution was neutralized, and sometimes a precipitate formed which could be isolated as described above. Occasionally, it was preferable to extract the aqueous solution with ether or chloroform, and after drying, evaporate or distill off the solvent. The extraction

method sometimes gave higher yields than simple filtration. In the case of the substituted toluenes, where sometimes a mixture of neutral and acidic products was observed, the general procedure was to extract the basic solution, and then acidify the aqueous phase. Usually the acidic product precipitated, and could be removed by filtration.

All products had sharp melting points within two degrees of literature values and gave undepressed mixing melting points and superimposable infrared spectra with authentic samples unless otherwise noted.

Acid workup by filtration of triphenylmethane oxidations gave $\geq 95\%$ yields of triphenylcarbinol in all solvents except pyridine. In solvents containing pyridine, a 5-10% yield of triphenylmethyl peroxide was isolated by washing the crude product (obtained by filtration or extraction from either basic or acidified aqueous reaction mixtures of triphenylmethane oxidations) on a filter with benzene. The solid remaining was pure peroxide, m.p. 185-6, identical with authentic material. The benzene soluble material was triphenylmethanol in the case of acidic workup, accounting for the balance of the reaction products.

Either filtration or extraction of the basic aqueous solutions from triphenylmethane oxidations gave triphenylmethyl hydroperoxide, except when the solvent contained DMSO, where the product was the carbinol. When the solvent was

dimethylformamide, the major product isolated was a DMF-triphenylmethyl hydroperoxide complex. The remainder was the uncomplexed hydroperoxide. After recrystallization from Skelly B, the complex had M.P. 60-61^o. This complex was identical with material obtained by dissolving authentic tri-tyl hydroperoxide in DMF, adding water, and filtering. The infrared of both materials (in chloroform) was identical, and was an exact superposition of the IR spectra of DMF and tri-tylhydroperoxide taken separately. Triphenylmethyl hydroperoxide could be recovered from the complex by dissolving it in Skelly B, washing with water, drying the Skelly B layer, and partial evaporation until crystallization occurred.

Quantitative elemental analysis of the complex (performed by Schwartzkopf Microanalytical Lab) gave 78.83% C, 6.31% H, and 1.82% N. Theoretical for a 1:2 DMF:hydroperoxide complex is 78.6% C, 6.24% H, and 2.24% N. Apparently the nitrogen determination is inaccurate.

The oxidation of *p*-methylbenzophenone in several solvents gave a neutral and an acidic product. The neutral product was separated by filtration of the basic aqueous reaction mixture. This product was dried and washed with hot absolute ethanol, M.P. 236-237^o. I.R. in chloroform shows a very simple spectrum with weak absorption at 3000-3200 cm⁻¹, sharp intense peaks at 1650 and 1600 cm⁻¹, weak absorption at 1445 and 1410 cm⁻¹, strong peaks at 1310 cm⁻¹ and 1275 cm⁻¹,

and other absorptions at 1000, 970, 950, 935, and 920 cm^{-1} . The infrared spectrum is very similar to that of *p*-methylbenzophenone, except the latter compound also has absorptions at 2900-3000 cm^{-1} . The structure assigned is *p,p'*-dibenzoylstilbene, lit. m.p. 234-235° (102). The I.R. spectrum is entirely consistent with this structure.

The oxidation of 4,5-methylenephenanthrene in *t*-butyl alcohol gave a neutral product, which was filtered from the aqueous solution and recrystallized 2 times from ethanol, m.p. 169-171°. Infrared showed the absence of any absorption in the 3000-4000 cm^{-1} region, but a strong carbonyl stretch at 1710 cm^{-1} (shoulder at 1740 cm^{-1}). This material is assigned the structure of 4,5-carbonylphenanthrene, lit. m.p. 170° (103).

The oxidation of 4,5-methylenephenanthrene in 80/20 DMSO gave on extraction of the acidified reaction mixture in water by chloroform, an oil which on treatment with hot ethanol and water yielded a solid. After recrystallization from aqueous ethanol the solid melted at 169-171°. Infrared spectra of this solid showed a strong broad absorption in the 4000-3000 cm^{-1} region, and a strong sharp peak at 1670-1690 cm^{-1} . These bands are assigned to a carboxyl group. The structure of this material is believed to be 4-phenanthroic acid, lit. m.p. 170-171° (104, 105).

Kruber (104) reports the conversion of 4,5-carbonyl-

phenanthrene to 4-phenanthroic acid in strong base, hence the assignment of this structure is reasonable.

The oxidation mixture of acenaphthene in 80/20 DMSO with potassium t-butoxide was poured into water, acidified, and the resulting precipitate filtered. Recrystallization from ethanol gave m.p. 250-270° (with sublimation). Infrared showed a doublet 1740, 1770 cm^{-1} , but no absorption in 3200-4000 cm^{-1} region. A sample of 1,8-naphthalene dicarboxylic acid (from L. Light & Co.) had identical m.p., and superimposable infrared with the oxidation product. A mixed m.p. was undepressed. Naphthalic acid is reported to have m.p. 270 and naphthalic anhydride m.p. 271-2° (106). Apparently both the oxidation product and the commercial material were the anhydride rather than the diacid, on the basis of the infrared spectra.

Products from methyl p-toluate oxidations were determined by gas-liquid chromatograph (g.l.c.). The reaction mixture from a methyl p-toluate (MPT) oxidation was acidified, evaporated to dryness on a steam bath, dissolved in DMF containing 20% THF, a trace of methanol added, and an excess of an ether solution of diazomethane added. Diazomethane was prepared by standard methods (107). A milliliter of glacial acetic acid was added to destroy any remaining diazomethane. The resulting solutions were concentrated, and injected on a 6' x 1/4" stainless steel column packed with 1% SE-30 on 100-110 mesh

Chromosorb P. Triphenylmethane was used as an internal standard. Known solutions containing dimethyl terephthalate, *p,p'*-dicarbomethoxystilbene, *p,p'*-dicarbomethoxybibenzyl, methyl *p*-toluate, and triphenylmethane were prepared and resolved on the chromatograph. Standard curves were prepared. Integration of recorder traces was by planimeter. Products and yields are given elsewhere in this thesis.

Gas-liquid chromatographic analysis of several co-oxidations were also performed. The same column and general method were used as in the MPT case, although column temperatures were different. Analysis of the products from the oxidation of triphenylmethane and fluorene in *t*-butyl alcohol and from the oxidation of triphenylmethane and cumene in 80/20 DMSO were done, and in each case internal standards used and known standard solutions run.

Analysis by g.l.c. of products in the interrupted oxidations of diphenylmethane and fluorene were performed. A 6' x 1/4" stainless steel column packed with 3% water insoluble UKON on Gas Chrom P (60-80 mesh) was used. Triphenylmethane was used as an internal standard, and standard solutions were prepared containing diphenylmethane, benzophenone, benzhydrol, and triphenylmethane in one case, and fluorene, fluorenone, fluorenol, and triphenylmethane in the other. DMSO addition products of either benzophenone or fluorenone could not be eluted from the column under any conditions tried. The gen-

eral procedure was to interrupt an oxidation at a predetermined time and either pour the reaction mixture in water, or in some cases add 10 ml of DMSO, shake once, and pour the reaction mixture in water. In both cases, the aqueous solution was acidified, and extracted twice with ether. The ether layers were separated, combined, washed with water twice, and dried. After concentration of the ether solutions to about 50 ml., a known volume of a standard solution of triphenylmethane was added, and the samples analyzed on the g.l.c.

The potassium salt of nitrobenzene radical anion was prepared by reaction of potassium metal with nitrobenzene. Carefully purified and dried tetrahydrofuran was placed in a 500 ml. 3-necked flask equipped with a mechanical stirrer, and addition funnel with a gas by-pass tube, and a nitrogen inlet. A solution of 5 ml. of nitrobenzene in 50 ml. THF was placed in the addition funnel, 2 g. of freshly cleaned potassium in small pieces placed in the 500 ml. flask with 150 ml. THF, and the apparatus purged with prepurified nitrogen. The nitrogen flow was reduced, stirring was started, and the nitrobenzene solution added slowly to the potassium. A brown-orange, finely divided solid slowly separated off the surface of the metal, and after about 2 hours, the metal had disappeared. This material was stored under nitrogen, and when needed was stirred. The solid was so finely divided, it

could be pipetted; under the stirring conditions the solution looked homogeneous. Samples were removed for oxidation and EST study with a syringe.

The oxidation was carried out in the oxidation apparatus described previously, but the procedure was different. The addition flask was replaced with a rubber septum, and the apparatus filled with oxygen, but otherwise completely empty. At time zero, a known volume of the slurry of nitrobenzene radical anion in THF was syringed into the oxidation flask through the septum, the timer started, and the shaker turned on. After reaction with oxygen, the resulting solution was analyzed for potassium superoxide and nitrobenzene. Superoxide analysis was by the method of Seyb and Kleinberg (108). This procedure involves measuring the gas (oxygen) evolution when a solution of 80% glacial acetic acid and 20% diethyl phthalate is dropped into the superoxide which had been cooled to zero degrees Centigrade. This analysis was also performed on the solid yellow material isolated by filtration of the oxygenated solution. Nitrobenzene was analyzed by g.l.c. in the manner previously described for methyl p-toluate, using an internal standard. E.S.R. spectra were taken on a Varian Associates instrument (6" magnet), using an aqueous sample cell.

In the isotope exchange reactions reported, triphenylmethane- α -d, and diphenylmethane- α -d₂ were allowed to react

under exactly identical conditions as the corresponding oxidations, except that prepurified nitrogen was used instead of oxygen. The reactions were stopped at a predetermined time by the addition of a large amount of water.

Fluorene-9,9-d₂ was exchanged in a specially constructed stainless steel apparatus. The apparatus consisted of two syringe needles silver-soldered into a stainless steel block. The block was so bored as to mix the two solutions entering through the syringe needles. The solution then exited from the block via a stainless steel tube which was about 12 inches long. The two syringe needles were so spaced that they fit into syringes mounted on a syringe pump. The syringe pump (Infusion pump No. 975, Harvard Apparatus Co.) consisted of a holder for the syringes and a block which drove the pistons of the syringes. The rate was variable. For the exchange of dideuterofluorene, two 50 ml. syringes were used. One was filled with base and solvent, the other with deuterofluorene and solvent. The syringes were placed in the syringe pump, and attached to the stainless steel apparatus. The pump was started, and the first several ml. allowed to exit from the steel tube rejected. A beaker of water was placed under the tube so that each drop of liquid emerging would fall into the water instantly after leaving the tube. The beaker was well stirred by a high speed magnetic stirrer. The volume of the stainless steel tube (which

extended from the point of mixing in the steel block) was measured to be 0.84 ml. The rate of flow of the syringes was measured using solvent of identical composition to that of the exchange experiments.

The aqueous reaction mixtures of the deuterio triphenylmethane and deuterofluorene exchange reactions were worked up by filtration. The resulting solids were recrystallized from aqueous alcohol, and analyzed for deuterium by mass spectroscopy. The aqueous reaction mixture of the diphenylmethane- α - d_2 exchange was extracted with ether. The ether layer was dried, and distilled to remove ether. The remaining oil was distilled in vacuum, and a diphenylmethane fraction analyzed for deuterium by mass spectroscopy.

Toluene- α - d_1 was exchanged in diphenyl sulfoxide at 100°C . The oxidation apparatus was used, except that prepurified nitrogen was used to degas the apparatus, and instead of the shaker, the apparatus was equipped with a magnetic stirring bar, and immersed in an oil bath at 100° . A high speed magnetic stirrer was placed below the oil bath. Diphenyl sulfoxide and solid potassium t-butoxide were weighed out and placed in the creased flask. Deuterotoluene was placed in the addition flask, and the contents of the apparatus allowed to warm to 100°C . After this occurred, the addition flask was tipped to admit the deuterotoluene, and the stirrer started. After a measured time, the mixture was worked up by

pouring into water, acidification, and extraction with pentane. The pentane layer was separated, washed several times with water, and dried. The pentane was distilled, and the remaining liquid fractionated in a microdistillation apparatus. A fraction boiling at 106° contained toluene and a trace of pentane by g.l.c. This fraction was analyzed for deuterium by N.M.R.

B. Mass Spectroscopy

All mass spectra were taken on an Atlas MAT CH-4 instrument. In the following tables, m/e is the ratio of mass per charge, in this case always singly charged positive ions, hence equal to the mass of the ion. Relative intensities are measured as peak heights, measured at a low ionizing voltage which was constant for a given molecule. Corrections for C^{13} contributions to peak intensities were made by standard techniques (109). See Tables 12, 13, and 14.

C. Analysis for Deuterium by N.M.R.

The analysis by N.M.R. of the toluene- α - d_1 preparation gave the following data: An unresolved multiplet at 3.0τ (integral 5.0) and a clean 1:1:1 triplet at 7.9τ (integral 2.06). The 3.0τ absorption is due to the aromatic ring, the triplet at 7.9τ is the $-CH_2D$ group. A 1:1:1 triplet is expected due to deuterium having a spin of 1. $J_{H-D} = 2.18$ c.p.s.

Table 12. Data from the mass spectra of isotopically labeled triphenylmethane

| | m/e | Relative intensity | Relative intensity ^a |
|---|-----|--------------------|---------------------------------|
| Triphenylmethane (standard) | 244 | 53.1 (1.0) | |
| | 245 | 11.5 (0.217) | |
| | 246 | 1.2 (0.0226) | |
| Triphenylmethane (deutero-prep.) | 244 | 4.4 | 4.4 |
| | 245 | 59.7 | 58.7 |
| | 246 | 13.7 | -- |
| (Triphenylmethane- α -d = 93.3%) | | | |
| Triphenylmethane (deutero after exchange) | 244 | 15.4 | 15.4 |
| | 245 | 13.2 | 9.9 |
| | 246 | 2.4 | |
| (Triphenylmethane- α -d = 39.1 %) | | | |

^aCorrected for C¹³.

Table 13. Data from the mass spectra of isotopically labeled diphenylmethane

| | m/e | Relative intensity | Relative intensity ^a |
|------------------------------------|-----|--------------------|---------------------------------|
| Diphenylmethane (standard) | 168 | 562.5 (1.0) | |
| | 169 | 89.5 (0.1565) | |
| | 170 | 5.65(0.01) | |
| Diphenylmethane (deutero-prep.) | 168 | 0.7 | 0.7 |
| | 169 | 4.85 | 4.75 |
| | 170 | 170.0 | 169.33 |
| | 171 | 22.2 | -- |
| | 172 | 1.7 | -- |

(Diphenylmethane = 97% d₂, 2.72% d₁, 0.4% d₀)

^aCorrected for C¹³.

Table 13. (continued)

| | m/e | Relative intensity | Relative intensity |
|---|-----|--------------------|--------------------|
| Diphenylmethane (exchange D-36) | 168 | 9.0 | 9.0 |
| | 169 | 96.0 | 94.72 |
| | 170 | 271.5 | 257.92 |
| | 171 | 38.4 | -- |
| | 172 | 2.75 | -- |
| (Diphenylmethane = 71.5% d ₂ , 26.2% d ₁ , 2.5% d ₀) | | | |
| Diphenylmethane (exchange D-35) | 168 | 4.6 | 4.6 |
| | 169 | 22.65 | 22.05 |
| | 170 | 41.1 | 37.91 |
| | 171 | 6.8 | -- |
| | 172 | 0.3 | -- |
| (Diphenylmethane = 58.7% d ₂ , 34.3% d ₁ , 7.13% d ₀) | | | |

Table 14. Data from the mass spectra of isotopically labeled fluorene

| | m/e | Relative intensity | Relative intensity ^a |
|---|-----|--------------------|---------------------------------|
| Fluorene (standard) | 166 | 80.0 (1.0) | |
| | 167 | 11.2 (0.14) | |
| | 168 | 4.15 (0.05) | |
| Fluorene (deutero-prep.) | 166 | 0.95 | 0.95 |
| | 167 | 10.30 | 10.17 |
| | 168 | 75.5 | 74.07 |
| | 169 | 10.55 | -- |
| | 170 | 0.70 | -- |
| (Fluorene = 87.0% d ₂ , 11.9% d ₁ , 1.1% d ₀) | | | |

^aCorrected for C¹³.

Table 14. (continued)

| | m/e | Relative intensity | Relative intensity |
|--|-----|--------------------|--------------------|
| Fluorene | 166 | 2.25 | 2.25 |
| (exchange D-49-B) | 167 | 29.7 | 29.38 |
| flow rate = | 168 | 192.5 | 188.38 |
| 4.35 ml./min.) | 169 | 24.9 | -- |
| | 170 | 1.6 | -- |
| (Fluorene = 85.7% d ₂ , 13.55% d ₁ , 1.0% d ₀) | | | |
| Fluorene | 166 | 4.45 | 4.45 |
| (exchange D-49-A) | 167 | 33.0 | 32.38 |
| flow rate = | 168 | 173.0 | 168.46 |
| 2.18 ml./min. | 169 | 21.9 | -- |
| | 170 | 1.8 | -- |
| (Fluorene = 82.2% d ₂ , 15.8% d ₁ , 2.17% d ₀) | | | |

An expansion of this triplet showed the same 1:1:1 intensity ratio, but further small splittings began to be resolved. The major secondary splitting appears to be a 1:2:1 triplet, possibly due to the two ortho hydrogens on the ring. $J_{H-H'} = 0.17$ c.p.s. The integration gives a value of 94% mono- α -d, but from the expansion of the triplet, this is probably a minimum value.

Analysis of the exchange product of the deuterotoluene in diphenyl sulfoxide by N.M.R. showed an unresolved multiplet at 3.0τ (integral 5.0) and a multiplet consisting of an unresolved peak with a smaller upfield shoulder, centered at 7.85τ (integral 2.41). Several other peaks were found at 8.5τ or higher. These were due to pentane which was an

impurity. Pentane does not absorb below ca. 8.5 τ . The 7.85 τ multiplet was shown to be due to approximately equal amounts of undeuterated toluene and mono-deuterated toluene. A synthetic 1:1 mixture of ordinary toluene and the starting monodeuterated toluene gave an identical pattern, with only slightly different intensities. Since if the chemical shift of the hydrogen in the monodeutero compound was identical with that of the hydrogens in undeuterated toluene, a symmetrical triplet (but with a 1:X:1 intensity pattern, where X would depend on the relative amounts of each) would be seen, deuterium caused an upfield shift on hydrogen. This was measured to be about 0.017 p.p.m. The integration indicates the toluene was 41% mono- α -d. The absence of further splitting of the 7.85 τ multiplet indicates the absence of any dideuterotoluene. N.M.R. spectra were taken on Varian Associates A-60 and HR-60 instruments.

D. Solvents and Bases

Commercially available t-butyl alcohol was always first purified before used as solvent or in preparation of base. Sodium was dissolved in t-butyl alcohol and oxygen bubbled through a warm (50°C) solution for several days. The resulting solution was usually black, and often dark material precipitated. It was then fractionally distilled under vacuum, the first fraction and a sizable pot residue being discarded.

This procedure was repeated once more with sodium, and then with potassium. The final distillate was stored over calcium hydride or used to prepare solutions of base.

All solvents and base solutions were stored in Pyrex vessels, with closure by ground glass stoppers.

Dimethyl sulfoxide was obtained from Crown Zellerbach, and dried over calcium hydride, distilled from calcium hydride in vacuum, and stored over calcium hydride.

Dimethylformamide was distilled under vacuum from calcium hydride, and stored over calcium hydride.

Pyridine was distilled, and stored over KOH pellets.

Hexamethylphosphoramide was obtained from Tennessee Eastman Corporation and distilled from calcium hydride, and stored over calcium hydride.

It was shown that a freshly distilled sample of any of these solvents (except pyridine) gave the same results in an oxidation as one which was stored over calcium hydride.

Sodium methoxide was used as obtained from Matheson, Coleman and Bell.

Potassium t-butoxide was prepared by adding a weighed amount of cleaned potassium to purified t-butyl alcohol. The resulting solutions were titrated with standardized acid, and normalities obtained were consistent with that calculated on the basis of potassium added. Potassium t-butoxide solutions prepared in this way were stable for months, turning only

slightly yellow, and losing titer gradually.

Solid potassium t-butoxide was used in oxidations in solvents containing no t-butyl alcohol. It was obtained from Mine Safety Appliance Co., and did contain some potassium carbonate and potassium hydroxide. It rapidly deteriorated on exposure to air.

Tetra-methylammonium t-butoxide was prepared by adding a solution of tetra-methylammonium bromide in DMSO to a solution of potassium t-butoxide in t-butyl alcohol, and filtering the insoluble potassium bromide. From 3.08 g. (0.02 moles) of tetra-methylammonium bromide dissolved in 56 ml of DMSO, and 20 ml. of a 1.0N potassium t-butoxide solution, 2.59 g. (0.0219 moles) of potassium bromide was removed by filtration.

The potassium hydroxide used was in pellet form, being ground to a powder before use, and was an 85% Mallinckrodt product.

E. Chemicals

The addition of α -naphthylmagnesium bromide to benzophenone gave diphenyl α -naphthylmethanol. The crude alcohol was reduced by HI to diphenyl α -naphthylmethane (110), and re-crystallized from aqueous ethanol, m.p. 139-141^o, lit. m.p. 139-140^o (110).

9-Methylfluorene was prepared by the alkylation of

9-sodiofluorene and methyl iodide (111). The product was recrystallized three times, from skelly B, m.p. 46-47°, lit. 45-47° (111). 9-Sodiofluorene was made by addition of sodium to fluorene in ether, filtered, washed several times with ether, and used for the preparation of 9-methylfluorene (111).

Triphenylmethyl peroxide was prepared by shaking triphenyl chloride with mercury in benzene, followed by rapid filtration, and exposure to air (112). The peroxide precipitated from a benzene solution was filtered, and gave after washing with solvent a product, m.p. 185-186°, lit. m.p. 185-186° (112).

Triphenylmethyl hydroperoxide was prepared by the action of approximately 90% hydrogen peroxide on triphenylmethyl chloride (113). The hydroperoxide precipitated after addition of water, and was recrystallized from skelly B, m.p. 84.5-85.5, lit. m.p. 81-3° (113).

p-Tolyltrimethylammonium iodide was prepared by addition of methyl iodide to p-toluidine in ether (114). The ammonium salt precipitated, and was purified by recrystallization in ethanol, m.p. 212-215° with sublimation, lit. m.p. 202° in sealed tube (114).

p-Benzoylbenzoic acid was made by oxidizing p-methylbenzophenone with acidic permanganate (115). Extraction of the hydrolyzed reaction mixture with sodium carbonate, followed by acidification gave the acid, which after recrystal-

lization in ethanol had m.p. 197-199°, lit. 197-200° (115).

Triphenylmethane- α -d was prepared by the addition of 3.6 ml. of deuterium oxide (>99.6%) to triphenylmethylsodium prepared by the reaction of 30 g. of trityl chloride (recrystallized from a mixture of 8 parts heptane, 1 part acetyl chloride) in 150 ml. of ethyl ether (sodium dried) with sodium-mercury alloy prepared from 6 g. of sodium and 54 g. of mercury. The trityl chloride was allowed to react with the amalgam for 140 min. and then quenched with the deuterium oxide. After 17 hours contact with the deuterium oxide, an excess of water was added, and triphenylmethane- α -d m.p. 90-91° recovered by evaporation of the ether solution. Recrystallization from 95% ethanol gave m.p. 91-92°, lit. for undeuterated material, 93° (116).

Fluorene -9,9-d₂ was made by adding D₂O to a solution of fluorene and potassium t-butoxide in dimethylformamide. Fluorene (6 g.) was dissolved in 200 ml. of DMF, and 100 g. of solid potassium t-butoxide were placed in a three-necked flask, equipped with a magnetic stir bar, nitrogen inlet, and condenser with a calcium chloride drying tube. Prepurified nitrogen was passed through the solution for several hours while it was stirred. Deuterium oxide (20 ml.) was added, and the solution stirred for another 6 hrs. under nitrogen. Another 80 ml. of deuterium oxide was added, the solution stirred for an additional 1/2 hr., and a large excess of

water added. The deuterated fluorene was filtered from the aqueous mixture, dried, and recrystallized from aqueous ethanol.

Diphenylmethane- α, α - d_2 was prepared by reduction of dichlorodiphenylmethane with lithium aluminum deuteride (117). Ether extraction, drying, and crude distillation, followed by fractionation on a microstill gave a fraction which had no aliphatic proton absorptions in NMR or IR spectra. The fraction was pure diphenylmethane by g.l.c.

Toluene- α - d_1 was prepared by hydrolysis of benzylmagnesium bromide with deuterium oxide. Benzylmagnesium bromide was prepared by usual methods (118). After completion of the Grignard synthesis, an excess of deuterium oxide was added, the solution was stirred for 1 hr., then water was added, enough sulfuric acid to homogenize the solution, and the ether layer separated, and dried. The ether was distilled off, and the resulting concentrate fractionated on a microstill. A middle fraction, b.p. 106-107°, was used for the exchange experiments.

t-Butyl 2-methylbutyrate was made by adding t-butyl alcohol to a solution of dimethylaniline and 2-methylbutyryl chloride in ether. The ether layer was separated, washed with sodium bicarbonate, dried, and distilled. The ether free concentrate was distilled to give an acid free product, b.p. 139°C.

Benzhydryl bromide was prepared by heating diphenylmethane and bromine at 150-160°C. (119). Distillation of the reaction mixture gave a product, b.p. 183° at 23 mm.

sym-Tetraphenylethane was prepared by treating benzhydryl bromide with zinc in ethyl acetate (119). Recrystallization from benzene gave the product in good yield, m.p. 210-211°, lit. 211° (119).

Methyl diphenylacetate was prepared by acid catalyzed esterification of diphenylacetic acid with methanol. The ester, after recrystallization from 95% ethanol, had a m.p. 60°, lit. 60° (120).

p-Benzhydryltetraphenylmethane was prepared by treating triphenylmethanol in refluxing glacial acetic acid with stannous chloride and hydrochloric acid under nitrogen (121). The solid material which formed was washed with ether and dried, m.p. 229-231°, lit. 228°C. (121).

Triphenylmethane was obtained from Matheson, Coleman, and Bell, and recrystallized twice from 95% ethanol, m.p. 93°C.

Diphenylmethane was an Eastman product, and was vacuum distilled before use.

α-, β-, and γ-picolines were obtained from Mr. E. Janzen. They were middle fractions from distillations under vacuum.

α-Methylnaphthalene, from Aldrich Chemical Co., was esti-

mated to be >98% pure α -isomer by g.l.c.

β -Methylnapthalene was a product of Ashland Oil Refining Co., and was >98% pure β -isomer by g.l.c.

Toluene was obtained from Dr. R. Kriens. G.l.c. showed no impurity.

α - and β -Ethylnapthalenes, from Aldrich, were \geq 98% pure isomers as shown by g.l.c.

Acenapthene was recrystallized from alcohol, m.p. 96° .

Fluorene was recrystallized from alcohol several times, m.p. $114-115^{\circ}$.

Benzhydrol and deuterobenzhydrol were obtained from Dr. E. Geels. Both were chemically pure by g.l.c.

Methyldiphenylmethane was prepared by Dr. J. Hunt. G.l.c. analysis showed \geq 98% purity, the trace impurity being ethanol.

Phenylacetylene was obtained from Aldrich, b.p. $142-143^{\circ}$.

p -Methylbenzophenone, an Eastman material, was recrystallized with Norite from aqueous ethanol, m.p. $59-60^{\circ}$.

Nitrobenzene was distilled before use, and was pale yellow.

m -Trifluoromethylnitrobenzene, obtained from Aldrich, was dried over molecular sieves. G.l.c. showed >98% purity.

9-Phenylfluorene was a recrystallized material obtained from Mr. R. Kocca, m.p. 148° .

Xanthidrol was recrystallized from aqueous ethanol, m.p.

120-122° (with sublimation).

Pyridine-N-oxide, from Aldrich, was dried and recrystallized from benzene to give a white solid.

Cyclopentadiene was obtained from Mr. S. Weiner, and had been freshly distilled from the dimer.

m- and p-Chlorotoluenes were obtained from Matheson, Coleman, and Bell. G.l.c. analysis showed the p-isomer to be 98% pure isomer, a trace of m-isomer being present. G.l.c. showed the meta isomer to contain a trace of toluene.

m-Methoxytoluene was dried over molecular sieves.

β,β-Diphenylpropionic acid was a student preparation, m.p. 154-156°.

1,1,2-Triphenylethane, obtained from Eastman, melted at 54-55°.

Methyl p-toluate was obtained from Eastman. I.R. showed no hydroxyl absorption.

Diphenylacetonitrile, benzhydryl chloride, and diphenylacetic acid were obtained from Eastman.

Cumene was a Phillips Petroleum product. Benzhydryl amine was from Matheson, Coleman, and Bell and was dried before use.

1,1-Diphenylacetone, 4,5-methylenephenanthrene, and p-phenyltoluene were Aldrich products. Diphenyl sulfoxide, m-fluorotoluene, and m- and p-bromotoluenes were from Eastman.

Acetophenone, benzyl chloride, and o-bromotoluene were

obtained from Matheson, Coleman, and Bell. Camphor was obtained from Geo. T. Walker Co.

o- and p-Fluorotoluenes were products of Pierce Chemical Co. o-Methyltoluene, o- and p-iodotoluenes, 8-methylquinoline, N,N-dimethyl p-toluidine, p-toluamide, and p-toluic acid were provided by Eastman.

m-Phenyltoluene was a product of Aldrich and 4-methylquinoline was obtained from K and K Labs.

Infrared spectra were obtained on a Perkin-Elmer IR-5. Gas-liquid chromatography was done on a A-350-B Aerograph dual-column instrument.

IV. RESULTS AND DISCUSSION

A. Introduction

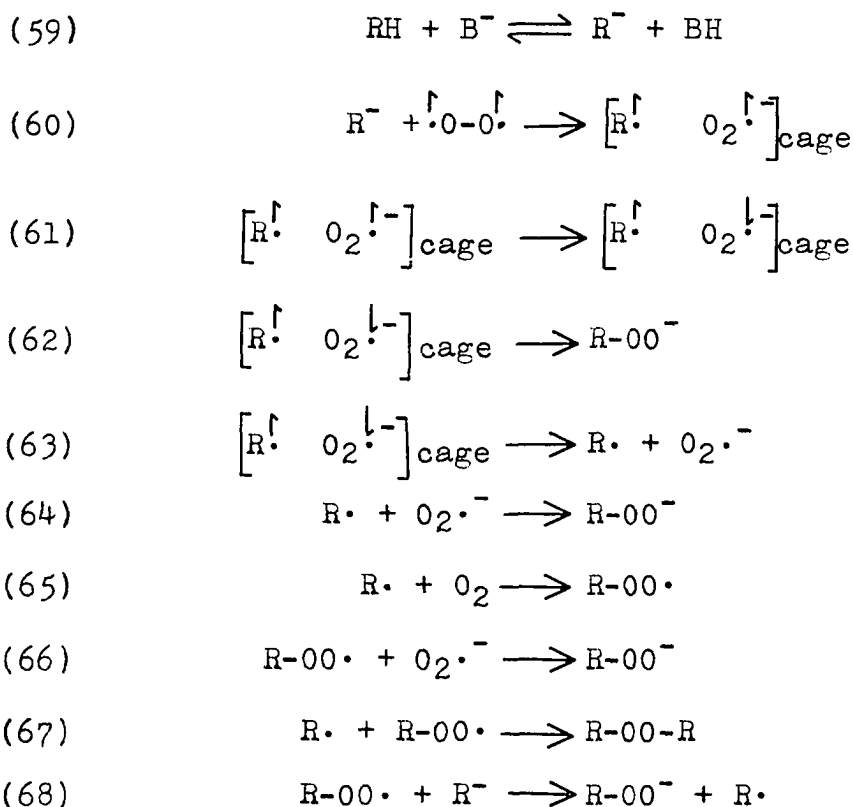
This section is divided into four parts: Introduction (A), Rates and Products (B), Kinetics and Catalysis (C), and Nitrobenzene Radical Anion (D).

The scope of the reaction between oxygen and carbanions is described in Part B. Products are identified, and yields are given. Rates as a function of solvent and structure are presented. Part B is further divided into four sections: (1) tertiary carbanions, (2) secondary carbanions, (3) primary carbanions, and (4) other carbanions.

Kinetic data is presented as evidence for the nature of the rate determining step in Part C, which is subdivided into (1) ionization, and (2) electron transfer. Section 1 presents the kinetic data for molecules whose slow step in base catalyzed autoxidations is shown to be the ionization of a C-H bond. The kinetic data for molecules where electron transfer is rate determining is given in Section 2.

Part D deals with the nitrobenzene radical anion. Implications of these results to the reactions of carbanions and oxygen are discussed.

The following mechanism is suggested on the basis of evidence to be presented, and partially on data from other sources (8, 16, 22, 25-29, 50).



A cage reaction is generally empirically defined as one which can not be prevented from occurring by the addition of a large excess of a more reactive substance (scavenger).

Hence the size or geometry of a cage will vary as the nature of reaction, reactants, solvent, and scavenger is changed.

Since no reaction occurs in the absence of base, reaction 59 must be the initial step, and is shown to be the rate determining step in some cases. The second step must be the interaction of a carbanion and oxygen (in the absence of catalyst). A direct, concerted addition of oxygen to a carbanion has been proposed to explain the lack of catalysis or inhibition by ferric ion or arsenic trioxide (30, 58), and

selectivity of product formation (16). An oxygen addition process involving electron transference in the transition state, but no intermediate, has been proposed (16). The required simultaneous change in multiplicity with reaction in either of these proposals is unique and unlikely (22). The product of the reaction of a carbanion and oxygen is undoubtedly an intermediate, consisting of a carbon radical and a superoxide ion (reaction 60). Reaction 61 is the spin relaxation step which may occur rapidly. Nelson and Bartlett (122) have provided evidence on the relative rates of spin relaxation and diffusion. By comparing the magnitude of the cage effect when radical pairs were produced whose spins were paired with pairs whose spins were parallel, they concluded that spin relaxation was complete before diffusion out of the cage could take place. These results make the coupling of free radical and superoxide ion in the cage, reaction 62, an attractive process, but by no means demands that all or most of the reaction proceed via this path. Nelson and Bartlett (122) found that for two cumyl radicals (from azocumene), produced with spins paired, there was about 28% cage coupling when an excess of a radical trapping reagent was present.

Le Berre and Berguer (50) have shown that trityl radical and superoxide ion readily react (reaction 64). Whether these two species could react in a cage before diffusion occurred is not known. Since superoxide ion is a very stable

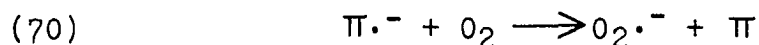
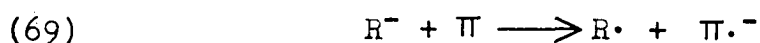
free radical, the combination of it with a carbon radical would probably be slower than the dimerization of two carbon radicals, but since the rate of spin relaxation of a stable radical anion such as superoxide ion may also be much different than the spin relaxation rate of a carbon radical, no conclusion is readily drawn. It seems unlikely that the cage reaction of a carbon radical and superoxide ion would occur to greater extent than for two carbon radicals.

No definitive evidence is available to demonstrate the relative merits of reaction 62 or the three step sequence, reactions 63, 65, and 66, but some evidence was obtained which shows that the three step sequence can occur. Triphenylmethyl peroxide was isolated from the oxidation of triphenylmethane in pyridine, and must be formed from the combination of a tritylperoxy radical, a trityl radical (reaction 67). The tritylperoxy radical can only form via reactions 63 and 65. Hydrogen abstraction by peroxy radicals occurs only slowly at 25^o as demonstrated by the lack of oxidation of cumene when present in an oxidation of triphenylmethane in 80/20 DMSO (cumene is not ionized in this solvent), but it is likely that a peroxy radical would react much faster with a superoxide ion, reaction 66, or a carbanion, reaction 68.

Reaction 68 is a propagating step, and may be important when initial electron transfer between carbanion and oxygen,

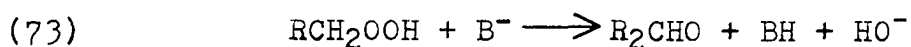
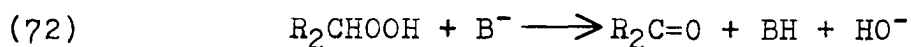
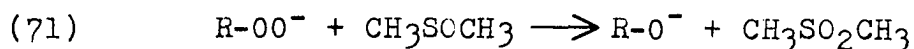
reaction 60, is slow. Russell *et al.* (29) have calculated a kinetic chain length of 21 for the nitrobenzene-catalyzed oxidation of fluorene in *t*-butyl alcohol. The electron transfer between oxygen and fluorenyl anion is slow, and reaction 68 is apparently important in this case.

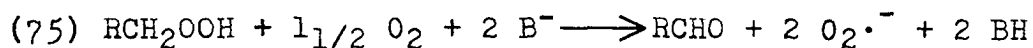
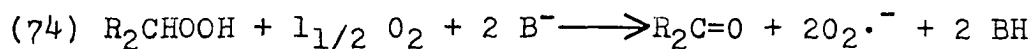
Reaction 69 is the well demonstrated electron transfer reaction (Π is an electron acceptor) (49). Nitrobenzene or substituted nitrobenzenes have been used as catalysts in base



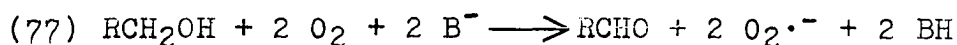
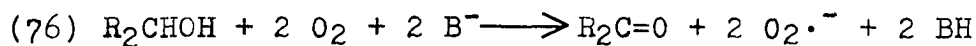
catalyzed autoxidations (25), and are shown to catalyze the oxidation when ionization is not the rate determining step. Reaction 70 is shown in this thesis to be fast for nitrobenzene = Π .

Hydroperoxides are observed as the oxidation products of tertiary hydrocarbons in the absence of DMSO. Hydroperoxides are reduced to alcohols by DMSO, reaction 71. The initial oxidation product of primary or secondary hydrocarbons is also apparently a hydroperoxide, which readily undergoes β -elimination, reactions 72 and 73, or further oxidation, reactions 74 and 75.





Primary or secondary alcohols produced in reaction 71 usually also oxidize further. The aldehydes produced via reactions 73, 74, or 75 are converted to carboxylic acids, possibly by the Cannizaro reaction.



B. Rates and Products

1. Tertiary carbanions

The base catalyzed autoxidation of triphenylmethane was studied in more detail in this thesis than any other compound. Janzen (25) oxidized triphenylmethane in 80/20 DMSO. His results are consistent with those reported here.

The products from the oxidation of triphenylmethane are shown in Table 15. Except in DMSO, triphenylmethyl hydroperoxide was the major product. In DMSO, only the alcohol was found. The reaction was very selective, only one product being formed except when pyridine was used as solvent. The yields given in Table 15 are of the recrystallized hydroperoxide or alcohol, and are minimum. The lower yields when hexamethylphosphoramide was the solvent may reflect difficulty in purifying the triphenylmethyl hydroperoxide, since no other

Table 15. Products from the oxidation of triphenylmethane

| Solvent | Product ^a | Yield ^b |
|--|--|--------------------|
| Pyridine | Triphenylmethyl hydroperoxide Trityl peroxide | 80% 10% |
| 80% Dimethylformamide- 20% <i>t</i> -butyl alcohol | Triphenylmethyl hydroperoxide ^c | 87% |
| 80% Dimethyl sulfoxide- 20% <i>t</i> -butyl alcohol | Triphenylmethanol | 95% |
| 80% Hexamethylphosphor- amide- 20% <i>t</i> -butyl alcohol | Triphenylmethyl hydroperoxide | 58% |
| Hexamethylphosphoramide | Triphenylmethyl hydroperoxide | 77% |

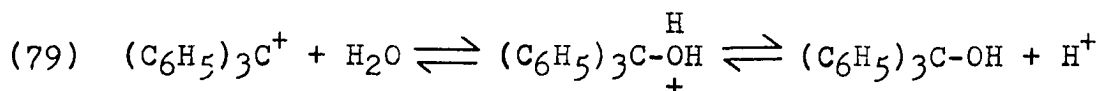
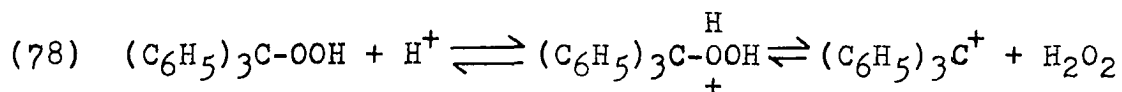
^aFrom unacidified reaction mixtures; addition of acid resulted in the isolation of triphenylmethanol in good yield rather than the hydroperoxide.

^bRecrystallized product.

^cInitial product isolated was a 1:2 complex of dimethylformamide and triphenylmethyl hydroperoxide, in 91% yield. The complex was easily converted to the hydroperoxide by washing an ether solution of it with water.

products were observed and the oxidation went to completion. It was found that to isolate the hydroperoxide, the solution must remain basic. Neutralization with strong acid (to pH 5 or lower) invariably led to the isolation of triphenylmethanol. Interestingly, the neutral or acidic solutions were more tractable, and the alcohol was isolated in 95% or better yield in all solvent except pyridine. The formation

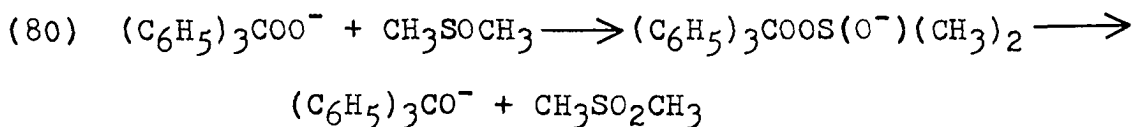
of the alcohol from the hydroperoxide in acid solution is most likely a S_N1 carbanium ion process. This process is a true equilibrium, for the triphenylmethyl hydroperoxide can be prepared from the alcohol in 90% hydrogen peroxide with a



trace of acid present (113). The product isolated from this equilibrium depends on the relative amounts of water and hydrogen peroxide present.

The formation of triphenylmethanol in basic 80/20 DMSO solution occurs by an oxygen transfer reaction. Dimethyl sulfoxide reduces triphenylmethyl hydroperoxide in basic solution to the alcohol, and is itself thereby oxidized to dimethyl sulfone. A precedent for this reaction is the oxidation of diphenyl sulfoxide to diphenyl sulfone by hydrogen peroxide (123). Triphenylmethyl hydroperoxide was mixed with a molar equivalent of DMSO in *t*-butyl alcohol containing an equivalent amount of potassium *t*-butoxide. The reaction was performed in a closed system, and no pressure change occurred. Triphenylmethanol was isolated in 94% yield, and dimethyl sulfone in 30% yield. The poor yield of dimethyl sulfone is due in large part to difficulties in isolation. It could not be eluted from any gas-liquid chromatography column tried, even from a column containing only 1% liquid phase at 330°. Since

it is very soluble in water as well as in t-butyl alcohol, the final isolation procedure involved hydrolysis, and acidification of the reaction mixture followed by evaporation to dryness on a steam bath. Boiling alcohol extraction of the residue gave the yield of dimethyl sulfone reported. Control experiments were run to establish the reaction. Triphenylmethyl hydroperoxide was recovered unchanged in quantitative yield from reaction with potassium t-butoxide in t-butyl alcohol. The hydroperoxide was also completely recovered from treatment with a large excess of 80/20 DMSO solution in the absence of any base. Hence the alcohol formation in DMSO is due to a simple oxygen transfer reaction between the ionized hydroperoxide and DMSO. The mechanism drawn is schematic, and not meant to distinguish between a concerted trans-



fer or two step sequence. This reaction is apparently very fast. Trityl hydroperoxide (0.1 M) and DMSO (0.1 M) in t-butyl alcohol containing potassium t-butoxide (0.1 M) react to form the alcohol in quantitative yield in two minutes or less. The actual rate may be much faster than the minimum required by the latter data for, as will be discussed in Section 2, this reaction is responsible for the formation of benzhydrol from diphenylmethyl hydroperoxide in the oxidation

of diphenylmethane, under conditions where a fast β -elimination can occur.

In pyridine containing solvents, triphenylmethyl peroxide was isolated in 5-10% yield (Table 16) from the oxidation of triphenylmethane. Triphenylmethyl hydroperoxide

Table 16. The isolation of triphenylmethyl peroxide from oxidations of triphenylmethane in pyridine

| Triphenylmethane ^a | Nitrobenzene ^a | Yield of trityl peroxide |
|-------------------------------|---------------------------|--------------------------|
| 0.1 | 0.00 | 10% |
| 0.1 | 0.044 | 6% |
| 0.1 | 0.39 | 2% |

^aMoles/liter.

comprised the balance of the reaction product, isolated in 80% yield. Triphenylmethyl peroxide could not be isolated from oxidations of triphenylmethane in any other solvent tried. The reason why trityl peroxide is isolated only in pyridine solvents is believed to be a specific solvent effect. Slough (124) found that potassium superoxide formed a strong charge-transfer complex with pyridine, but not with DMF or DMSO. The reaction of oxygen with triphenyl carbanion produces trityl radical and superoxide ion, initially in a cage. In the usual solvents, such as DMSO, DMF, or HMPA, spin relax-

ation probably occurs in the cage, and the product hydroperoxide is either formed by coupling in the cage, or diffusion of the intermediates followed by the reaction of trityl radical with oxygen, and electron transfer from a superoxide ion to the product trityl peroxy radical. When pyridine is the solvent, most superoxide radical ions are probably complexed, and presumably much less reactive. This gives the trityl peroxy radicals a greater lifetime, apparently long enough to intercept some trityl radicals, and form trityl peroxide. The formation of trityl peroxide is strong evidence against concerted addition of oxygen to carbanions, and sets an upper limit of 90% for the cage coupling process. Since the efficiency of pyridine as a trapping reagent is unknown, and is probably not high, no information on the actual extent of the cage process is obtained.

The variation of yield of trityl peroxide when nitrobenzene was added may be due partially to increased difficulty in isolating this product. A possible explanation is that the nitrobenzene radical anion formed by electron transfer from the triphenyl carbanion is uncomplexed by pyridine, and a trityl peroxy radical may accept an electron more readily from it than from the complexed superoxide. On the other hand, nitrobenzene radical anion reacts rapidly with oxygen, and may not have an appreciable lifetime.

The rate of oxidation of triphenylmethane is shown as a

function of solvent in Table 17. In all solvents listed, the stoichiometry of the oxidation was one mole of oxygen absorbed per mole triphenylmethane. The observed rates correlate with the polarity of the solvent, being faster in the more polar media. This solvent effect is consistent with the slow step being the ionization of triphenylmethane, but does not demand

Table 17. The effect of solvent on the autoxidation of triphenylmethane^a

| Solvent ^b | Initial rate ^c |
|--|---------------------------|
| <u>t</u> -Butyl alcohol | 0.00 |
| Pyridine (80%)- <u>t</u> -butyl alcohol (20%) | 0.02 |
| Pyridine ^{d,e} | 0.16 |
| Dimethylformamide (80%)- <u>t</u> -butyl alcohol (20%) | 0.39 |
| Dimethyl sulfoxide (80%)- <u>t</u> -butyl alcohol (20%) | 1.10 |
| Hexamethylphosphoramide (80%)- <u>t</u> -butyl alcohol (20%) | 1.28 |
| Hexamethylphosphoramide ^e | 2.3 ^f |

^aRoom temperature, pressure of oxygen = 749 mm, 25 ml of a vigorously shaken solution, 0.1 M triphenylmethane, 0.2 M potassium t-butoxide.

^bSolvent mixtures in volume %.

^cMoles oxygen per mole triphenylmethane per minute.

^dHeterogeneous.

^eSolid potassium t-butoxide used.

^fMinimum rate, probably diffusion controlled.

it since the same qualitative trend is observed for fluorene. The effect of the nature of base is seen in Table 18. The rate given for potassium hydroxide is probably a minimum since potassium hydroxide is not soluble to the extent of 0.2 M in 80/20 DMSO. The rate of oxidation increases as the

Table 18. The effect of the nature of the base on the rate of oxidation of triphenylmethane^a

| Base | Initial rate ^b |
|--|---------------------------|
| Potassium hydroxide ^c | 0.06 |
| Sodium methoxide | 0.18 |
| Potassium <u>t</u> -butoxide | 1.10 |
| Tetramethylammonium <u>t</u> -butoxide | 1.10 |

^aDimethyl sulfoxide (80%)-t-butyl alcohol (20%), triphenylmethane 0.1 M, base 0.2 M, 25 ml of a vigorously shaken solution at room temperature and 749 mm of oxygen.

^bMoles of oxygen per mole of triphenylmethane per minute.

^cSaturated.

anionic portion of the base becomes more efficient at ionizing C-H bonds, i.e., the conjugate acid of the base becomes weaker. Although the effectiveness of an ionic base depends in part on how dissociated it is (18), there was no difference between potassium t-butoxide and tetramethylammonium t-butoxide. Generally the larger and more polarizable the

cation, the more dissociated the base (18). Russell and Konaka¹ found that for the oxidation of triphenylmethane in 80/20 DMSO, the relative rate of oxidation varied with the nature of the cation: lithium t-butoxide 1.0, sodium t-butoxide 2.1, and potassium t-butoxide 5.5. These data are in good accord with the usual trends (18). The reason that tetramethylammonium t-butoxide is no more effective than potassium t-butoxide is that the latter is already completely dissociated. Specific solvation of potassium ion in DMSO solution has been invoked to explain similar results for other reactions (18).

A large kinetic deuterium isotope effect for the oxidation of triphenylmethane in 80/20 DMSO with potassium t-butoxide was found. $k_H/k_D = 7.2$

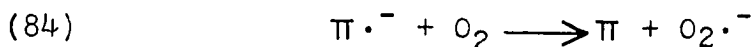
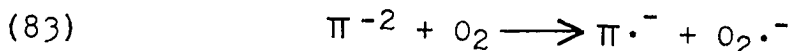
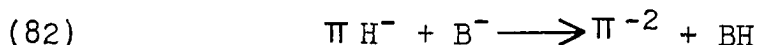
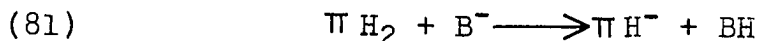
A co-oxidation of 0.1 M triphenylmethane and 0.1 M cumene in 80/20 DMSO containing 0.2 M potassium t-butoxide led to the oxidation of only triphenylmethane. The same rate and stoichiometry was observed as when triphenylmethane alone was oxidized. Cumene was recovered in near quantitative yield, and no oxidation products derived from cumene could be detected.

The direction and magnitude of the solvent and base effects, and the large isotope effect is strong evidence that

¹G. A. Russell and R. Konaka, Ames, Iowa. Effect of nature of base. Private communication. 1965.

the rate of oxidation is equal to the rate of ionization of triphenylmethane. This will be proven in Section B.

The rate and products for the oxidation of other hydrocarbons which ionize to give a tertiary carbanion is presented in Table 19. Diphenyl- α -naphthylmethane oxidations are very similar, although somewhat faster, than triphenylmethane oxidations. Kinetic data to show that diphenyl- α -naphthylmethane oxidations are ionization rate controlled are presented in Section C. The effect of varying X in R_2CHX , where X is a hydrocarbon group, can be seen in Table 19. For oxidation in 80/20 DMSO, the relative rates are given in Table 20. The oxidations of triphenylmethane, diphenyl- α -naphthylmethane, and diphenylmethane are ionization rate controlled as shown in Section C. It is quite likely that 1,1-diphenylethane is also. sym-Tetraphenylethane does not give oxygenated products, and probably oxidizes by a somewhat different mechanism than triphenylmethane. Russell *et al.* (29) have postulated for oxidations where dehydrogenation is observed rather than oxygenation the following mechanism:



(π represents an aromatic or unsaturated system.) Evidence that this pathway at least in part is likely is the larger

Table 19. Oxidation of some tertiary hydrocarbons

| Hydrocarbon ^a | Solvent ^b | Initial rate ^c | Stoichiometry ^d | Product ^e |
|-------------------------------|--|---------------------------|----------------------------|--|
| 9-Phenylfluorene | <u>t</u> -Butyl alcohol | 0.44 | 0.72 | --f |
| 9-Phenylfluorene | Dimethyl sulfoxide (80%)- <u>t</u> -butyl alcohol (20%) | 3.2 | 1.0 | 9-Phenyl-9-fluorenol (73%) |
| 9-Methylfluorene | <u>t</u> -Butyl alcohol | 0.36 | 0.95 | 9-Methyl-9-hydroperoxyfluorene (69.7%) |
| 9-Methylfluorene ^g | <u>t</u> -Butyl alcohol | 2.26 | 1.0 | -- |
| 9-Methylfluorene | Dimethyl sulfoxide (80%)- <u>t</u> -butyl alcohol (20%) | 3.9 | 1.0 | 9-Methyl-9-fluorenol (79.3%) |
| 1,1-Diphenylethane | Dimethyl sulfoxide (80%)- <u>t</u> -butyl alcohol (20%) | 0.018 | 0.57 | -- |

^a0.1 M Hydrocarbon; 0.2 M potassium t-butoxide.

^bSolvent mixtures in volume %.

^cMoles oxygen per mole hydrocarbon per minute.

^dMoles oxygen per mole hydrocarbon at completion.

^eMinimum yields of recrystallized products.

^fProbably mixture of alcohol and hydroperoxide.

^gIn the presence of .195 M nitrobenzene.

Table 19. (continued)

| Hydrocarbon | Solvent | Initial rate | Stoichiometry | Product |
|---|--|--------------|---------------|---|
| 1,1-Diphenylethane ^g | Dimethyl sulfoxide (80%)- <u>t</u> -butyl alcohol (20%) | 0.035 | 1.15 | -- |
| 1,1-Diphenylethane | Hexamethylphosphoramide | 0.61 | 0.84 | 1,1-Diphenyl ethanol (--) |
| Diphenyl- α -naphthyl- methane ^h | Dimethyl sulfoxide (80%)- <u>t</u> -butyl alcohol (20%) | 1.64 | 1.0 | Diphenyl- α - naphthylmethanol (95%) |
| <u>sym</u> -Tetraphenyl- ethane ^h | Dimethyl sulfoxide (80%)- <u>t</u> -butyl alcohol (20%) | 0.025 | 1.4 | Tetraphenyl- ethene (96%) |

^h0.05 M.

Table 20. Relative rates of oxidation in dimethyl sulfoxide (80%)-t-butyl alcohol (20%)^a

| Hydrocarbon ^b | Relative rate ^c |
|-------------------------------------|----------------------------|
| Diphenyl- α -naphthylmethane | 1.22 ^d |
| Triphenylmethane | 1.0 ^d |
| Diphenylmethane | 0.63 ^d |
| <u>sym</u> -Tetraphenylethane | 0.023 |
| 1,1-Diphenylethane | 0.016 |

^aContaining 0.2 M potassium t-butoxide.

^b0.1 M.

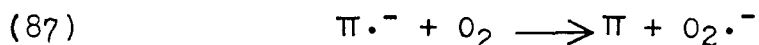
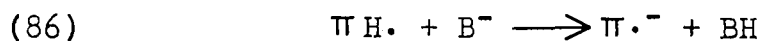
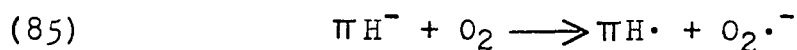
^cRelative to triphenylmethane.

^dCalculated from kinetic rate constants given in Section C.

stoichiometry (1.4 moles oxygen per mole ethane). Stoichiometries this large were never observed for the other hydrocarbons in Tables 19 and 20. Secondly, when the sym-tetraphenylethane oxidation mixture was poured into water, a vigorous foaming occurred. This is a qualitative test for significant amounts of superoxide. Actual isolation of potassium superoxide was not attempted.

The relative rates in Table 20 are in qualitative agreement with the generally accepted electronic effects of α -naphthyl, phenyl, hydrogen, and methyl, if ionization of the

tertiary hydrogen is the rate controlling process. If the electron transfer with oxygen is rate controlling, diphenylmethane might be expected to be the slowest, since generally secondary radicals are less stable than tertiary. The diphenylmethyl substituent is in qualitatively the place that an ionization rate controlled process would be expected to put it. Possibly instead of the dianion reacting with oxygen, the mono-anion does, followed by loss of a proton, and then another electron transfer. In any case, the oxidation of sym-tetraphenylethane does not measure a single ionization rate, unless reaction 81 occurs slowly, and is followed by reactions 85-87.



As with triphenylmethane, hydroperoxides were isolated in the oxidation of 9-phenylfluorene only in the absence of DMSO.

Fluorene, 9-phenylfluorene, and 9-methylfluorene all have approximately the same rate in 80/20 DMSO (Fluorene results in Part 2). In t-butyl alcohol, 9-phenylfluorene and 9-methylfluorene oxidize about twenty times faster than fluorene. (Fluorene oxidizes at a rate of 0.02 moles oxygen/mole fluorene-minute in t-butyl alcohol.) In t-butyl alcohol, for fluorene, and probably for 9-phenylfluorene and

9-methylfluorene, the rate of electron transfer from the carbanion to oxygen is the slowest step. The rate of 9-phenylfluorene in t-butyl alcohol is probably not as accurate a measure of the rate of electron transfer as the other two fluorene compounds. The stoichiometry of the 9-phenylfluorene oxidation is only 0.72 in contrast to the 1.0 observed in the other two cases. The product of this oxidation seems to be a mixture of alcohol and hydroperoxide from the infrared spectrum. Presumably the same phenomena noted by Sprinzak (30) in the oxidation of 9-phenylfluorene and other fluorenes in pyridine is occurring here. Sprinzak (30) found at 40°, that alcohols were the products isolated, and the oxygen stoichiometries were around 0.5. At 0° however, the products were hydroperoxides, and 1.0 stoichiometries were found. The phenomenon was explained by the reaction of the hydroperoxide with the carbanion, which reaction was demonstrated independently of the oxidation. Sprinzak (30) writes the mechanism for this reaction as a nucleophilic displacement of the carbanion on the unionized hydroperoxide. The hydroperoxide is probably ionized however, and the displacement could be

(88)
$$R_3C^- + R'_3COOH \longrightarrow R_3COH + R'_3CO^-$$

written as a carbanion displacing an alkoxide ion. This latter mechanism has the drawback of charge repulsion.

Differences between results reported here for t-butyl alcohol and by Sprinzak (30) for pyridine are probably due to

differences in the ionizing ability of the solvents. Pyridine is a better ionizing solvent than t-butyl alcohol. In the case of 9-phenylfluorene, there is probably somewhat more carbanion present in pyridine solution than in t-butyl alcohol, and hence the displacement occurs somewhat more readily in the former solvent.

For 9-methylfluorene, one would expect much less carbanion present in t-butyl alcohol than in the case of 9-phenylfluorene. There is, for example, a much slower oxidation in the case of 1,1-diphenylethane in 80/20 DMSO than for triphenylmethane in 80/20 DMSO, conditions where both substances oxidize at the rate of ionization. Evidence that this explanation is correct is the fact that 9-methylfluorene has a stoichiometry of 1.0 and yields only the hydroperoxide in t-butyl alcohol. In pyridine, where again a larger amount of carbanion would be present, the alcohol was obtained (30).

The fact that fluorene oxidizes at a much slower rate than 9-methylfluorene is excellent evidence that the rate of electron transfer is the slow step for these oxidations. As was mentioned in the discussion of the triphenylmethane series, a secondary carbanion would be expected to electron transfer more slowly than a tertiary. Proof that the rate of electron transfer is much slower than the rate of ionization for fluorene in t-butyl alcohol is presented in Part 2 of Section 2.

The near identity of the rates of oxidation of fluorene, 9-phenylfluorene, and 9-methylfluorene in 80/20 DMSO is probably due to the fact that in this solvent the oxidation rate is so fast that it may be controlled by the diffusion of oxygen into the solvent, and is also about as fast as can be measured accurately by the volumetric technique employed.

The product of the oxidation of 9-methylfluorene in *t*-butyl alcohol was not unequivocally established as the hydroperoxide. It had an infrared spectrum which was similar, but not identical, to the alcohol. The main difference was that the hydroxyl band was shifted about 20 wave numbers higher. This same shift was found between triphenylmethanol and triphenylmethyl hydroperoxide. The melting point of the methylfluorene product was 152°C. The hydroperoxide is reported to melt at 150°C (30), and the alcohol melts at 174°C (125). On this basis, the reasonable assignment was made.

Cumene did not oxidize in 100% HMPA. Apparently it did not ionize in that solvent, or any other tried.

Data on the oxidation of some compounds bearing resemblance to the previous tertiary hydrocarbons in that they can all be represented by R_2CHX is given in Table 21. "X" in this case, however, is not a hydrocarbon group, but is a strongly electronegative substituent. The rates are about in the order expected if ionization was the rate limiting process, but for the compounds which oxidize very rapidly

Table 21. Oxidation of some substituted tertiary hydrocarbons^a

| Compound ^b | Initial rate ^c | Stoichiometry ^d | Product ^e |
|-------------------------------------|---------------------------|----------------------------|---|
| Benzhydryl amine | 0.10 | 1.2 | DMSO-benzophenone adduct ^f (--) |
| Diphenylacetic acid | 0.86 | 1.0 | Benzilic acid (74%) |
| 1,1-Diphenyl acetone | 1.87 | 1.27 | DMSO-benzophenone adduct ^f (40%) |
| Methyl diphenylacetate ^g | 3.1 ^h | 1.0 | Benzilic acid (83%) |
| Diphenylacetonitrile ^g | 2.9 ^h | 1.0 | DMSO-benzophenone adduct ^f (26%) |
| Benzhydryl chloride ^g | 3.2 ^h | 1.0 | DMSO-benzophenone adduct ^f (52%) |
| Benzhydryl bromide ^g | 2.4 ^h | 1.0 | DMSO-benzophenone adduct ^f (--) |

^aIn dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) containing 0.2 M potassium *t*-butoxide; 25 ml of solvent at room temperature and 749 mm of oxygen.

^b0.1 M.

^cMoles oxygen per mole compound per minute.

^dMoles oxygen absorbed at completion per mole compound used.

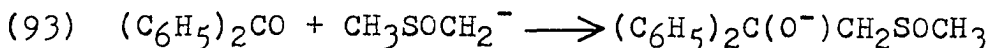
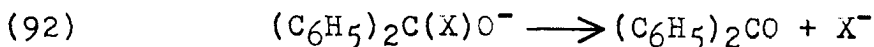
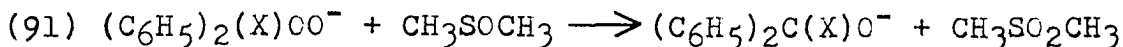
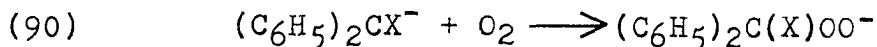
^eYields are of recrystallized product, and are minimum.

^f1,1-Diphenyl-(1-methylsulfinyl)-ethanol.

^g0.05 M.

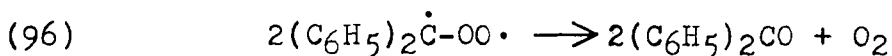
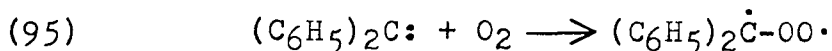
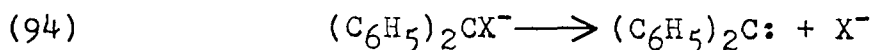
^hRates may be diffusion controlled, and are somewhat approximate.

(initial rates of 1.5 or greater) small differences can be due to experimental error. For example, a rate of 3.0 moles of oxygen per mole of substrate per minute implies for an oxidation of 2.5 mmoles of substrate (0.1 M in 25 ml) that the reaction is over in about 33 seconds. Actually these are initial rates, and the reaction velocity decreases with time, but measuring an initial rate of that magnitude is difficult. The mechanism of the oxidation of these compounds is thought to be similar to that proposed for triphenylmethane in 80/20 DMSO, with the addition of a ketone forming step, and a DMSO condensation to give the adduct in some cases.



Reaction 92 is apparently important when "X" is a chloro, bromo, cyano, or amino group. Some oxidation product of 1,1-diphenylacetone also undergoes a ketone forming elimination. Benzilic acid and methyl benzilate are stable under the reaction conditions. An alternate path to benzophenone is via α -elimination of the carbanion formed in reaction 89, and reaction of the carbene or carbenoid product with oxygen. The reaction of diphenylmethylene with oxygen is known to

give benzophenone (126-130). Some aspects of the mechanism will be discussed in Part 2 of this section.



The larger stoichiometry observed for 1,1-diphenylacetone is probably due to oxidation of the methyl group in some molecules. The larger stoichiometry for benzhydryl amine may be due to oxidation of the amino group, but generally only aromatic amines oxidize (26).

An aliphatic ester with a tertiary α -hydrogen was oxidized in 80/20 DMSO. *t*-Butyl 2-methylbutyrate oxidized at a rate of 0.39 moles of oxygen per mole of ester per minute, and had an overall stoichiometry of 1.0. When nitrobenzene (0.2 M) was present, the rate was increased only about 20%, but the stoichiometry changed to 1.8 moles oxygen absorbed per mole ester. A vigorous evolution of oxygen was noted on pouring the reaction mixture from the latter oxidation into water, indicating the presence of superoxide. No evolution was noted in the case of the uncatalyzed oxidation.

2. Secondary carbanions

Diphenylmethane was oxidized in a variety of solvents. It had been previously oxidized in 80/20 DMSO by Janzen (25). The product isolated after oxygen absorption ceased was

benzophenone in all solvents except DMSO, where the product was the DMSO-benzophenone adduct, 1,1-diphenyl-1-(methylsulfinyl)-ethanol. This adduct was first discovered by Russell *et al.* (26) and shown to readily form from benzophenone and DMSO in the presence of potassium *t*-butoxide. The product, initial rate, and stoichiometry of the oxidation of diphenylmethane as a function of solvent is presented in Table 22. The products were isolated and identified in each solvent. Gas-liquid partition chromatography detected only benzophenone in near quantitative yield at the completion of oxidations in all solvents except DMSO. In 80/20 DMSO, Janzen (25) found a 96% yield of the DMSO-benzophenone adduct. This was confirmed. The rates of oxidation parallel closely those observed in the triphenylmethane oxidation. The initial rate of oxidation of diphenylmethane is believed to be identical with the rate of ionization. Evidence for this is the solvent effect, which is very similar to that found for triphenylmethane, and a deuterium isotope effect of 8.1. This evidence is further supported by kinetic data to be presented in Section C. The initial rate of oxidation of diphenylmethane is probably equal to the rate of ionization in all solvents except HMPA.

The most interesting aspect of the oxidation of diphenylmethane is the change in stoichiometry with solvent. Janzen (25) reported a ratio of 3.36 moles of oxygen absorbed per

Table 22. The oxidation of diphenylmethane^a

| Solvent ^b | Initial rate ^c | Stoichiometry ^d | Product |
|---|---------------------------|----------------------------|-----------------------------|
| <u>t</u> -Butyl alcohol | 0.0 | | |
| Pyridine (80%)- <u>t</u> -butyl alcohol | 0.02 | -- | -- |
| Pyridine ^{e,f} | 0.15 | 1.4 ^g | Benzophenone |
| Dimethylformamide (80%)- <u>t</u> -butyl alcohol (20%) | 0.37 | 1.0 | Benzophenone |
| Dimethyl sulfoxide (80%)- <u>t</u> -butyl alcohol (20%) | 1.0 | 2.66 | DMSO-benzophenone adduct |
| Hexamethylphosphoramide (80%)- <u>t</u> -butyl alcohol (20%) | 1.09 | 1.1 | Benzophenone |
| Hexamethylphosphoramide | 2.9 ^h | 2.65 | Benzophenone |

^a0.1 M diphenylmethane, 0.2 M potassium t-butoxide in 25 ml of solution at room temperature and 749 mm of oxygen.

^bSolvent mixtures in volume %.

^cMoles oxygen per mole diphenylmethane per minute.

^dMoles oxygen when absorption ceases per mole diphenylmethane initially.

^eSolid potassium t-butoxide used.

^fHeterogeneous.

^gAfter 35 minutes.

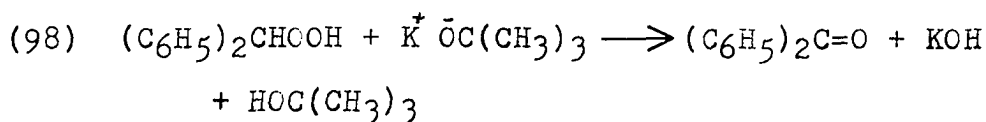
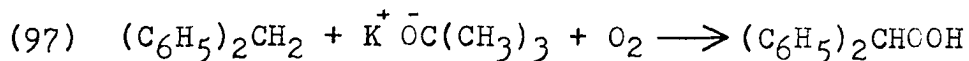
^hMinimum rate.

mole diphenylmethane in 80/20 DMSO, and was able to explain this result when he isolated a 60% yield of benzhydrol after 1.53 moles of oxygen per mole diphenylmethane had been absorbed. Benzhydrol is known to oxidize to benzophenone in 80/20 DMSO with potassium t-butoxide at a much slower rate than diphenylmethane (101). The rate difference allows the intermediate to be isolated. The stoichiometry of the oxidation of benzhydrol in 80/20 DMSO was found to vary with the concentration of potassium t-butoxide by Geels (101) and was 1.65 moles of oxygen per mole benzhydrol when a three time excess of base was used. From the stoichiometry data in Table 22, it can be seen that if about 1.6 moles of oxygen per mole diphenylmethane was used for the oxidation of benzhydrol, the oxidation of diphenylmethane to benzhydrol required about one mole of oxygen per mole of diphenylmethane, consistent with the stoichiometries observed for the tertiary hydrocarbons.

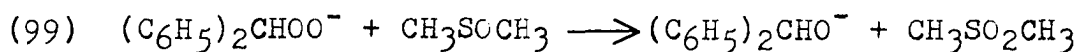
The oxidation of diphenylmethane in either 80/20 DMF or 80/20 HMPA required only 1 mole of oxygen per mole diphenylmethane. In these solvents, benzophenone is isolated in high yield, and the oxidation does not proceed through benzhydrol as an intermediate.

Almost certainly, the initial oxidation product is diphenylmethyl hydroperoxide, in analogy with the oxidation of triphenylmethane. Secondary hydroperoxides are known to

undergo a facile β -elimination to give ketones (31). Thus in 80/20 DMF or 80/20 HMPA, the initially formed hydroperoxide quickly undergoes β -elimination to benzophenone.



In 80/20 DMSO by contrast, the hydroperoxide must be very quickly reduced to benzhydrol by DMSO, as triphenylmethyl hydroperoxide was shown to rapidly be reduced to triphenylmethanol in DMSO solution. The β -elimination reaction to



form benzophenone is rapid, hence the DMSO reduction of a hydroperoxide must be a very fast reaction. Of course, under the oxidation conditions, DMSO is present in huge excess and this may swamp out the elimination reaction.

Table 23 presents data from experiments where the oxidation of diphenylmethane was interrupted at an intermediate stage. In some cases, water was added immediately to prevent further reaction, and in other cases, 10 milliliters of DMSO were added, the reaction mixture shaken several times, and then water added. The reaction mixtures were then analyzed by g.l.p.c. For oxidation in 80/20 DMSO, benzhydrol was found in high yield after one molar equivalent of oxygen had been absorbed. The oxidation of diphenylmethane in HMPA

Table 23. Interrupted oxidations of diphenylmethane^a

| Solvent ^c | Stoichiometry ^d | Interruption procedure | % Product ^b | | |
|---|----------------------------|------------------------|------------------------|--------------------|---------------------|
| | | | $\phi_2\text{CH}_2$ | $\phi_2\text{C=O}$ | $\phi_2\text{CHOH}$ |
| Dimethyl sulfoxide (80%)- <u>t</u> -butyl alcohol (20%) ^e | 1.0 | H ₂ O | 7 | 2 | 85.5 |
| Hexamethylphosphoramide | 1.0 | H ₂ O | 25 | 48 | 0 |
| Hexamethylphosphoramide | 0.94 | DMSO; H ₂ O | 30 | 0.5 | 4 |
| Hexamethylphosphoramide | 1.29 | DMSO; H ₂ O | 8.6 | 0.6 | 2 |
| Hexamethylphosphoramide | 1.58 | DMSO; H ₂ O | 0.3 | 70 | 0 |

^a0.1 M diphenylmethane, 0.4 M potassium t-butoxide in 25 ml. of solution.

^bBy g.l.p.c. using internal standards.

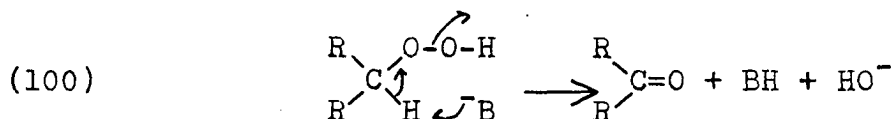
^cSolvent mixtures in volume %.

^dMoles of oxygen per mole of diphenylmethane when interrupted.

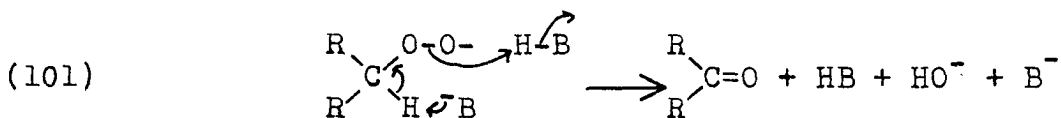
^e0.2 M potassium t-butoxide.

(100%) was intriguing since the stoichiometry was found to be about 2.5. There can be some error in this figure, since HMPA slowly absorbs oxygen in the presence of potassium t-butoxide. However more than 1.5 molar equivalents of oxygen were absorbed very rapidly, and the stoichiometry is at least 2.0. It was therefore quite amazing to find that if the oxidation was stopped after one molar equivalent of oxygen had been absorbed, and water added, about 48% of the product was benzophenone and 25% was unoxidized diphenylmethane. All yields quoted are based on starting diphenylmethane. If this reaction mixture had not been hydrolyzed, it would have absorbed 1.5 more molar equivalents of oxygen. Some insight into this reaction is provided when an oxidation of diphenylmethane in HMPA was stopped after one mole of oxygen per mole of diphenylmethane had been absorbed, DMSO added, the reaction mixture shaken, and then water added. This reaction mixture contained by g.l.p.c. less than 1% benzophenone, and did contain 4% benzhydrol. 30% Diphenylmethane was also present. Clearly, at least some hydroperoxide was present, and was reduced by the DMSO. Unfortunately, how much can not be estimated, as the disappearance of benzophenone can also be due to condensation with DMSO to produce the adduct. The adduct could not be analyzed by g.l.p.c. Since a reasonable mass balance was gotten in the absence of DMSO, probably about 40% of the adduct was present.

The probable explanation of these results is that the intermediate oxidation product of diphenylmethane in HMPA is the hydroperoxide, which does not β -eliminate in this solvent. Since triphenylmethyl hydroperoxide could be isolated from HMPA in the oxidation of triphenylmethane, there is no reason to expect any difficulty with hydroperoxide formation, or reaction with solvent in this case. The β -elimination reaction is usually written with a base attacking the α -hydrogen of an unionized hydroperoxide, hydroxide ion being

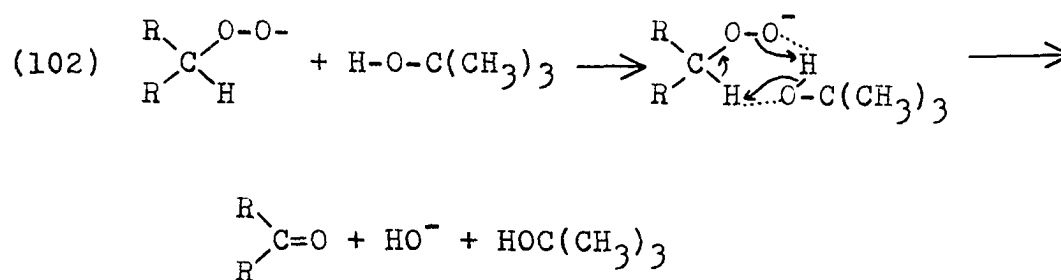


expelled. Actually, in strongly basic solvents like 80/20 DMF, 80/20 DMSO, or HMPA, the proton bound to oxygen must be very acidic, and it is unlikely that any unionized hydroperoxides are present. It seems preferable, although there is no evidence, to write the β -elimination in 80/20 DMF or 80/20 HMPA as follows:



The elimination of an oxide ion would seem highly unlikely. Whether or not proton transfer to the hydroperoxide oxygen is simultaneous with abstraction of the α -proton can not be decided; the dianion ($\text{R}_2\text{C-O-O}^{-2}$) could be a transient intermediate in these solvents. It is true that benzhydrol does

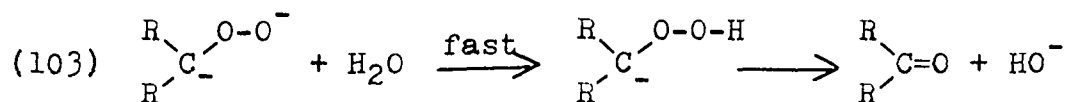
not form a dianion in 80/20 DMSO (see Section C) but the dianion of benzhydrol requires the like charges to be much closer, and is probably much less favorable to dianion formation than the hydroperoxide. An alternative possibility for the elimination mechanism would be participation by t-butyl alcohol in a cyclic hydrogen bonded structure, which could open to give the ketone. The only disadvantage to this



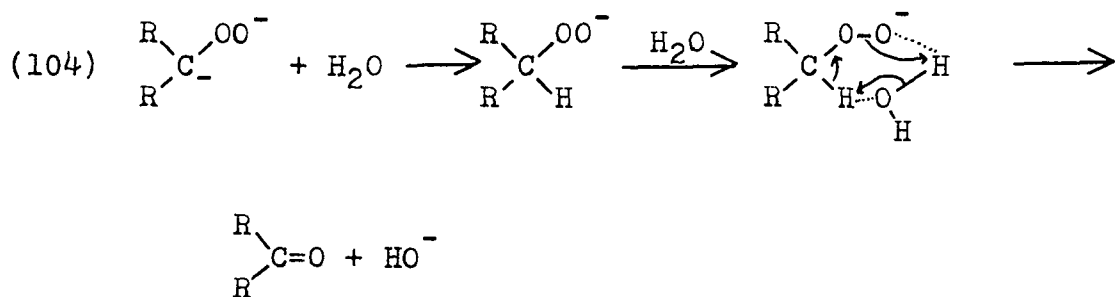
process is requiring a very weak base, t-butyl alcohol, to abstract a proton bound to carbon. This may be overcome by the driving force due to ketone formation.

The explanation for the curious results in HMPA is probably that proton transfer does not occur. The only acidic protons which are present are in t-butyl alcohol molecules formed from potassium t-butoxide in the ionization step, and since the maximum amount of these would be one equivalent relative to diphenylmethane or oxidation product, a process involving proton transfer would be much slower than in the solvents containing 20% t-butyl alcohol. The 48% yield of benzophenone from hydrolysis of an interrupted oxidation after one molar equivalent of oxygen had been absorbed lends

credence to the idea that the actual species present is the dianion of diphenylmethyl hydroperoxide, and that kinetic protonation on oxygen by water leads to immediate β -elimination and ketone formation. Alternatively the protonation

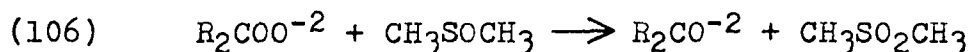
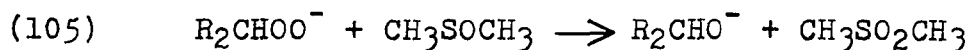


could take place on carbon, followed by protonation on oxygen, abstraction of the α -proton, then elimination. The latter sequence could be made less clumsy if a hydrogen bonding catalyst like water participated:



This latter scheme would explain the data equally well if the mono-anion was the predominate species in HMPA.

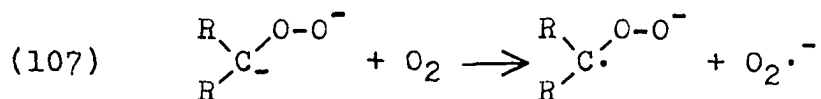
The formation of benzhydrol when DMSO is added to the interrupted oxidation could be due to reaction with either the mono-anion or the di-anion of the hydroperoxide. The



latter process is less attractive, since no analogy is known,

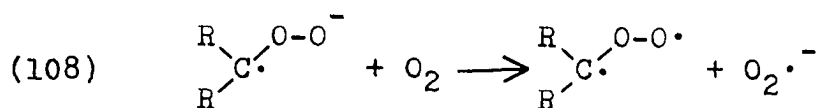
and the dianion of benzhydrol, the product required, does not readily form in 80/20 DMSO. HMPA is a more basic medium, however. The rather poor yield of benzhydrol from the DMSO treatment may be due to the lack of reaction of the hydroperoxide dianion with DMSO; what is formed could come from the reaction of the ionized hydroperoxide (monoanion), which is probably in equilibrium with the dianion form. Another explanation of the poor benzhydrol yield is that DMSO could act as a source of protons, hence catalyzing the β -elimination. The possibility that the yield of benzhydrol obtained is an accurate reflection of the amount of hydroperoxide present seems remote on the basis of the stoichiometries observed and the yields of benzophenone obtained.

The continued uptake of oxygen when the reaction is not interrupted is probably due to oxidation of the hydroperoxide. No examples of this process are known. By analogy with the mechanism due to Russell *et al.* (29), for the oxidation of 9-fluoreno1, a radical anion is proposed as an intermediate. This radical anion is not however, the resonance stabilized ketyl which is well known, and which has been identified in alcohol oxidations. This "oxologue" of a ketyl is unknown.

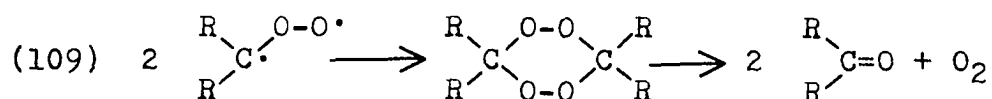


If this radical anion reacted with oxygen, a di-radical could

be produced. Dimerization of two di-radicals, followed by



rearrangement could lead to benzophenone. This di-radical has been proposed as an intermediate in the reaction of di-



phenylmethylene with oxygen (126-130), a process which leads to benzophenone as product. The cyclic oxide intermediate was actually isolated in one case (126).

Evidence for this type of overall process is the evolution of large amounts of oxygen when water is added to the completed oxidation, indicating the presence of superoxide. The mechanism predicts a stoichiometry of 2.5, which is observed.

The base catalyzed autoxidation of fluorene in pyridine was studied by Sprinzak (30). The oxidation was studied in *t*-butyl alcohol by Moye (8) and was extensively investigated in 80/20 DMSO and other solvents by Janzen (25). A table illustrating the effect of solvent on the oxidation of fluorene was given in the literature section of this thesis. 9-Fluorenone was the product isolated in all solvents except in DMSO-*t*-butyl alcohol mixtures where the DMSO-fluorenone adduct (9-(methylsulfinyl)-fluorene-9-ol) was isolated (25).

The effect of solvent on the rate and stoichiometry of the oxidation of fluorene is shown in Table 24. The relative rates are similar to those reported by Janzen (25). Products of these oxidations were determined by gas-liquid partition

Table 24. Oxidation of fluorene^a

| Solvent ^b | Stoichiometry ^c | Initial rate ^d |
|---|----------------------------|---------------------------|
| <u>t</u> -Butyl alcohol | 1.09 | 0.035 |
| Dimethylformamide (80%)- <u>t</u> -butyl alcohol (20%) | 1.16 | 2.7 ^e |
| Dimethyl sulfoxide (80%)- <u>t</u> -butyl alcohol (20%) | 1.14 | 2.8 ^e |
| Hexamethylphosphoramide (80%)- <u>t</u> -butyl alcohol (20%) | 1.22 | 2.9 ^e |
| Hexamethylphosphoramide ^f | 2.5 | 3.7 ^e |

^a0.1 M fluorene, 0.2 M potassium t-butoxide in 25 ml of solution at room temperature and 749 mm of oxygen.

^bSolvent mixtures in volume %.

^cMoles of oxygen per mole of fluorene.

^dMoles of oxygen per mole of fluorene per minute.

^eMinimum rate, probably diffusion controlled.

^f0.4 M potassium t-butoxide (solid).

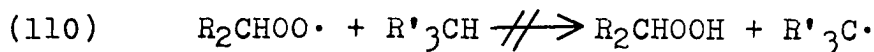
chromatography, and 9-fluorenone was present in close to quantitative yield in *t*-butyl alcohol, 80/20 DMF, and 80/20 HMPA. A 10-20% yield of fluorenone was found for oxidations in 80/20 DMSO or HMPA (100%). The major product in 80/20 DMSO is the DMSO-fluorenone adduct. The reason for the poor yield of fluorenone in HMPA was not determined.

The stoichiometry of the oxidation of fluorene was nearly 1 mole of oxygen per mole of fluorene in all cases except 100% HMPA. Apparently in 80/20 DMSO, 9-hydroperoxyfluorene undergoes β -elimination to give fluorenone faster than it can be reduced by DMSO to the alcohol, in contrast to the results for diphenylmethane. This result is reasonable since Russell *et al.* (29) and Geels (101) have evidence that the dianion of fluorenone forms under conditions where the dianion of benzhydrol does not form. The abstraction of the α -proton by base would hence be much more rapid for 9-hydroperoxyfluorene than for the diphenylmethyl hydroperoxide. No 9-fluorenone could be detected by g.l.p.c. in any fluorene oxidation.

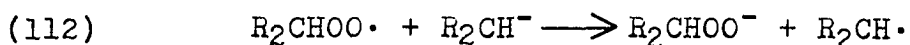
An increased stoichiometry in the oxidation of fluorene in 100% HMPA relative to other solvents was observed. The stoichiometry of 2.5 moles of oxygen per mole of fluorene is similar to that observed for diphenylmethane in this solvent. Gas-liquid partition chromatography analysis of an oxidation of fluorene in HMPA interrupted after 1 mole of oxygen per

mole of fluorene had been absorbed showed only fluorene and fluorenone to be present, even when treated with DMSO prior to hydrolysis. Although in the case of fluorene the only evidence is the increase in stoichiometry, the same mechanism is likely for the oxidation of diphenylmethane in 100% HMPA as that proposed for diphenylmethane. The lack of formation of fluorenol on addition of DMSO to an oxidation in HMPA is reasonable, since none formed in 80/20 DMSO oxidation. The initially formed hydroperoxide apparently can not easily eliminate in HMPA, and must oxidize instead.

A co-oxidation of fluorene and triphenylmethane in t-butyl alcohol containing potassium t-butoxide, conditions under which triphenylmethane alone does not oxidize and is not ionized, resulted in the oxidation of only fluorene. No change in rate or stoichiometry was found compared to the oxidation of fluorene alone, and triphenylmethane was recovered in near quantitative yield by g.l.c. No triphenylmethanol could be detected by g.l.c. This observation rules out any reaction whereby peroxy radical abstract hydrogen atoms in a chain propagating step, since the α -hydrogens of triphenyl-



methane and fluorene have similar reactivities toward peroxy radicals (131). It does not rule out the presence of peroxy radicals, since electron transfer reactions of peroxy radicals and superoxide radical anion or carbanions would be



expected to be quite rapid. Evidence that some kind of chain propagation process does occur in the oxidation of fluorene is presented by Russell et al. (29). They find a kinetic chain length of 21 in the nitrobenzene catalyzed oxidation of fluorene. The reaction of peroxy radical and carbanion is postulated to be this process.

The oxidation of fluorene-9,9-d₂ in t-butyl alcohol with potassium t-butoxide had exactly the same initial rate and stoichiometry as the oxidation of undeuterated fluorene. Absolutely no differences were observed. The lack of an isotope effect means the rate of oxidation of fluorene is not controlled by the rate of ionization. The rate of exchange of the dideuterio fluorene in t-butyl alcohol containing potassium t-butoxide was found to be more than fifty times faster than the rate of oxidation under the same conditions. Details of this experiment will be discussed in Part 2 of Section C.

The oxidation of fluorene can not be catalyzed or inhibited by compounds such as ferric chloride or arsenic trioxide which are effective in long chain free radical autoxidations. Russell et al. (26) found that nitrobenzene or substituted nitrobenzenes greatly catalyze the rate of oxidation of fluorene in t-butyl alcohol. Janzen (25) found that

a plot of log rate of oxidation of fluorene against σ for a number of substituted nitrobenzenes gave a straight line. The same ρ was obtained from a plot of log rate of electron transfer of fluorenyl anion versus σ for the substituted nitrobenzenes (25). Hence for fluorene, the rate of oxidation is controlled by the rate of electron transfer.

In Part 2 of Section C, a means of measuring rates of ionization by measuring rates of oxidation as a function of catalyst concentration is presented. Kinetic data consistent with the conclusion that the rate of oxidation of fluorene in t-butyl alcohol in the absence of catalyst is controlled by the rate of electron transfer of fluorenyl anion to oxygen will also be presented.

The oxidation of a few other compounds which ionize to give secondary carbanions was studied. Table 25 presents the rates and products observed.

Cyclopentadiene and 4,5-methylene phenanthrene were oxidized in t-butyl alcohol and 80/20 DMSO. The rate of oxidation of 4,5-methylene phenanthrene was very similar to the rate of oxidation of fluorene in either t-butyl alcohol or 80/20 DMSO. 4,5-Carbonylphenanthrene was isolated in poor yield from the oxidation in t-butyl alcohol. Some 4-phenanthroic acid was isolated from the oxidation of 4,5-methylene-phenanthrene in 80/20 DMSO. Kruber (104) reported the conversion of 4,5-carbonylphenanthrene to 4-phenanthroic acid

Table 25. Oxidation of some compounds containing secondary hydrogen atoms^a

| Compound | Solvent ^b | Initial rate ^c | Stoichiometry ^d | Product |
|--|-------------------------|---------------------------|----------------------------|--|
| Benzyl chloride ^e | HMPA ^f | 1.22 | 1.14 | <u>trans</u> -Stilbene (trace) |
| Acenaphthene | 80/20 DMSO ^g | 0.15 | 2.28 | Napthalic anhydride ^h (63%) |
| 4,5-Methylenephenanthrene ⁱ | <u>t</u> -Butyl alcohol | 0.04 | 1.8 | 4,5-Carbonyl phenanthrene |
| 4,5-Methylenephenanthrene ⁱ | 80/20 DMSO ^g | 3.7 | 1.32 | 4-Phenanthroic acid |
| Camphor ^e | 80/20 DMSO ^g | 0.39 | 2.06 | |

^a0.1 M substrate, 0.2 M potassium t-butoxide in 25 ml of solution at room temperature and 749 mm of oxygen.

^bSolvent mixtures in volume %.

^cMoles of oxygen per mole of substrate per minute.

^dMoles of oxygen per mole substrate.

^e0.6 M potassium t-butoxide (solid).

^fHMPA = hexamethylphosphoramide.

^gDimethyl sulfoxide (80%)-t-butyl alcohol (20%).

^hNo acenaphthylene could be isolated.

ⁱ0.05 M substrate.

Table 25. (continued)

| Compound | Solvent | Initial rate | Stoichiometry | Product |
|--|-------------------------|-------------------|---------------|--------------------------------|
| Camphor ^e | HMPA ^f | 2.35 | 2.28 | |
| Cyclopentadiene | <u>t</u> -Butyl alcohol | 0.52 ^j | 1.32 | |
| Cyclopentadiene | 80/20 DMSO ^g | 1.1 | 1.81 | |
| α -Ethyl-naphthalene ^k | HMPA ^f | 0.6 | 4.66 | α -Naphthoic acid (51%) |
| β -Ethyl-naphthalene ^k | HMPA ^f | 0.67 | 4.82 | β -Naphthoic acid (59%) |

^jUnchanged by the addition of 195% nitrobenzene relative to substrate.

^k0.8 M potassium t-butoxide (solid).

in strong base. The larger stoichiometry than that observed for fluorene may be due to oxidative degradation of the ketone. The rate of oxidation of cyclopentadiene in t-butyl alcohol was not enhanced by the addition of nitrobenzene. The oxidation of cyclopentadiene in t-butyl alcohol is probably not ionization rate controlled. Fluorene oxidizes much more slowly in t-butyl alcohol than cyclopentadiene, but the rate of ionization of fluorene in t-butyl alcohol as measured by the rate of exchange of dideuterio fluorene or the rate of electron transfer (see Section C) is much faster than the rate of oxidation of cyclopentadiene. The pK_a of cyclopentadiene was measured to be 14-15 by Dessy et al. (92) whereas fluorene is assigned a pK_a of 25 by McEwen (65). Dessy et al. (92) also found that cyclopentadiene exchanged about 5000 times faster than fluorene in DMF with triethylamine as base. From the comparison in Table 26, it would seem highly unlikely that the rate of oxidation of cyclopentadiene in t-butyl alcohol is controlled by the ionization of a carbon-hydrogen bond.

Acenaphthene oxidized in 80/20 DMSO to give naphthalic anhydride. The anhydride spontaneously formed on neutralizing the basic reaction mixture, which contained an ion of the diacid. About 24% starting material was recovered in this oxidation, and it is believed that a deficient amount of base was present. Acenaphthylene was not isolated from partial

Table 26. Relative rates of oxidation of secondary hydrocarbons^a

| Compound | Relative rate ^b |
|---------------------------|----------------------------|
| Fluorene | 2.8 |
| Cyclopentadiene | 1.1 |
| 4,5-Methylenephenanthrene | 3.7 |
| Diphenylmethane | 1.0 |

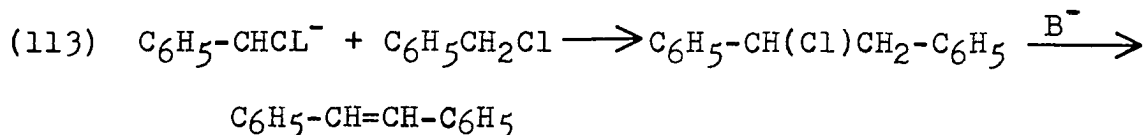
^a0.1 M substrate, 0.2 M potassium *t*-butoxide in 25 ml of dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) at room temperature and 749 mm of oxygen.

^bRelative to diphenylmethane.

oxidation of acenaphthene, and oxidized very slowly under identical conditions, hence is not an intermediate in this oxidation. The acenaphthene oxidation probably proceeds through a ketone or diketone intermediate, and possibly through an alcohol. The minimum stoichiometry would be 3 moles of oxygen per mole of acenaphthene, and it would be greater if there is an alcohol intermediate. The observed 2.28 stoichiometry is equivalent to about 3 when the 24% recovery of starting material is taken into account.

The oxidation of benzyl chloride had a fast initial rate, but the rate rapidly decreased, and after three minutes was only slightly greater than the solvent blank. This unusual decrease may be due to solvolysis of the chloride to produce

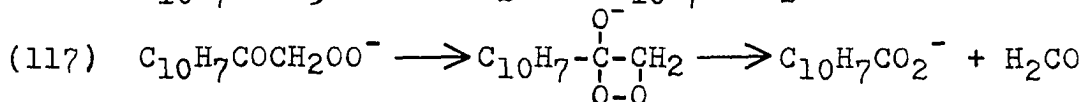
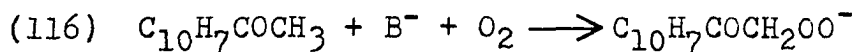
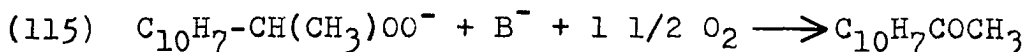
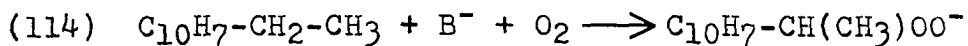
an ether or alcohol, which do oxidize much more slowly. The formation of trans-stilbene may be another reason for the decrease, since its formation is probably not via an autoxidative pathway. A condensation-elimination mechanism seems most reasonable.



Camphor oxidized in either 80/20 DMSO or HMPA and absorbed about 2 moles of oxygen per mole of camphor. This stoichiometry is consistent with a mechanism involving an alcohol or hydroperoxide as an intermediate. If the intermediate α -hydroperoxy ketone underwent β -elimination to produce camphor quinone, a stoichiometry of only 1 would be expected. A crude mixture was obtained from the oxidation in HMPA, but no pure products could be isolated. Camphoric acid is reported to be a product (in 5-10% yield) from the oxidation of camphor in t-butyl alcohol (9).

Both α - and β -ethylnapthylene oxidized in HMPA to the corresponding naphthoic acid in good yield. About 6 equivalents of base were needed to obtain the maximum uptake of oxygen, which approached 5 moles per mole of ethylnapthalene. In Part 3 of this section, it is reported that the methyl-napthalenes absorb about 3 moles of oxygen per mole, and hence the stoichiometry observed in the ethylnapthalene oxidation is consistent with complete oxidation of the ethyl

group, probably via the methyl naphthyl ketone. The equations below are only a schematic interpretation of the course of the oxidation, and are not intended as a detailed mechanism.



Acetophenone absorbs somewhat more than 1 mole of oxygen per mole in t-butyl alcohol, so the decomposition of the ω -hydroperoxy methyl ketone via a cyclic intermediate is probably not the only pathway to the acid. The formaldehyde probably also oxidizes, or else the hydroperoxy ketone, since the stoichiometry is larger than predicted by the four reactions above. A vigorous gas evolution on hydrolysis with water indicates that superoxide is formed in this oxidation.

3. Primary carbanions

Although triphenylmethane and diphenylmethane rapidly react with oxygen in 80/20 DMSO containing potassium t-butoxide, toluene is not oxidized. The addition of nitrobenzene does not cause any reaction. Toluene is apparently unionized in this solvent. In HMPA (100%), toluene oxidizes very slowly, as has also been reported by Hofmann et al. (42). Both of the isomeric methylnaphthalenes are reported to

oxidize rapidly in HMPA, but very slowly in 80/20 DMSO (25). Table 27 presents data for the oxidation of the methylnaphthalenes. The α -isomer oxidized more rapidly than the β -isomer in HMPA (100%), which is expected if the rate of oxidation was a measure of the rate of ionization, since the pK_a 's for the analogous acids are 3.7 for α -naphthoic acid and 4.16 for β -naphthoic acid (132). However one of the criteria

Table 27. Oxidation of methylnaphthalenes^a

| Isomer | Solvent ^b | Initial rate ^c | Stoichiometry ^d | Product |
|----------|-------------------------|---------------------------|----------------------------|--------------------------------|
| α | 80/20 DMSO ^e | ≤ 0.01 | | |
| β | 80/20 DMSO ^e | ≤ 0.01 | | |
| α | 80/20 HMPA ^f | ≤ 0.01 | | |
| β | 80/20 HMPA ^f | ≤ 0.01 | | |
| α | HMPA ^g | 1.35 | 3.46 | α -Naphthoic acid (88%) |
| β | HMPA ^g | 1.17 | 3.09 | β -Naphthoic acid (82%) |

^a0.1 M substrate, 0.6 M potassium t-butoxide (solid) in 25 ml of solution at room temperature and 749 mm of oxygen.

^bMixtures in volume %.

^cMoles of oxygen per mole of substrate per minute.

^dMoles of oxygen per mole substrate.

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

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

^gHexamethylphosphoramide.

for an ionization rate limited oxidation is that the reaction must be first order in substrate and first order in base. This is not true for the oxidation of α -methylnapthalene in HMPA as will be shown in Section C. The rate of oxidation may be determined by the rate of electron transfer in this case, but the catalysis test could not be used since nitrobenzene itself oxidized rapidly in HMPA containing potassium t-butoxide.

The three isomeric picolines (methylpyridines) were oxidized. Picolines were oxidized in 80/20 DMF by Bartok et al. (39) and in a variety of solvents by Janzen (25). Table 28 shows the results obtained in this study. The relative rates of oxidation agree very well with those obtained by Janzen (25). The only difference in results is that a much larger stoichiometry is observed in this study for the oxidation of the picolines in HMPA (100%) than that reported by Janzen (25). This is apparently due to the use of only two equivalents of base by that author, while 5-6 equivalents are apparently required for complete oxidation. The rate of oxidation of γ -picoline in 80/20 DMSO was greatly increased by the addition of nitrobenzene, hence the rates are believed to reflect the ease of electron transfer from carbanion to oxygen. The products of oxidation of the methylpyridines in 80/20 DMF are reported to be the corresponding picolinic acids (39). The observed stoichiometries are consistent with

Table 28. The oxidation of methylpyridines and methylquinolines^a

| Compound | Solvent ^b | Initial rate ^c | Stoichiometry ^d |
|-----------------------------------|-----------------------------|---------------------------|----------------------------|
| γ -Picoline | 80/20 Pyridine ^e | 0.0 | -- |
| δ -Picoline | Pyridine | 0.337 | 1.37 |
| γ -Picoline | 80/20 DMF ^f | 0.042 | 1.25 |
| δ -Picoline | 80/20 HMPA ^g | 0.058 | 1.52 |
| δ -Picoline | 80/20 DMSO ^h | 0.545 | 2.63 |
| δ -Picoline | HMPA ⁱ | 1.25 | 1.47 |
| α -Picoline | HMPA ⁱ | 1.37 | 2.43 |
| β -Picoline | HMPA ⁱ | 0.56 | 2.28 |
| δ -Picoline ^j | 80/20 DMSO ^h | 0.425 | -- |
| δ -Picoline ^{j,k} | 80/20 DMSO ^h | 1.14 | -- |
| 4-Methylquinoline | HMPA ⁱ | 5.0 | 2.44 |
| 8-Methylquinoline | HMPA ⁱ | 0.88 | 3.06 |

^a0.1 M substrate, 0.6 M potassium t-butoxide (solid) in 25 ml of solution at room temperature and 749 mm of oxygen.

^bSolvent mixtures in volume %.

^cMoles of oxygen per mole of substrate per minute.

^dMoles of oxygen per mole of substrate.

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

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

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

^hDimethyl sulfoxide (80%)-t-butyl alcohol (20%).

ⁱHexamethylphosphoramide.

^j0.25 M potassium t-butoxide.

^kIn the presence of 0.195 M nitrobenzene relative to substrate.

oxidation to the acid, since about the same ratios were observed for the methyl naphthalenes which yield only the acids. In the case of γ -picoline in HMPA, however, the low stoichiometry may indicate that dimeric products were formed. Since a vigorous oxygen evolution occurred when the reaction mixtures (for all the methyl compounds in HMPA) were poured into water, superoxide is apparently formed. This is also consistent with what was observed for the methyl naphthalenes.

A large number of substituted toluenes were oxidized, mostly in HMPA. The initial rates, stoichiometries, and products of these oxidations are given in Table 29. The oxidations of *p*-methylbenzophenone and methyl *p*-toluate in 80/20 DMSO had been studied by Janzen (25). The effect of solvent on the oxidation of *p*-methylbenzophenone is shown in Table 29. The solvent effect is similar to that observed for fluorene, except that *p*-methylbenzophenone does not oxidize in *t*-butyl alcohol. It is apparently not ionized in that solvent, since the addition of nitrobenzene did not cause any oxygen absorption. The rate of oxidation in 80/20 DMSO is increased by the addition of nitrobenzene, indicating that the electron transfer between carbanion and oxygen is probably the slow or rate determining step. This is probably true also for the other solvents used, with the exception of 80/20 pyridine. The formation of dimer (*p,p'*-dibenzoylstilbene) is also evidence that ionization is much faster than

Table 29. Oxidation of substituted toluenes^a

| X-C ₆ H ₄ -CH ₃ X = | Solvent ^b | Initial rate ^c | Stoichio- metry ^d | Product |
|---|-----------------------------|------------------------------|---------------------------------|---|
| p-Benzoyl | <u>t</u> -Butyl alcohol | 0.00 ^e | -- | -- |
| p-Benzoyl | 80/20 Pyridine ^f | 0.045 | 3.2 | p-Benzoylbenzoic acid (78%) |
| p-Benzoyl | Pyridine | 2.4 | 3.1 | p-Benzoylbenzoic acid (66%) |
| p-Benzoyl | 80/20 HMPA ^g | 0.96 | 2.1 | Dimer ^h (19%) p-Benzoylbenzoic acid (68%) |
| p-Benzoyl | 80/20 DMF ⁱ | 1.22 | 1.94 | Dimer ^h (45%) p-Benzoylbenzoic acid (41%) |

^a0.1 M substrate, 0.6 M potassium t-butoxide in 25 ml of solution at room temperature and 749 mm of oxygen.

^bSolvent mixtures in volume %.

^cMoles of oxygen per mole of substrate per minute.

^dMoles of oxygen per mole of substrate.

^eNo oxidation in the presence of 0.195 M nitrobenzene relative to substrate.

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

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

^hp,p'-Dibenzoylstilbene.

ⁱDimethylformamide (80%)-t-butyl alcohol (20%).

Table 29. (continued)

| X-C ₆ H ₄ -CH ₃ X = | Solvent | Initial rate | Stoichio- metry | Product |
|---|-------------------------|-----------------|--------------------|---|
| p-Benzoyl | 80/20 DMSO ^j | 1.65 | 3.40 | -- |
| p-Benzoyl ^k | 80/20 DMSO ^j | 3.0 | 3.5 | -- |
| p-Benzoyl | HMPA ^l | 3.2 | 2.9 | Dimer ^h (10%) p-Benzoylbenzoic acid (82.5)% |
| p-Phenyl | 80/20 DMSO ^j | 0.00 | | -- |
| p-Phenyl | HMPA ^l | 1.0 | 2.87 | p-Phenylbenzoic acid (88%) |
| m-Phenyl | HMPA ^l | 0.079 | 1.0 ^m | m-Phenylbenzoic acid (15%) |
| p-Carbomethoxy ⁿ | 80/20 DMSO ^j | 0.36 | 0.86 | -- |
| p-Carbomethoxy ^o | HMPA ^l | 1.35 | 3.3 | -- |

^jDimethyl sulfoxide (80%)-t-butyl alcohol (20%).

^kIn the presence of 0.195 M nitrobenzene relative to substrate.

^lHexamethylphosphoramide.

^mAfter 60 minutes.

ⁿ40 ml of solution, 0.1 M substrate, 0.2 M potassium t-butoxide.

^o0.056 M substrate.

Table 29. (continued)

| X-C ₆ H ₄ -CH ₃ X = | Solvent | Initial rate | Stoichio- metry | Product |
|---|-------------------------|-----------------|--------------------|-------------------------------------|
| p-Trimethylammonium | 80/20 DMSO ^j | 0.024 | -- | -- |
| p-Trimethylammonium ^k | 80/20 DMSO ^j | 0.34 | 3.6 | -- |
| p-Carboxy ^p | HMPA ^l | 0.019 | -- | -- |
| p-Carboamide | HMPA ^l | 0.034 | -- | -- |
| <u>m</u> -Methoxy | HMPA ^l | 0.025 | 1.2 ^q | <u>m</u> -Methoxybenzoic acid (26%) |
| <u>o</u> -Methyl | HMPA ^l | 0.066 | 2.3 | <u>o</u> -Toluic acid (31%) |
| Hydrogen | HMPA ^l | 0.039 | 1.0 ^r | -- |
| <u>o</u> -Fluoro | HMPA ^l | 0.194 | 2.0 | <u>o</u> -Fluorobenzoic acid (29%) |
| <u>m</u> -Fluoro | HMPA ^l | 0.784 | 2.5 | <u>m</u> -Fluorobenzoic acid (72%) |
| p-Fluoro | HMPA ^l | 0.016 | -- | -- |
| <u>m</u> -Chloro | HMPA ^l | 1.08 | 2.27 | <u>m</u> -Chlorobenzoic acid (66%) |

^pProbably carboxylate salt in basic solution.

^qAfter 300 minutes.

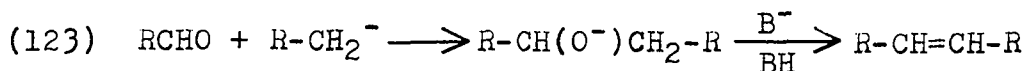
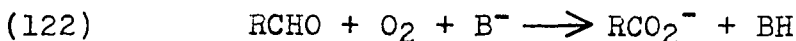
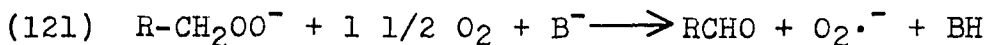
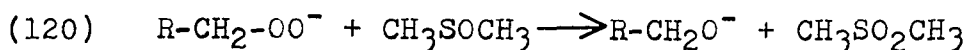
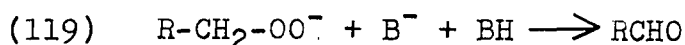
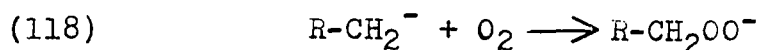
^rAfter 113 minutes.

Table 29. (continued)

| X-C ₆ H ₄ -CH ₃ X = | Solvent | Initial rate | Stoichio- metry | Product |
|---|-------------------|-----------------|--------------------|------------------------------------|
| <u>p</u> -Chloro | HMPA ¹ | 0.49 | 2.07 | <u>p</u> -Chlorobenzoic acid (42%) |
| <u>o</u> -Bromo | HMPA ¹ | 1.7 | 2.7 | <u>o</u> -Bromobenzoic acid (23%) |
| <u>m</u> -Bromo | HMPA ¹ | 1.26 | 2.16 | <u>m</u> -Bromobenzoic acid (68%) |
| <u>p</u> -Bromo | HMPA ¹ | 0.74 | 2.34 | <u>p</u> -Bromobenzoic acid (43%) |
| <u>o</u> -Iodo | HMPA ¹ | 1.94 | 2.42 | -- ^s |
| <u>p</u> -Iodo | HMPA ¹ | 1.09 | 2.18 | <u>p</u> -Iodobenzoic acid (56%) |

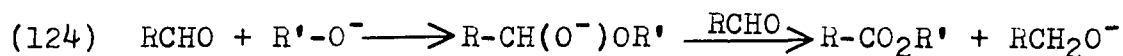
^sProduct was a brown oil.

oxidation, since the mechanism of dimer formation is believed to be via the carbanion and an aldehyde. The aldehyde is a postulated intermediate in the oxidation of the toluene to the benzoic acid. The same oxidation mechanism which was proposed for diphenylmethane or fluorene is believed to be valid for the oxidation of toluenes and other methyl aromatic compounds, with the difference that instead of a ketone being formed, an aldehyde is produced, and the aldehyde oxidizes to the carboxylic acid, or in some cases is trapped by a carbanion and converted to the stilbene-type dimer. The mechan-



ism for the conversion of aldehydes to carboxylic acids was not studied, but there are at least two possible pathways in basic solution. Aldehydes are known to spontaneously react with air to produce acids, possibly by abstraction of the aldehydic hydrogen by oxygen or traces of impurities, followed by a free-radical chain process involving peroxy radicals. The per-acid product predicted by this mechanism would not survive hydrolysis with water. The second possibility is

that a Cannizaro reaction could occur. A base catalyzed disproportionation such as the Cannizaro reaction should occur readily in the highly basic solvents used in the oxidations.



In general, fair yields of the corresponding benzoic acids were isolated from the oxidation of substituted toluenes in HMPA. Yields are generally as good, and in some cases better, than the dichromate oxidation technique (133) which requires 18 hours in an autoclave.

Dimeric products from the oxidation of toluenes were discovered in only two cases in this investigation. Janzen (25) found that methyl *p*-toluate oxidations gave rise to *p,p'*-stilbene dicarboxylic acid and terephthalic acid in 80/20 DMSO. The oxidation of methyl *p*-toluate in 80/20 DMSO was investigated by g.l.c. in this study, after esterification of the reaction mixture. Dimethyl terephthalate, *p,p'*-dicarbomethoxystilbene, and methyl *p*-toluate were observed. No *p,p'*-dicarbomethoxybibenzyl was observed. The yields of the "terephthalate" and "stilbene" were poor, due in large part to the recovery of starting material. Methyl *p*-toluate hydrolyzes very quickly in 80/20 DMSO when the slightest trace of water or hydroxide ion is present. Presumably ester exchange is very rapid also. *p*-Benzoyltoluene oxidizes in 80/20 DMF to give almost 50% *p,p'*-dibenzoylstilbene and 40%

p-benzoylbenzoic acid. No p,p'-dibenzoylbibenzyl was found. A smaller percentage of dimer was isolated in HMPA. The amount of dimer formed probably depends on the relative rates of ionization and electron transfer, being largest when the ionization is rapid, and the electron transfer is slow. The possibility that the dimer slowly oxidizes to the benzoic acid was not investigated. Apparently DMSO adducts of oxidation products from p-benzoyltoluene were obtained in 80/20 DMSO, but were not completely characterized.

The relative rates of oxidation, log relative rates of oxidation, and σ^- -constants for some of the substituted toluenes are given in Table 30. The log relative rates of oxidation for some meta-substituted toluenes are plotted against σ^- in Figure 3. A reasonable correlation can be seen, although the point for m-methoxytoluene is badly away from the line drawn through the other points. The correlation could be a reflection of either an ionization process or an electron transfer reaction. Probably the slow step is an electron transfer for all the meta substituted toluenes except m-methoxy.

The log relative rates for the oxidations of para substituted toluenes are plotted versus σ^- in Figure 4. The line is drawn at the same position as for the meta substituents in Figure 3 to facilitate comparison. There is a lot of scatter, and a good correlation does not exist. Plotting

Table 30. Relative rates of oxidation of substituted toluenes^a

| X-C ₆ H ₄ -CH ₃ X = | Relative rate | Log relative rate | σ ^b |
|---|---------------|-------------------|----------------|
| Hydrogen | 1.0 | 0.00 | 0.00 |
| <u>o</u> -Fluoro | 5.0 | 0.7 | |
| <u>m</u> -Fluoro | 20.0 | 1.3 | .39 |
| <u>p</u> -Fluoro | 0.41 | -0.39 | .07 |
| <u>m</u> -Chloro | 27.8 | 1.44 | .37 |
| <u>p</u> -Chloro | 12.5 | 1.1 | .23 |
| <u>o</u> -Bromo | 43.5 | 1.64 | |
| <u>m</u> -Bromo | 32.3 | 1.51 | .39 |
| <u>p</u> -Bromo | 19.0 | 1.28 | .23 |
| <u>o</u> -Iodo | 50.0 | 1.70 | |
| <u>p</u> -Iodo | 27.9 | 1.45 | .28 |
| <u>m</u> -Methoxy | 0.86 | -0.07 | .12 |
| <u>o</u> -Methyl | 1.7 | 0.23 | |
| <u>p</u> -Carboxy | 0.49 | -0.31 | 0.00 |
| <u>p</u> -Carbomethoxy | 34.6 | 1.54 | .39 |
| <u>p</u> -Phenyl | 25.7 | 1.41 | -.01 |
| <u>m</u> -Phenyl | 2.0 | 0.3 | .06 |
| <u>p</u> -Benzoyl | 82.0 | 1.91 | .46 |

^a0.1 M substrate, 0.6 M potassium t-butoxide in 25 ml of HMPA at room temperature and 749 mm of oxygen; vigorously shaken.

^bValues from Hine (134).

Figure 3. Oxidation of meta substituted toluenes (0.1 M) in hexamethylphosphoramide containing potassium t-butoxide (0.6 M)

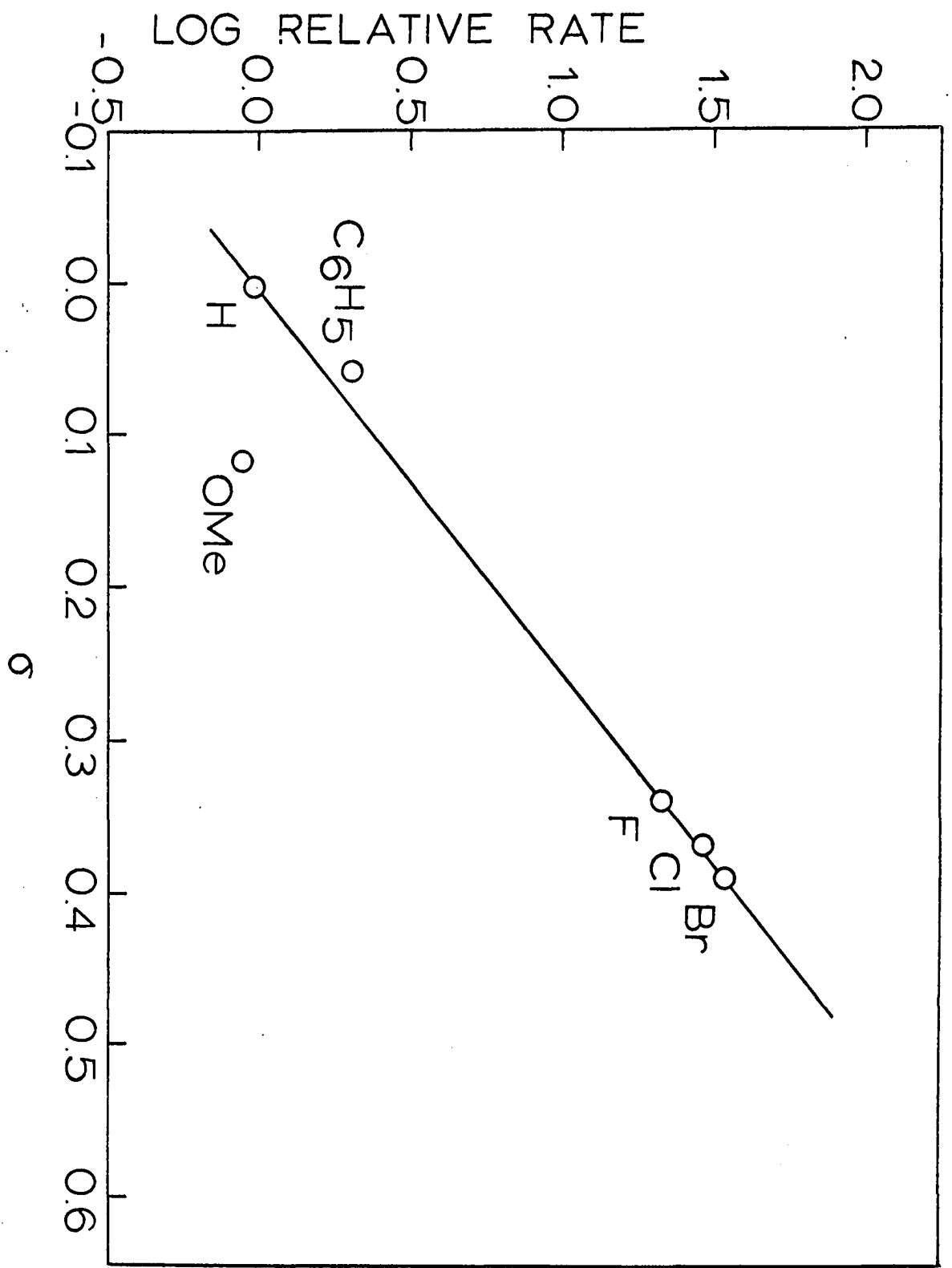
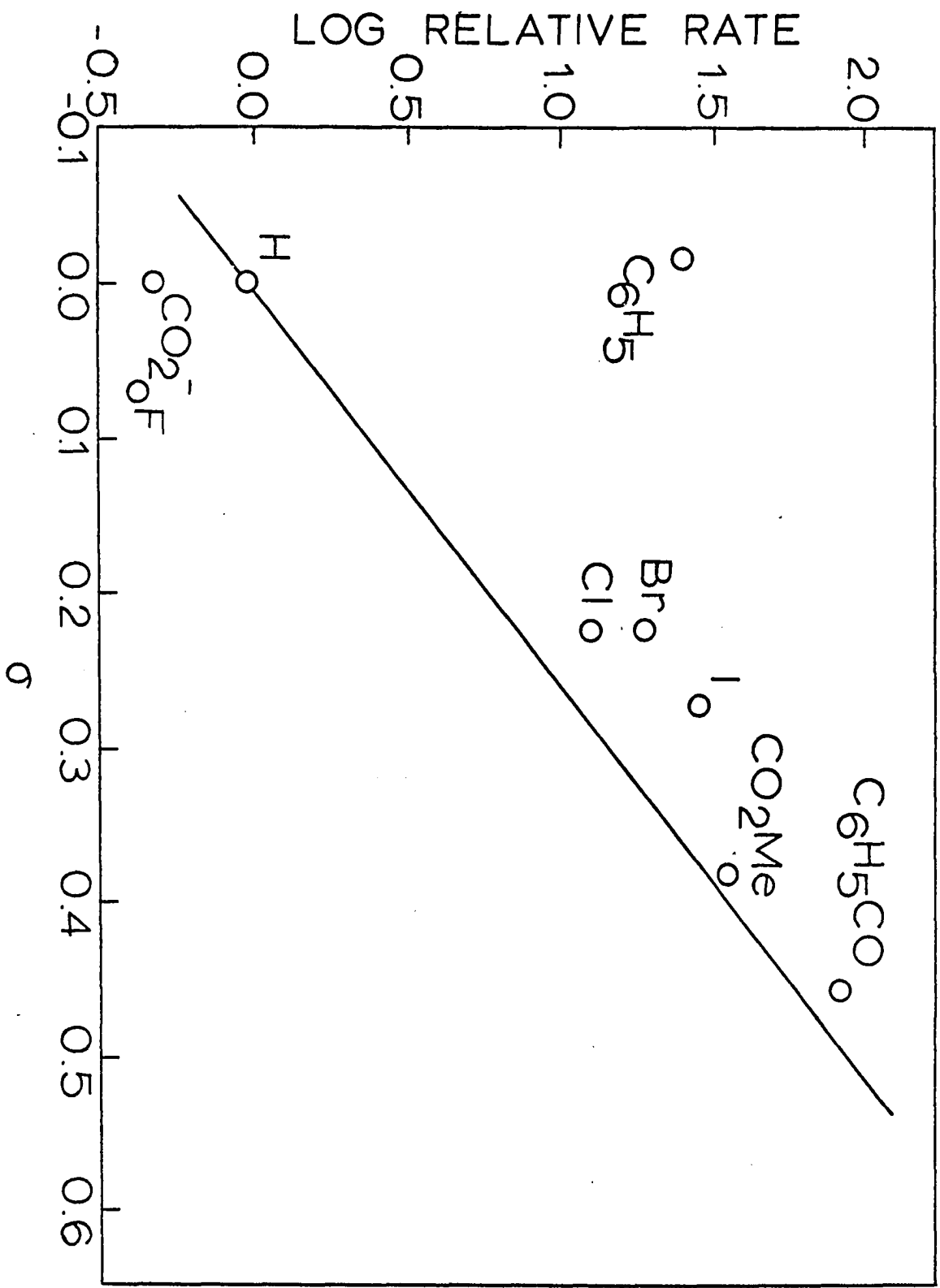


Figure 4. Oxidation of para substituted toluenes (0.1 M) in hexamethylphosphoramide containing potassium t-butoxide (0.6 M)



the log rates against σ^- does not improve the correlation, for while some points are improved, others become worse. Part of the scatter may be due to differences in rate determining steps in the oxidations. Methyl p-toluate and p-methylbenzophenone oxidations are probably electron transfer rate controlled, while p-fluorotoluene and p-toluic acid oxidations may well be controlled by the rate of ionization. The additional possibility that a pre-equilibrium step in the ionization process may be involved in HMPA is discussed in Section C.

The autoxidation of acetophenone will be discussed in Part 2 of Section C.

4. Other carbanions

The oxidation of phenylacetylene in various solvents was attempted, and the results are shown in Table 31. Phenylacetylene did not react with oxygen in t-butyl alcohol or 80/20 pyridine containing potassium t-butoxide in the absence of copper ion. The addition of nitrobenzene in these solvents did not cause any oxygen absorption. Oxygen was absorbed by phenylacetylene in 80/20 DMSO or HMPA containing potassium t-butoxide, but very slowly in the absence of catalyst. The oxidation of phenylacetylene in 80/20 DMSO was strongly catalyzed by nitrobenzene. Since phenylacetylene has a pK_a of 21 (65), and is reported to exchange at a rate

Table 31. The oxidation of phenylacetylene^a

| Solvent ^b | Catalyst ^c | Stoichio- metry ^d | Initial rate ^e | Product |
|-----------------------------|----------------------------|---------------------------------|------------------------------|---------------------------|
| <u>t</u> -Butyl alcohol | None ^f | -- | 0.00 | -- |
| 80/20 Pyridine ^b | None | -- | 0.00 | -- |
| 80/20 DMSO ^h | None | -- | 0.006 | -- |
| HMPA ⁱ | None | -- | 0.018 | -- |
| 80/20 DMSO ^h | 0.39 <u>M</u> Nitrobenzene | 2.0 | 0.126 | Benzoic acid ^j |

^a0.1 M Phenylacetylene, 0.25 M potassium t-butoxide in 25 ml of solvent, vigorously shaken at room temperature and 749 mm of oxygen.

^bSolvent mixtures in volume %.

^cCupric chloride was not mixed with the potassium t-butoxide solution until the reaction began.

^dMoles of oxygen per mole of phenylacetylene.

^eMoles of oxygen per mole of phenylacetylene per minute.

^fNo oxidation occurred in the presence of 0.39 M nitrobenzene.

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

^hDimethyl sulfoxide (80%)-t-butyl alcohol (20%).

ⁱHexamethylphosphoramide.

^jIsolated from a complex mixture of products.

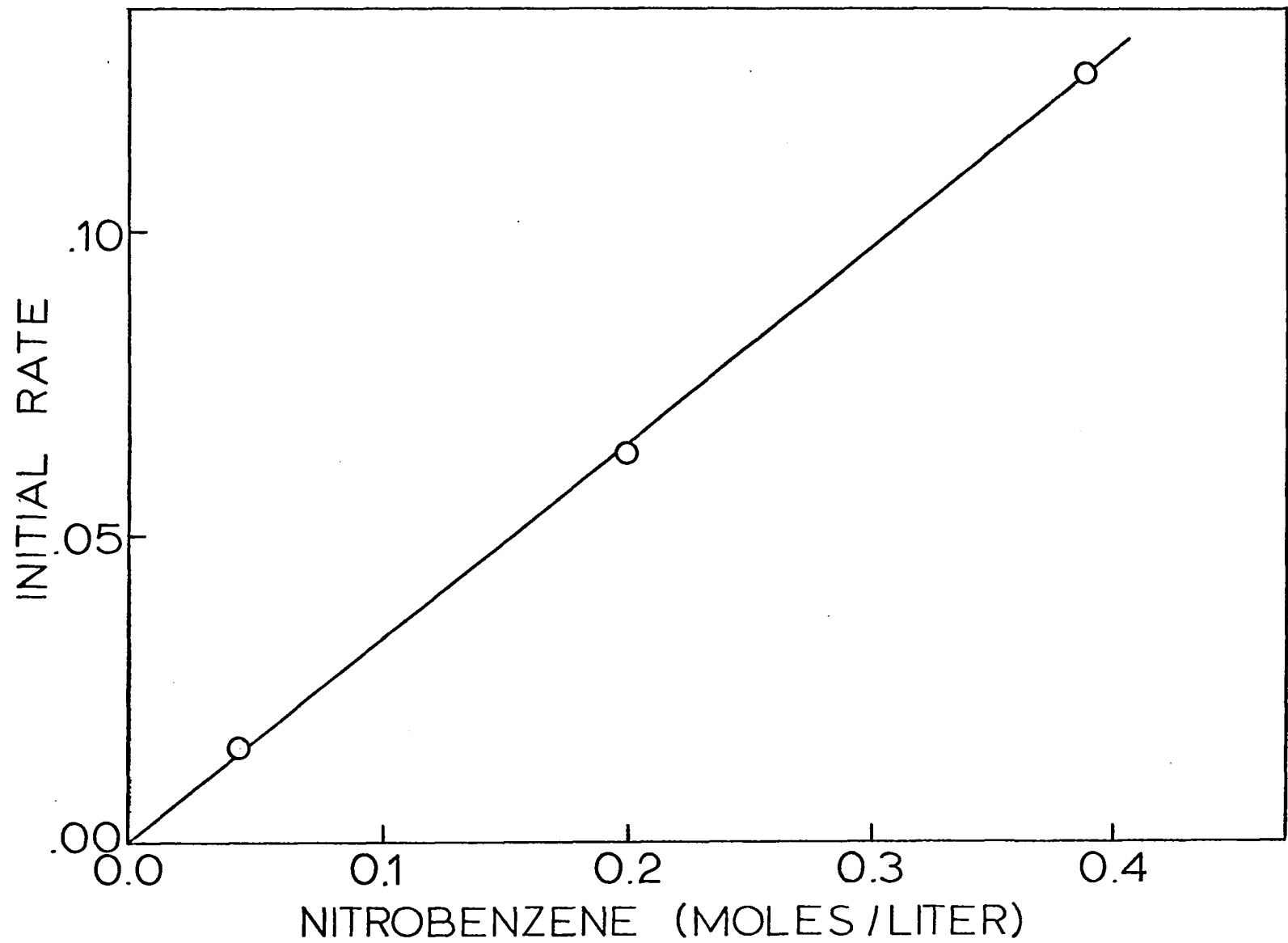
Table 31. (continued)

| Solvent | Catalyst | Stoichio- metry | Initial rate | Product |
|-------------------------|-------------------------------|--------------------|-----------------|---------------------------|
| 80/20 DMSO ^h | 0.2 <u>M</u> Nitrobenzene | 1.2 | 0.05 | |
| 80/20 DMSO ^h | 0.04 <u>M</u> Nitrobenzene | 0.71 | 0.0156 | |
| 80/20 DMSO ^h | 0.05 <u>M</u> Cupric chloride | 0.50 | 0.15 | Diphenyldiacetylene (70%) |
| <u>t</u> -Butyl alcohol | 0.05 <u>M</u> Cupric chloride | 0.35 | 0.038 | Diphenyldiacetylene (70%) |

about 30 times faster than fluorene in DMF (92) (fluorene has a pK_a of 25 (65)), it probably ionizes very rapidly in t-butyl alcohol, and even more so in 80/20 DMSO. The large rate increase on addition of catalyst in 80/20 DMSO is proof that the rate of ionization is much faster than the rate of electron transfer with oxygen. Figure 5 shows the initial rate of oxidation of phenylacetylene plotted as a function of nitrobenzene concentration. The good straight line is evidence that the catalyzed oxidation is first order in nitrobenzene, and hence the electron transfer step is the rate limiting step in the oxidation. The lack of reaction of phenylacetylene with oxygen in t-butyl alcohol even when nitrobenzene is present must be due to a solvent effect on the electron transfer step. Similar trends (although not so drastic) are seen in the oxidations of fluorene and acetophenone. The variation in stoichiometry of the oxidation of phenylacetylene in 80/20 DMSO with nitrobenzene concentration is unusual, since variation of stoichiometries was not observed in the catalyzed oxidations of fluorene and acetophenone. The effect in the phenylacetylene oxidation is probably due to destruction of nitrobenzene.

The nitrobenzene catalyzed oxidation of phenylacetylene in 80/20 DMSO containing potassium t-butoxide gave a complex mixture of products. An infrared spectrum of this mixture showed strong carbonyl and hydroxyl bands, indicative of

Figure 5. Oxidation of phenylacetylene (0.1 M) in dimethyl sulfoxide (80%)-t-butyl alcohol (20%) containing potassium t-butoxide (0.25 M) as a function of nitrobenzene concentration; initial rate in moles oxygen per mole phenylacetylene per minute



carboxylic acids. The only compound isolated in pure form was benzoic acid, in poor yield. No neutral compounds could be found.

Phenylacetylene also oxidized in 80/20 DMSO with potassium t-butoxide when cupric chloride was added. Cupric chloride also catalyzed the oxidation of phenylacetylene in t-butyl alcohol, although at a slower rate than in 80/20 DMSO, consistent with the solvent on electron transfer reactions noted previously. The product in both solvents was diphenyldiacetylene, probably in close to quantitative yield. No acidic products could be isolated.

The reaction of cupric ion and phenylacetylene to produce diphenyldiacetylene is well known (135-137). Weak bases, such as amines, are known to catalyze the reaction (137). The action of oxygen on copper phenylacetylide in ammonia to produce diphenyldiacetylene has been reported (138). The ionization of the acetylinic C-H bond is thus the necessary first step in the reaction of cupric ion and phenylacetylene. Phenylacetylene radicals have been proposed as intermediates in the reaction of phenylacetylene with cupric ion to produce diphenyldiacetylene (139).

The data for the cupric chloride catalyzed oxidation in basic solution is in accord with a mechanism involving ionization of phenylacetylene, reaction of the carbanion with cupric ion, and dimerization of two copper acetylide species.

The exact structure of composition of the copper acetylide species was not investigated.

The oxygen absorption arises from the reaction of oxygen with cuprous ion. A solution of 2.5 mmoles of cuprous chloride in 80/20 DMSO containing excess potassium t-butoxide absorbed about 2.5 mmoles of oxygen. When the reaction mixture was poured into water, a large amount of oxygen was evolved. In this case, cuprous ion reacted with oxygen to produce superoxide ion, and judging from the stoichiometry and hydrolysis test, superoxide was the major or sole reduction product of oxygen. The product after hydrolysis seemed to be a copper oxide, but its composition was not determined.

The stoichiometry in the cupric chloride catalyzed oxidation of phenylacetylene, 1/2 mole of oxygen per mole of phenylacetylene, is not consistent with the formation of superoxide, and indeed no oxygen evolution was observed when reaction mixtures were hydrolyzed. The probable reaction path is formation of copper peroxide. The change in stoichiometry may be due to dimerization of the copper acetylide species, but retention of the copper in a complexed form until oxygen reacts, thus giving a single oxygen molecule an opportunity to accept two electrons.

The observation that acids are produced in the nitrobenzene catalyzed oxidation of phenylacetylene, consistent with the formation of oxygenated products in other nitrobenzene

catalyzed oxidations, and the fact that dimer is produced (but no acids) in the cupric ion catalyzed oxidation suggests the mechanisms of the two catalysts are different. Free radicals are produced from electron transfer of carbanions with nitrobenzene, and when nitrobenzene is used as an oxidation catalyst, only oxygenated products are observed, suggesting that oxygen intercepts the radicals. The cupric ion catalyzed oxidation of phenylacetylene can not have a free radical as an intermediate since no acids are observed, and the only product (in good yield) is a dimer. The only reasonable intermediate is a copper acetylide.

Nitrobenzene and substituted nitrobenzenes are observed to absorb oxygen in highly basic solvents. Nitrobenzene absorbs oxygen very slowly in 80/20 DMSO containing potassium t-butoxide. The better electron acceptor (25) meta-trifluoromethylnitrobenzene oxidizes very rapidly in 80/20 DMSO with potassium t-butoxide. The product from the oxidation of nitrobenzene in 80/20 DMSO is a mixture of ortho and para nitrobenzoic acids (140). The mechanism suggested is methylation by DMSO (140), followed by oxidation. Nitrotoluenes

(125) $\text{CH}_3\text{SOCH}_2^- + \text{C}_6\text{H}_5\text{NO}_2 \longrightarrow \text{CH}_3\text{SOCH}_2-\text{C}_6\text{H}_5-\text{NO}_2^-$

(126) $\text{CH}_3\text{SOCH}_2-\text{C}_6\text{H}_5-\text{NO}_2^- + \text{B}^- \longrightarrow \text{O}_2\text{NC}_6\text{H}_5\text{CH}_2^- + \text{CH}_3\text{SO}^- + \text{BH}$

are known to oxidize in 80/20 DMSO to give nitrobenzoic acids (25).

Nitrobenzene reacts with oxygen very rapidly in HMPA

(100%) containing potassium t-butoxide. Products from this reaction have not been determined, but presumably an addition-elimination sequence followed by oxidation is operating in this case also.

C. Kinetics and Catalysis

1. Ionization

The oxidation of triphenylmethane was described in Section B. Since the reaction of triphenylmethane with oxygen had a clean 1:1 stoichiometry, a detailed kinetic study was made. The rate of absorption of oxygen as a function of triphenylmethane concentration, potassium t-butoxide concentration, oxygen pressure, and presence of nitrobenzene was studied. The results are displayed in Table 32. The first four entries illustrate the effect of oxygen pressure and nitrobenzene on the rate of oxidation. There is no catalysis by nitrobenzene, and the rate of oxidation at 609 mm of Hg is the same as at 749 mm. The increase in rate at an oxygen pressure of 402 mm must be due to an experimental error; if the rate reflected the reaction of the carbanion with oxygen, a first order dependence would be expected, and at lower pressures the rate should be smaller. The variation in initial rate with hydrocarbon concentration at constant base concentration is plotted in Figure 6. The straight line obtained is evidence that the oxidation is first order in tri-

Table 32. The oxidation of triphenylmethane^a

| $(C_6H_5)_3CH$ ^b | $KOC(CH_3)_3$ ^b | O_2 pressure ^c | Initial rate ^d |
|-----------------------------|----------------------------|-----------------------------|---------------------------|
| 0.025 | 0.05 | 749 | 1.27 |
| 0.025 | 0.05 | 609 | 1.31 |
| 0.025 | 0.05 | 402 | 1.81 |
| 0.025 | 0.05 | 749 | 1.33 ^e |
| 0.025 | 0.10 | 749 | 2.02 |
| 0.0125 | 0.186 | 749 | 1.52 ^f |
| 0.025 | 0.20 | 749 | 6.42 |
| 0.05 | 0.20 | 749 | 11.6 |
| 0.10 | 0.20 | 749 | 22.5 |
| 0.049 | 0.045 | 749 | 2.65 |
| 0.049 | 0.09 | 749 | 5.2 |
| 0.049 | 0.135 | 749 | 7.85 |

^a25 ml of dimethyl sulfoxide (80%)-t-butyl alcohol, vigorously shaken at room temperature.

^bMoles/liter.

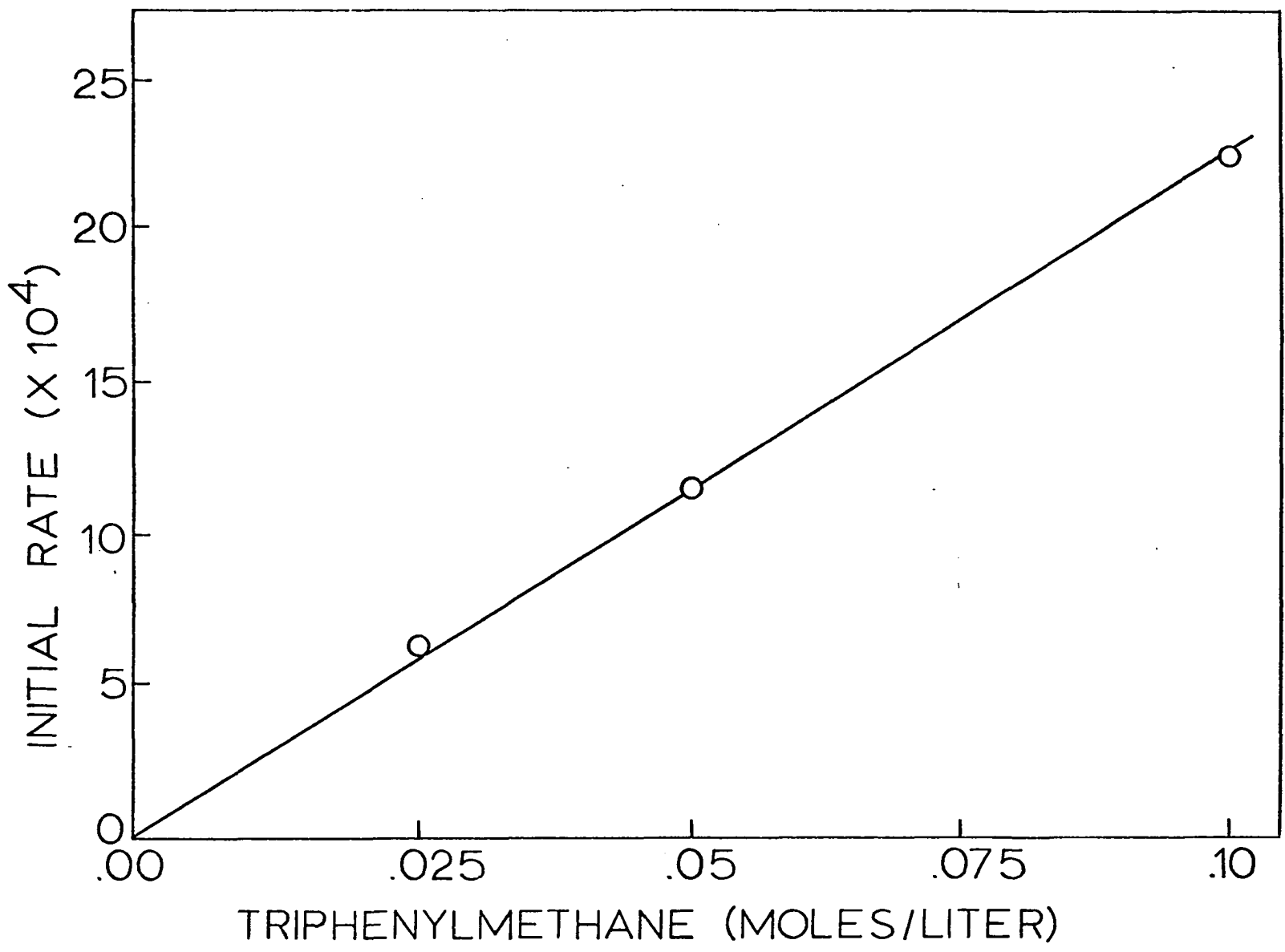
^cmm of Hg.

^dMoles/liter-sec x 10⁴.

^eIn the presence of 0.098 M nitrobenzene.

^f50 ml of solvent.

Figure 6. Oxidation of triphenylmethane in dimethyl sulfoxide (80%)-
t-butyl alcohol (20%) containing potassium t-butoxide (0.2 M);
initial rate in moles per liter per second



phenylmethane. In Figure 7, the variation of initial rate with base concentration is shown for constant triphenylmethane concentration. Again a good straight line is obtained, showing the reaction is first order in potassium t-butoxide. A representative oxidation of triphenylmethane in 80/20 DMSO is plotted on Figure 8.

An alternative method to demonstrate the dependence of the rate of oxidation of triphenylmethane on substrate concentration and base concentration is to derive a kinetic expression and test it by plotting functions which should be linearly related to see if a straight line is obtained, and calculating rate constants for a variety of initial concentrations to see if the rate constant remains at the same value, as it should if the kinetic expression derived is valid for the reaction.

If ionization of the C-H bond is the rate limiting step in the oxidation of triphenylmethane, the following kinetic expression should be valid:

$$(127) \quad \frac{-d[RH]}{dt} = k_1 [RH] [B^-]$$

(The symbols RH and B⁻ will be used throughout to denote hydrocarbon and base respectively.)

For an oxidation where the base was present in large excess, or for the initial portion of any oxidation before much had been consumed, the base is essentially a constant,

Figure 7. Oxidation of triphenylmethane (0.049 M) in dimethyl sulfoxide (80%)-t-butyl alcohol (20%) containing potassium t-butoxide; initial rate in moles per liter per second

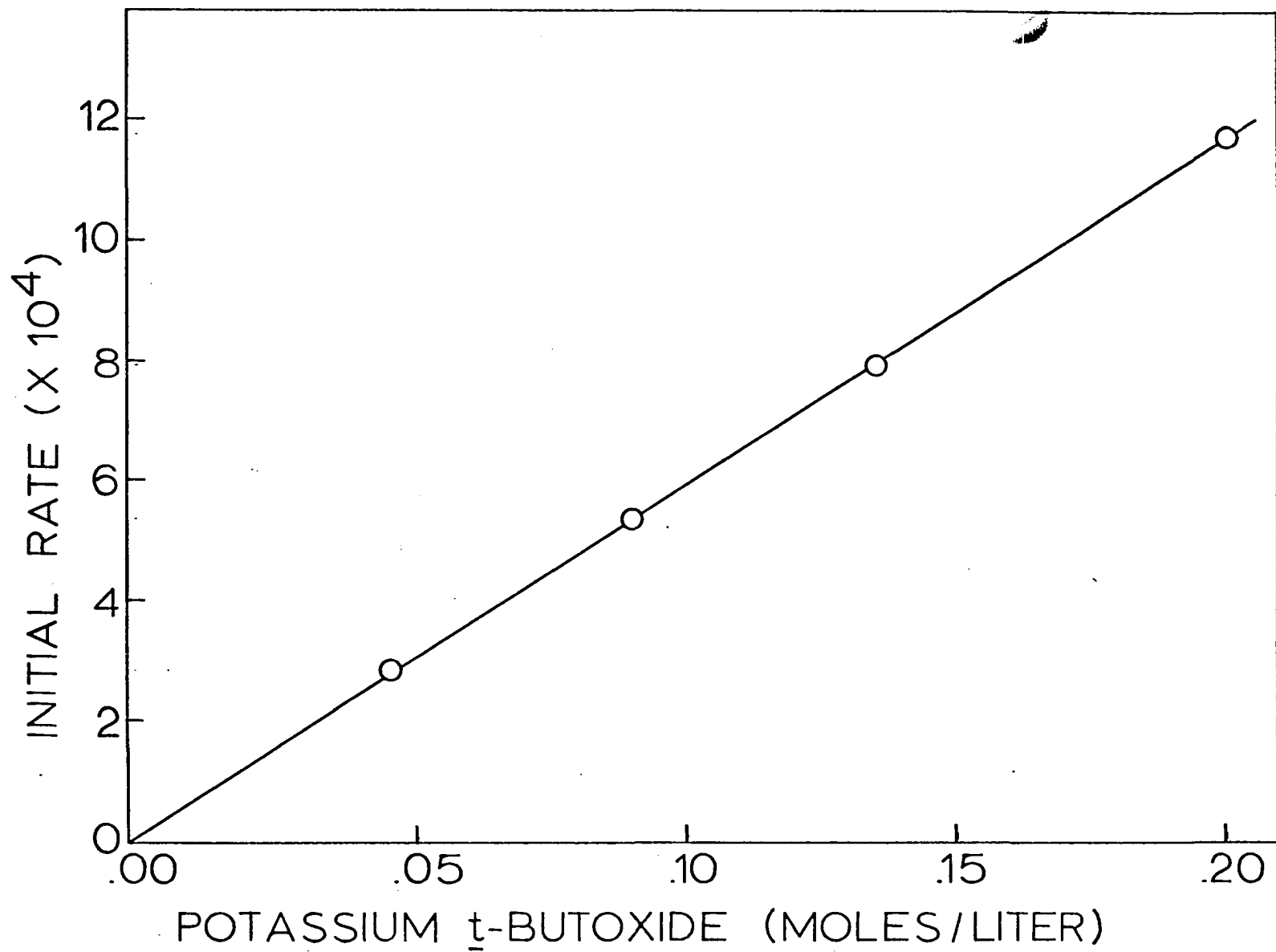
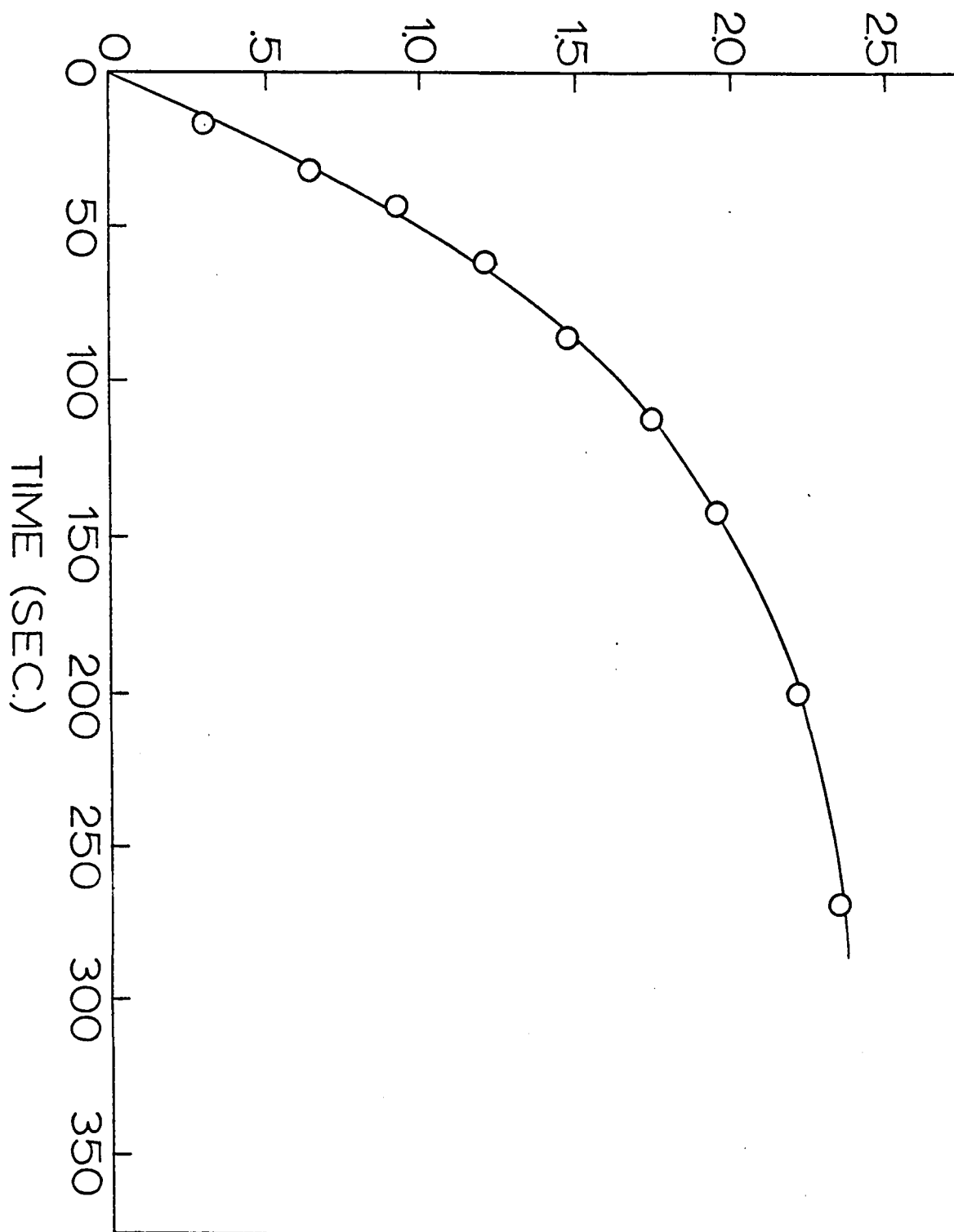


Figure 8. Oxidation of triphenylmethane (0.025 M) in dimethyl sulfoxide (80%)-t-butyl alcohol (20%) containing potassium t-butoxide (0.1 M)

OXYGEN ABSORBED (MOLES/LITER X 10²)



and the rate equation simplifies to a first order expression, which can be easily integrated.

$$(128) \quad \frac{-d[\text{RH}]}{[\text{RH}]} = k_1 [\text{B}^-] dt$$

$$(129) \quad \int_{[\text{RH}]_0}^{[\text{RH}]_t} \frac{-d[\text{RH}]}{[\text{RH}]} = \int_{t=0}^t k_1 [\text{B}^-] dt$$

$$(130) \quad -(\ln[\text{RH}]_t - \ln[\text{RH}]_0) = k_1 [\text{B}^-] (t-0)$$

$$(131) \quad \ln[\text{RH}]_0 - \ln[\text{RH}]_t = k_1 [\text{B}^-] t$$

$$(132) \quad \ln \frac{[\text{RH}]_0}{[\text{RH}]_t} = k_1 [\text{B}^-] t$$

The overall stoichiometry for all triphenylmethane oxidations was cleanly 1 mole of oxygen per mole of triphenylmethane. If the stoichiometric relationship holds at all times during the oxidation, the triphenylmethane concentration can be expressed in terms of the oxygen absorbed.

$$(133) \quad [\text{RH}]_t = [\text{RH}]_0 - [\text{O}_2]_t$$

Substituting yields equation 134. This equation was

$$(134) \quad \ln \frac{[\text{RH}]_0}{[\text{RH}]_0 - [\text{O}_2]_t} = k_1 [\text{B}^-] t = k_1 t$$

used to calculate rate constants. The concentration of oxygen was calculated from the volume absorbed, which was corrected to S.T.P. and converted into moles of oxygen. The concentration was then calculated by dividing the moles of

oxygen by the volume of the solution. Since the logarithmic term is a ratio of concentrations, moles of triphenylmethane and moles of oxygen could be used. The same rate constants will be gotten by either calculation, and are presented in Table 33. The second order rate constant, k_1 , is very nearly constant for all conditions. The variation seen is apparently due to temperature fluctuations, since much better reproducibility was obtained when the oxidations were thermostated.

In order to graph the oxidation of triphenylmethane, equation 134 was rearranged. Since $\ln[\text{RH}]_0$ is a constant, a

$$(135) \quad \ln[\text{RH}]_0 - \ln([\text{RH}]_0 - [\text{O}_2]_t) = k_1 [\text{B}^-]t$$

plot of $\ln([\text{RH}]_0 - [\text{O}_2]_t)$ against t should yield a straight line whose slope is $-k_1 [\text{B}^-]$ ($= k_1$) and whose intercept would be $\ln[\text{RH}]_0/k_1 [\text{B}^-]$. In practice, semi-log paper was used, and $[\text{RH}]_0 - [\text{O}_2]_t$ was plotted in the logarithmic direction against t . Identical rate constants for a particular oxidation were obtained whether they were calculated by equation 134, calculated from the slope of a semi-log plot, or calculated from the slope of a plot of initial rate versus base or hydrocarbon concentration such as Figures 6 and 7.

A typical semi-log plot is shown in Figure 9. The oxidation run was the same one plotted in Figure 8. Excellent pseudo first order kinetics were obtained over more than 95% reaction. A 300% excess concentration of base is important

Table 33. Rate constants from the oxidation of triphenylmethane^a

| $(\text{C}_6\text{H}_5)_3\text{CH}$ ^b | $\text{KOC}(\text{CH}_3)_3$ ^b | O_2 pressure ^c | k_1 ^d | $k_1 = k_1/B$ ^e |
|--|--|------------------------------------|--------------------|----------------------------|
| 0.025 | 0.05 | 749 | 0.007 | 0.140 |
| 0.025 | 0.10 | 749 | 0.0103 | 0.103 |
| 0.025 | 0.20 | 749 | 0.034 | 0.169 |
| 0.049 | 0.135 | 749 | 0.0213 | 0.155 |
| 0.049 | 0.091 | 749 | 0.0116 | 0.128 |
| 0.05 | 0.20 | 749 | 0.0296 | 0.148 |
| 0.10 | 0.20 | 749 | 0.0341 | 0.171 |
| 0.025 | 0.05 | 609 | 0.0073 | 0.145 |
| 0.025 | 0.05 | 402 | 0.0082 | 0.164 |
| 0.025 | 0.05 | 749 | 0.0075 | 0.151 ^f |
| 0.10 | 0.20 | 749 | 0.0257 | 0.128 ^g |

^a25 ml of dimethyl sulfoxide (80%)-t-butyl alcohol (20%) vigorously shaken at room temperature.

^bMoles/liter.

^cmm.

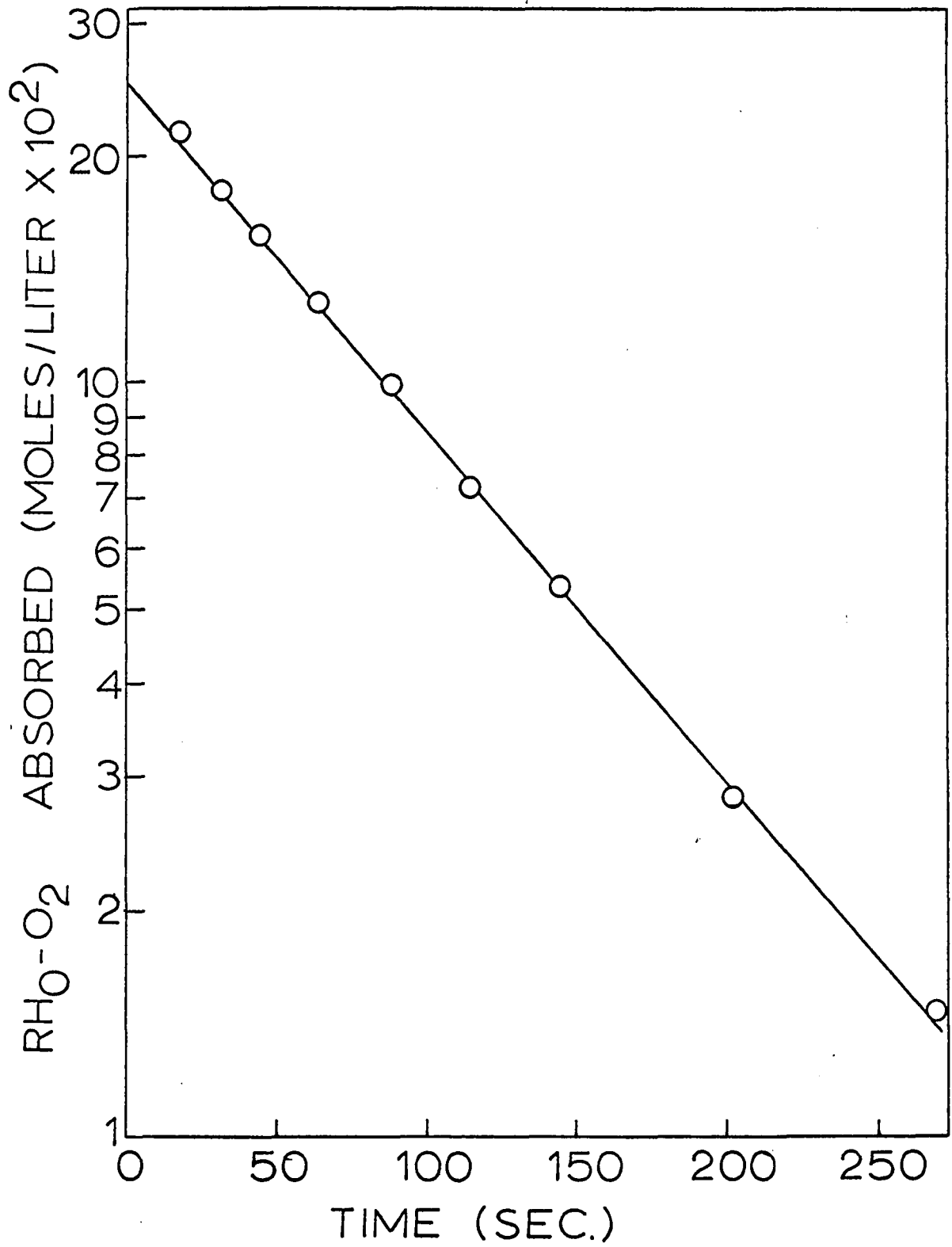
^dSec⁻¹.

^eLiter/mole-second.

^fIn the presence of 0.098 M nitrobenzene.

^gIn the presence of 0.39 M nitrobenzene.

Figure 9. Oxidation of triphenylmethane (0.025 M) in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) containing potassium *t*-butoxide (0.10 M); the ordinate axis is constructed logarithmically; RH_0 = initial concentration of triphenylmethane



for good pseudo first order kinetics, since in graphs of some oxidations with equal amounts of triphenylmethane and potassium t-butoxide, the rate became slower than the initial straight line predicted after about 60-70% completion.

Better reproducibility was obtained when oxidations were thermostated. The improved precision and effect of temperature are shown in Table 34.

The variation of rate with temperature allows the enthalpy and entropy of activation to be calculated. The

Table 34. Effect of temperature on the rate of oxidation of triphenylmethane^a

| Temperature ^b | (C ₆ H ₅) ₃ CH ^c | KOC(CH ₃) ₃ ^c | k ₁ ^d |
|--------------------------|---|---|-----------------------------|
| 24.5 | 0.0995 | 0.197 | 0.136 |
| 24.5 | 0.0455 | 0.197 | 0.136 |
| 24.5 | 0.0995 | 0.103 | 0.129 |
| 29.5 | 0.0492 | 0.197 | 0.179 |
| 29.5 | 0.0492 | 0.234 | 0.170 |
| 34.5 | 0.0492 | 0.0936 | 0.234 |

^a25 ml of dimethyl sulfoxide (80%)-t-butyl alcohol (20%), vigorously shaken at 749 mm of oxygen.

^bDegrees centigrade.

^cMoles/liter.

^dLiter/moles-second.

activation energy (E_a) can be calculated from the Arrhenius equation:

$$(136) \quad k = A e^{-E_a/RT}$$

which can be rewritten

$$\ln k = -\frac{E_a}{RT} + \ln A$$

The Arrhenius equation predicts that $\ln k$ is linearly related to $1/T$, and this is shown for the oxidation of triphenylmethane in 80/20 DMSO in Figure 10. A straight line is found, although oxidations were run at only three temperatures. The activation energy was calculated by combining two equations:

$$(138) \quad \ln k_2 = -\frac{E_a}{RT_2} + \ln A$$

$$(139) \quad -(\ln k_1 = \frac{-E_a}{RT_1} + \ln A)$$

$$(140) \quad \ln k_2 - \ln k_1 = \frac{-E_a}{RT_2} + \frac{E_a}{RT_1}$$

$$(141) \quad \ln (k_2/k_1) = \frac{E_a (T_2 - T_1)}{R T_2 T_1}$$

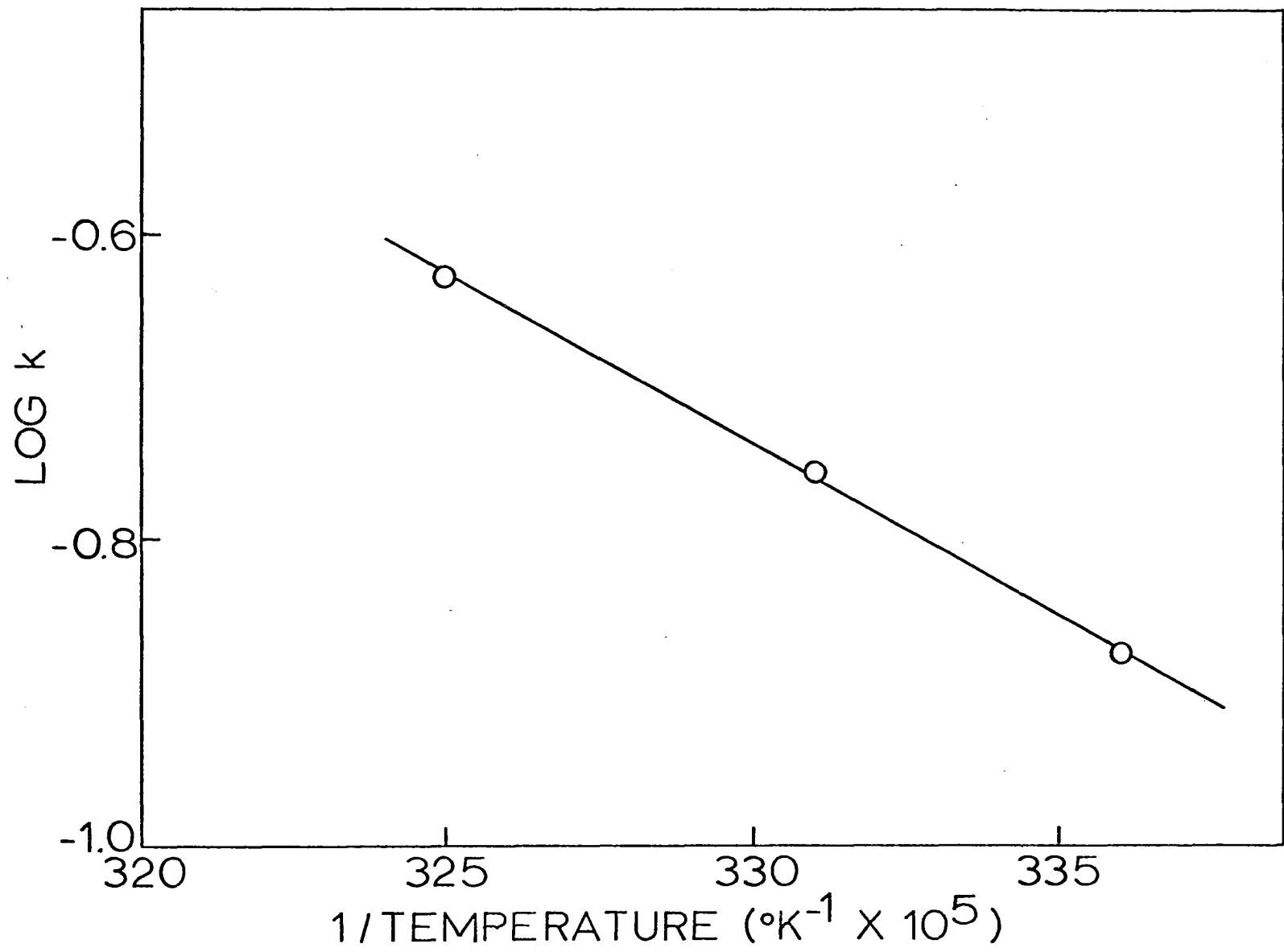
$$(142) \quad E_a = 2.303 \frac{R T_2 T_1}{T_2 - T_1} \log (k_2/k_1)$$

The activation energy varied slightly depending on which pair of temperatures was used, but the average value using all three possible pairs was calculated to be $10.4 \pm .4$ kcal/mole. The activation enthalpy can be calculated since (141):

$$(143) \quad \Delta H^\ddagger = E_a - RT$$

From this equation, ΔH^\ddagger is calculated to be $9.8 \pm .4$ kcal/mole. The usual equation was rearranged and used to calculate the entropy of activation (141).

Figure 10. Oxidation of triphenylmethane in dimethyl sulfoxide (80%)-
t-butyl alcohol (20%) containing potassium t-butoxide at
various temperatures; k = rate constant



$$(144) \quad k = \frac{k'T}{h} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}$$

$$(145) \quad \ln k = \ln \frac{k'T}{h} + \frac{\Delta S^\ddagger}{R} + \frac{\Delta H^\ddagger}{RT}$$

$$(146) \quad \Delta S^\ddagger = R(2.303 \log k - 2.303 \log \frac{k'T}{h} + \frac{\Delta H^\ddagger}{RT})$$

The value obtained was $\Delta S^\ddagger = -29.4$ e.u. This value is consistent with a bimolecular transition state containing a unit charge, but in a polar solvent (62). The activation parameters are consistent with the ionization process, but do not demand it.

The effect on the rate constant by varying the percentage of DMSO in mixtures of DMSO and *t*-butyl alcohol was also studied. The data obtained is given in Table 35, and a plot of log oxidation rate constant as a function of percent DMSO is shown in Figure 11. The plot is approximately linear, agreeing with data of Cram (63) who found a linear relation between % DMSO and log rate constant within the limits 80% DMSO and 20% DMSO for the racemization of 2-methyl-3-phenylpropionitrile. Presumably, the correlation exists because the entropy of activation is linearly related to the % DMSO in this region. However, either above 80% DMSO or below 20% DMSO, the linear relationship is invalid (63) and the situation is more complex.

A complete kinetic investigation of the oxidation of

Table 35. The oxidation of triphenylmethane in various mixtures of dimethyl sulfoxide and t-butyl alcohol^a

| % Dimethyl sulfoxide ^b | k_1 ^c | $-\log k_1$ |
|-----------------------------------|----------------------|-------------|
| 80% | 0.175 ^d | 0.747 |
| 70% | 0.038 ^d | 1.42 |
| 60% | 0.0127 ^d | 1.90 |
| 52% | 0.00417 ^e | 2.38 |
| 25% | 0.000224 | 3.65 |

^aThermostated at 29.5°.

^bRemainder of solvent is t-butyl alcohol.

^cLiter/mole-second.

^dAverage of several determinations.

^eUnthermostated, room temperature was 27°.

α -deuteriotriphenylmethane in 80/20 DMSO was also performed. Results from unthermostated runs are summarized in Table 36. A typical oxidation of deuteriotriphenylmethane in 80/20 DMSO is shown in Figure 12. There is an obvious lack of precision in the data of Table 36, but accepting a 10-15% deviation, there is no effect on varying the oxygen pressure or adding nitrobenzene. Figure 13 displays the variation of oxidation rate with hydrocarbon concentration, and a reasonable linear relationship is observed. Figure 14 presents the change in oxidation rate with change in base concentration,

Figure 11. Oxidation of triphenylmethane in various dimethyl sulfoxide-
t-butyl alcohol mixtures containing potassium t-butoxide;
k = rate constant

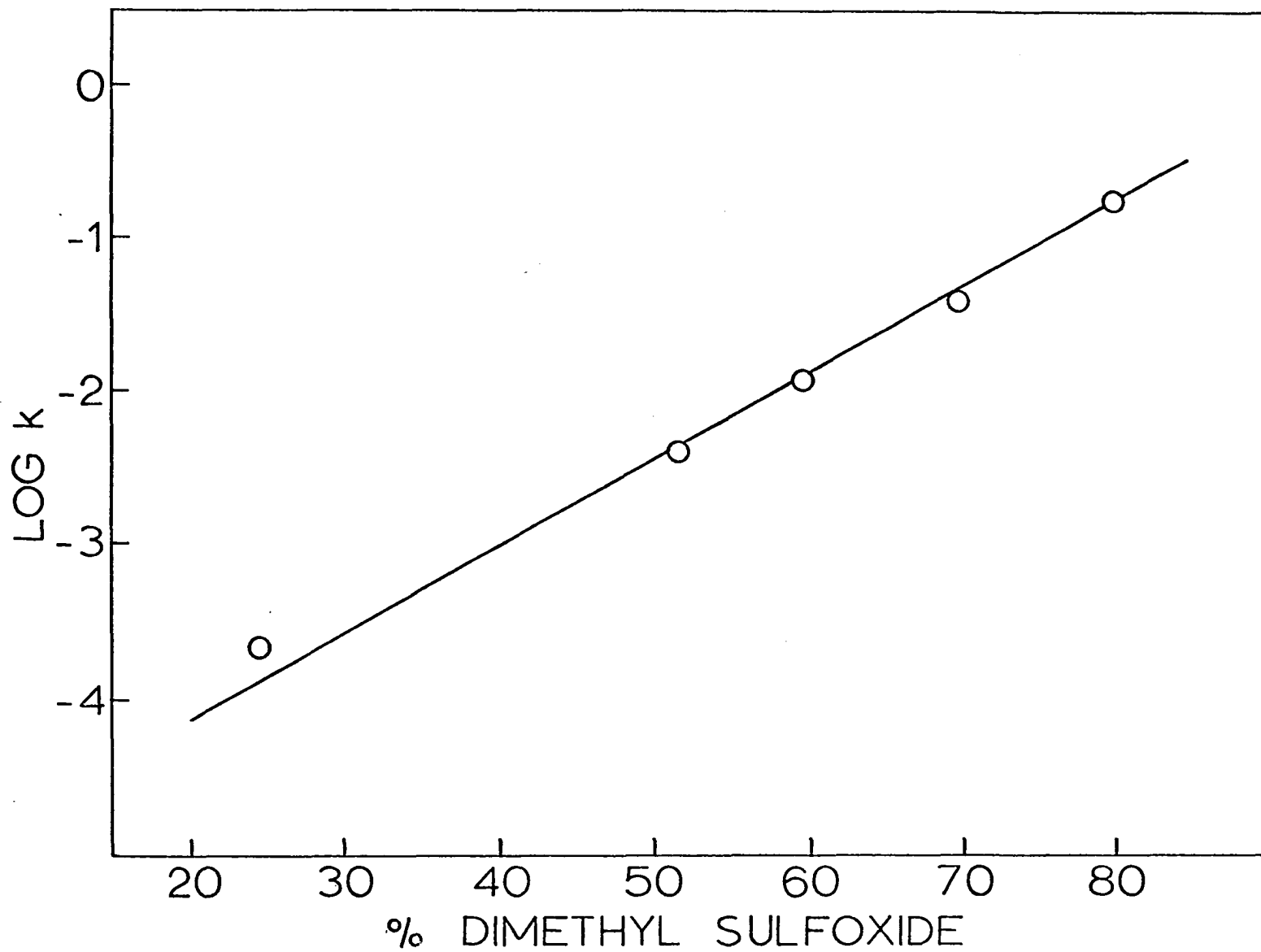


Figure 12. Oxidation of triphenylmethane- α -d (0.049 M) in dimethyl sulfoxide (80%)-t-butyl alcohol (20%) containing potassium t-butoxide (0.199 M)

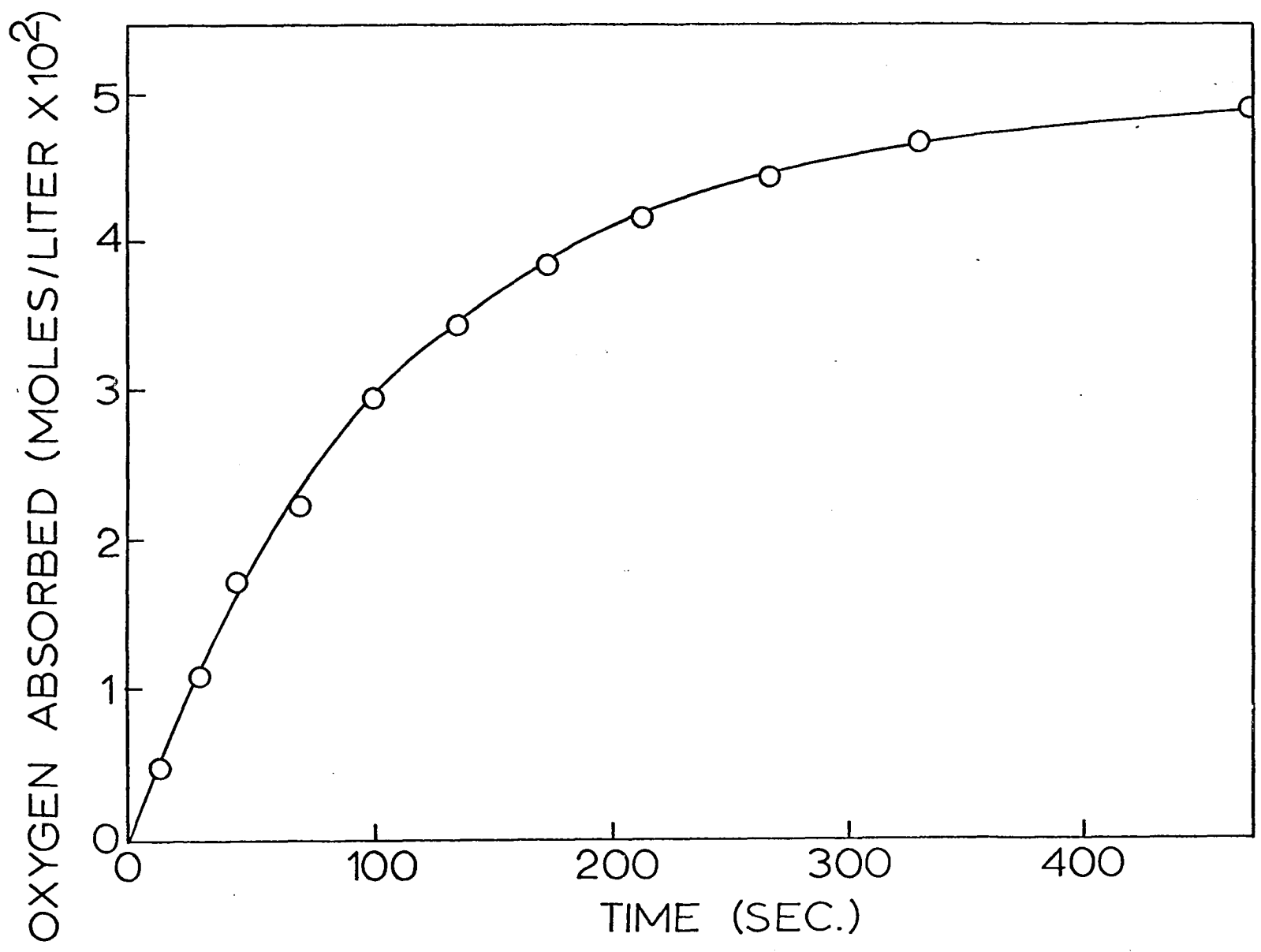


Figure 13. Oxidation of triphenylmethane- α -d in dimethyl sulfoxide (80%)-
t-butyl alcohol (20%) containing potassium t-butoxide (0.199 M);
initial rate in moles per liter per second

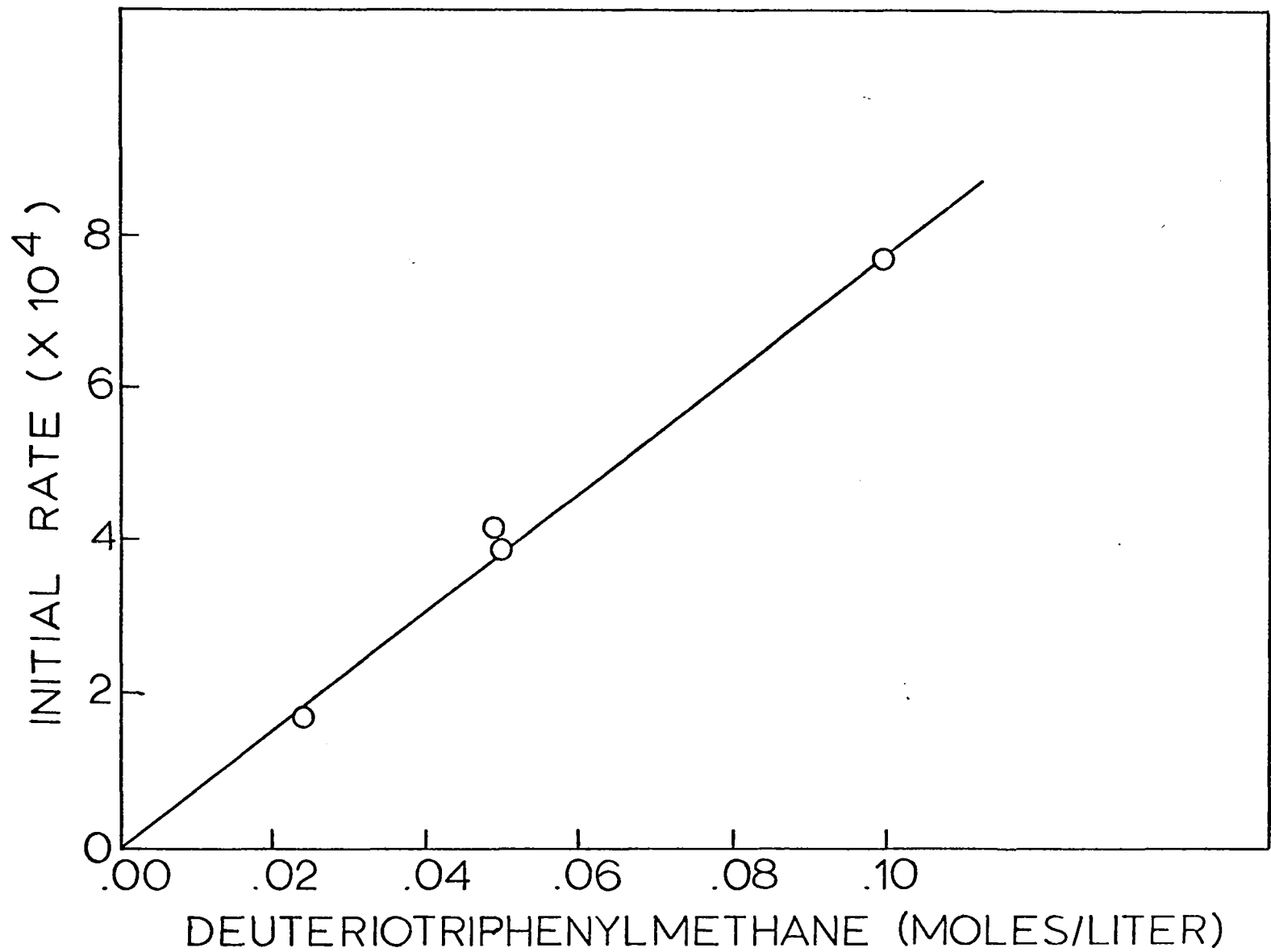


Figure 14. Oxidation of triphenylmethane- α -d (0.049 M) in dimethyl sulfoxide (80%)-t-butyl alcohol (20%) containing potassium t-butoxide; initial rate in moles per liter per second

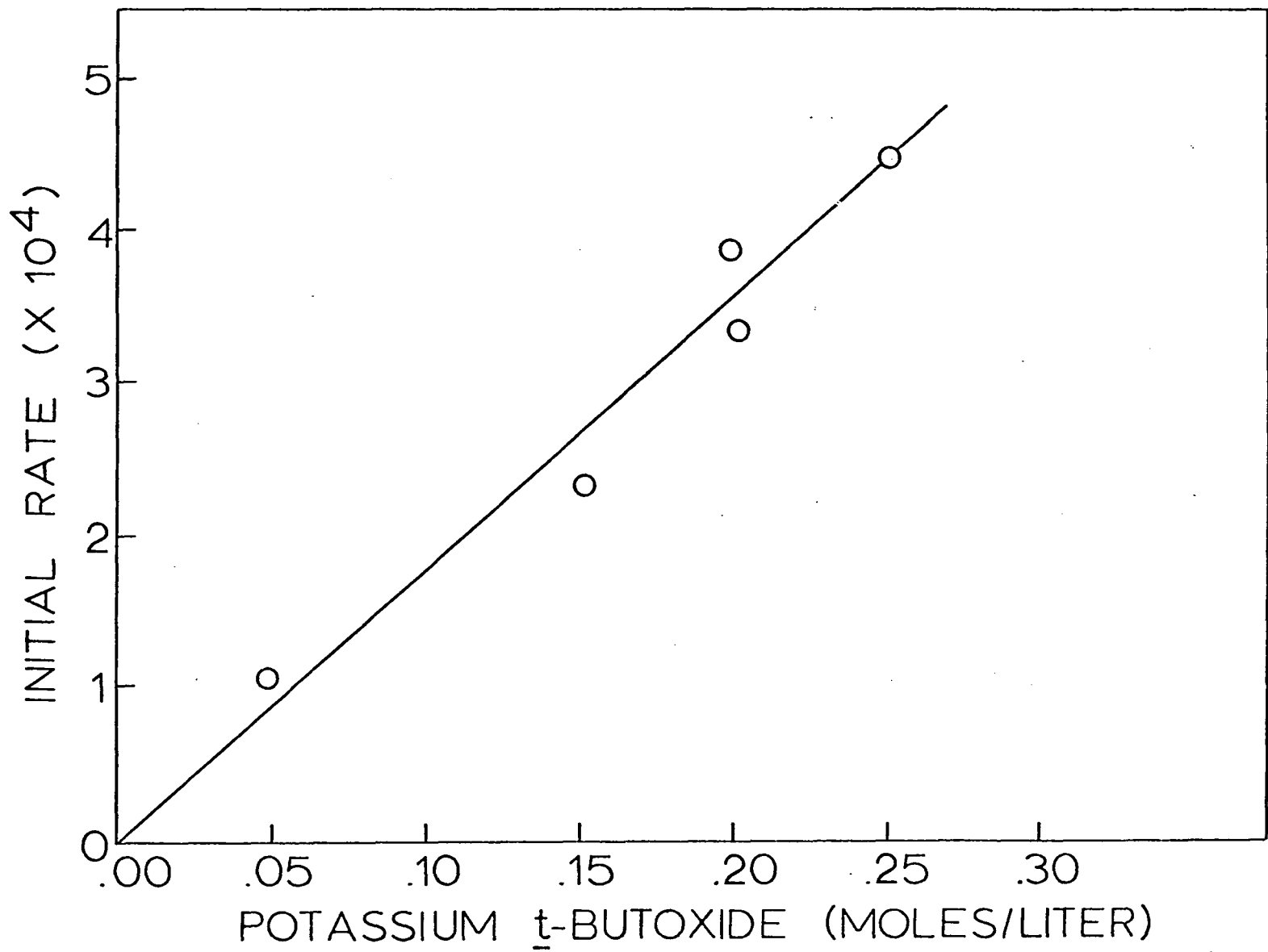


Table 36. Oxidation of α -deuteriotriphenylmethane in dimethyl sulfoxide (80%)-t-butyl alcohol (20%)^a

| $(C_6H_5)_3CD$ ^b | $KOC(CH_3)_3$ ^b | Initial rate ^c |
|-----------------------------|----------------------------|---------------------------|
| 0.0505 | 0.199 | 3.88 |
| 0.0995 | 0.199 | 7.64 |
| 0.049 | 0.199 | 4.21 |
| 0.0245 | 0.199 | 1.77 |
| 0.049 | 0.199 | 3.50 ^d |
| 0.0245 | 0.199 | 1.13 ^e |
| 0.049 | 0.051 | 1.08 |
| 0.049 | 0.154 | 2.32 |
| 0.049 | 0.205 | 3.35 |
| 0.049 | 0.256 | 4.45 |

^a25 ml of a vigorously shaken solution at 749 mm of oxygen and room temperature.

^bMoles/liter.

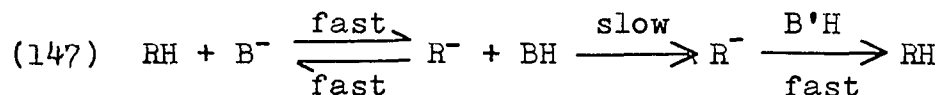
^cMoles/liter-second.

^dAt 391 mm of oxygen.

^e0.098 M nitrobenzene present.

at constant initial hydrocarbon concentration. The points are clustered near a straight line. These relationships are evidence that in the oxidation of deuteriotriphenylmethane, as was observed for the undeuterated compound, the rate

determining step is ionization. The rate constant for the oxidation of deuteriotriphenylmethane in 80/20 DMSO containing potassium *t*-butoxide, and thermostated at 24.5° (calculated as described previously) is $k_1 = 0.0186 \pm .005$ liter/mole-second, the average of three determinations. Since the average rate constant for the oxidation of undeuterated triphenylmethane in 80/20 DMSO at 24.5° was $k_1 = 0.134 \pm 0.003$ liter/mole-second, a kinetic isotope effect (k_H/k_D) of 7.2 is found. The size of this isotope effect demands that a carbon-hydrogen bond is broken in the rate determining step. The magnitude also rules out the rapid pre-equilibria which was found by Cram in 100% DMSO (142). The lack of a hydrogen-



deuterium isotope effect in the base catalyzed exchange of 2-methyl-3-phenylpropionitrile in 100% DMSO (142) and the absence of a deuterium-tritium isotope effect in the exchange of toluene in 100% DMSO (76) are the major pieces of evidence supporting such a mechanism. Streitwieser and Van Sickle (71) found a large isotope effect for the exchange of toluene in cyclohexylamine. k_H/k_D was calculated to be 10-12 from k_D/k_T which was measured. The pre-equilibrium mechanism is excluded in cyclohexylamine on the basis of the large isotope effect (71), and it can not be important in 80/20 DMSO for the same reason. It is interesting to note that although it

was understood that pure DMSO was quantitatively a much better solvent for base catalyzed reactions, no one (63) seemed to realize that the addition of only 20% t-butyl alcohol could completely change the mechanism of exchange, and probably other base-catalyzed reactions.

Triphenylmethane- α -d was exchanged under conditions identical to the oxidation, except that nitrogen was substituted for oxygen. The rate constant for exchange was calculated from the percent deuterium present, obtained by mass spectroscopy. The raw data are given in the Experimental Section. The exchange and an oxidation were performed at 27° under identical conditions, using the same batch of solvent and base, and within a few minutes of each other. The rate constants, for 80/20 DMSO containing potassium t-butoxide, were $k_{\text{exchange}} = 0.0209$ liter/mole-second and $k_{\text{oxidation}} = 0.0189$ liter/mole-second. Both second order rate constants are experimental, and uncorrected. Since the starting triphenylmethane was 93.1% mono- α -d, some of the oxidation is due to the undeuterated material. This does not affect the calculation of the exchange rate constant (by the same equation as the oxidation) since the change in deuterium is what is being measured, but it does affect the oxidation rate constant. If the calculation of the oxidation rate constant is corrected by assuming that essentially all the undeuterated material is oxidized in 2 minutes, and (experimentally an

oxidation of undeuterated triphenylmethane is greater than 95% complete in this time) an oxidation rate constant of 0.0214 liter/mole-second is obtained. This correction is not strictly valid, but would seem to be reasonable. The exchange rate constant was not corrected for replacement of hydrogen by deuterium (back reaction) or replacement of deuterium by deuterium. Streitwieser et al. (70) made these corrections in exchange reactions in cyclohexylamine, and found it lowered the experimental rate constant about 10%. However, they were using a ten times more concentrated solution in deuterated species, and deuterium buildup in the solvent was important. In this case, it is probably unimportant, and a correction would be expected to be much smaller than 10%.

Diphenyl- α -naphthylmethane was oxidized in 80/20 DMSO containing potassium t-butoxide at a variety of conditions. The calculated rate constants are given in Table 37. By comparing runs at a given temperature, it can be seen that there is no effect on lowering the oxygen pressure or adding nitrobenzene. Similarly, since the same value of the rate constant is obtained at different base and hydrocarbon concentrations, the reaction is consistent with the kinetic treatment, i.e., first order in hydrocarbon and first order in base. In view of results from other oxidations, the precision in the room temperature oxidations of diphenyl- α -

Table 37. The oxidation of diphenyl- α -naphthylmethane in dimethyl sulfoxide (80%)-t-butyl alcohol (20%)^a

| Temperature | Diphenyl- α -naphthylmethane ^b | KOC(CH ₃) ₃ ^b | k ₁ ^c |
|-------------------|--|---|-----------------------------|
| 32-33 | 0.0504 | 0.199 | 0.193 |
| 32-33 | 0.0231 | 0.199 | 0.193 |
| 32-33 | 0.0231 | 0.1025 | 0.192 |
| 24.5 ^d | 0.0242 | 0.197 | 0.179 |
| 24.5 ^d | 0.0242 | 0.197 | 0.167 |
| 28-29 | 0.0484 | 0.197 | 0.165 |
| 28-29 | 0.0484 | 0.197 | 0.167 ^e |
| 28-29 | 0.0484 | 0.197 | 0.167 |
| 28-29 | 0.0484 | 0.197 | 0.172 ^f |

^a25 ml of a vigorously shaken solution at 749 mm of oxygen.

^bMoles/liter.

^cLiter/mole-second.

^dThermostated.

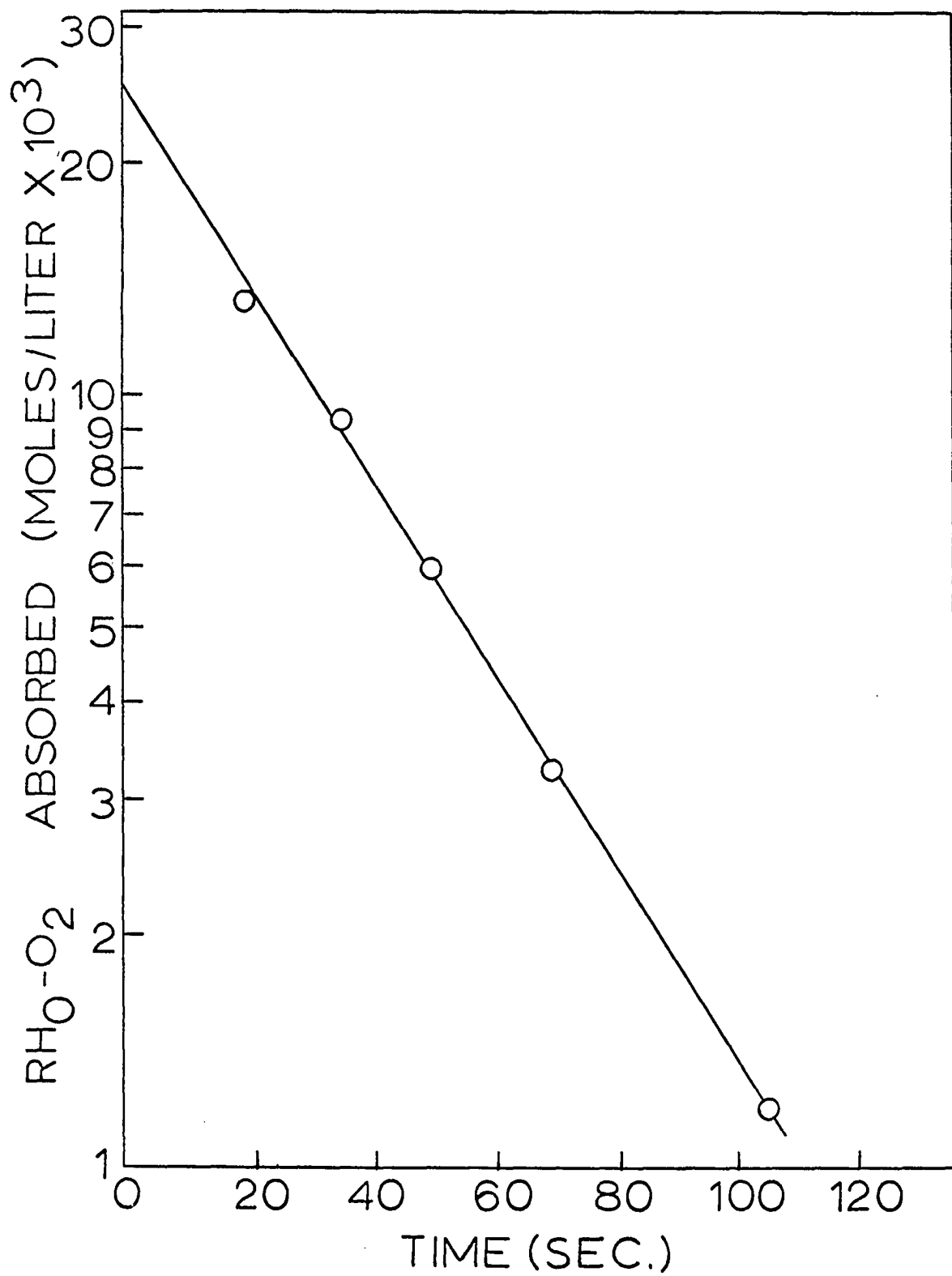
^eIn the presence of 0.098 M nitrobenzene.

^fAt 391 mm of oxygen.

naphthylmethane is probably fortuitous. At 24.5^o, the rate constant is 0.173 ± 0.004 liter/mole-second. A typical oxidation is graphed in the semi-log manner on Figure 15.

The oxidation of diphenylmethane was treated kinetically

Figure 15. Oxidation of diphenyl- α -naphthylmethane (0.0242 M) in dimethyl sulfoxide (80%)-t-butyl alcohol (20%) containing potassium t-butoxide (0.197 M) at 24.5^o; the ordinate axis is constructed logarithmically; RH_0 = initial diphenyl- α -naphthyl methane concentration



by the same scheme as used for triphenylmethane. Although the overall stoichiometry is greater than 2:1, the initial reaction, which results in the formation of benzhydrol as an isolable product has a stoichiometry of 1:1, and the rate of oxidation of benzhydrol is slow enough compared to the initial rate of oxidation of diphenylmethane that there was a good possibility of analyzing the first step kinetically. Actually, surprisingly good results were obtained. Table 38 presents data from oxidations of diphenylmethane in 80/20 DMSO under a variety of conditions. Reasonable precision was obtained for runs at a given temperature. No significant change is observed in the rate constant in Table 38, when the concentration of diphenylmethane or potassium t-butoxide is varied. The accuracy of the rate constants is poorer than for triphenylmethane since in the diphenylmethane oxidations, a semi-log plot did not give a straight line. Figure 16 presents the semi-log plot of a typical diphenylmethane oxidation in 80/20 DMSO. Note that the rate increases faster than a straight line would predict; this is due to oxidation of the benzhydrol which is formed in the first step. The rate constants were all calculated from the first point since there was less benzhydrol oxidation. Unfortunately an error in the first point can not be detected. In the triphenylmethane graphs, a straight line was always obtained, and if the initial point was slightly in error it could be readily

Table 38. Rate constants from the oxidation of diphenylmethane in dimethyl sulfoxide (80%)-t-butyl alcohol (20%)^a

| Temperature | $(C_6H_5)_2CH_2$ ^b | $KOC(CH_3)_3$ ^b | k_1 ^c |
|-------------------|-------------------------------|----------------------------|--------------------|
| 31-32 | 0.025 | 0.05 | 0.148 |
| 31-32 | 0.0643 | 0.20 | 0.183 |
| 31-32 | 0.0643 | 0.20 | 0.182 |
| 31-32 | 0.0167 | 0.20 | 0.177 |
| 25-26 | 0.05 | 0.234 | 0.087 |
| 25-26 | 0.10 | 0.234 | 0.092 |
| 25-26 | 0.10 | 0.234 | 0.12 |
| 24.5 ^d | 0.0643 | 0.197 | 0.089 |
| 24.5 ^d | 0.0643 | 0.197 | 0.105 |
| 24.5 ^d | 0.10 | 0.197 | 0.07 |
| 24.5 ^d | 0.10 | 0.197 | 0.075 |

^a25 ml of a vigorously shaken solution at 749 mm of oxygen.

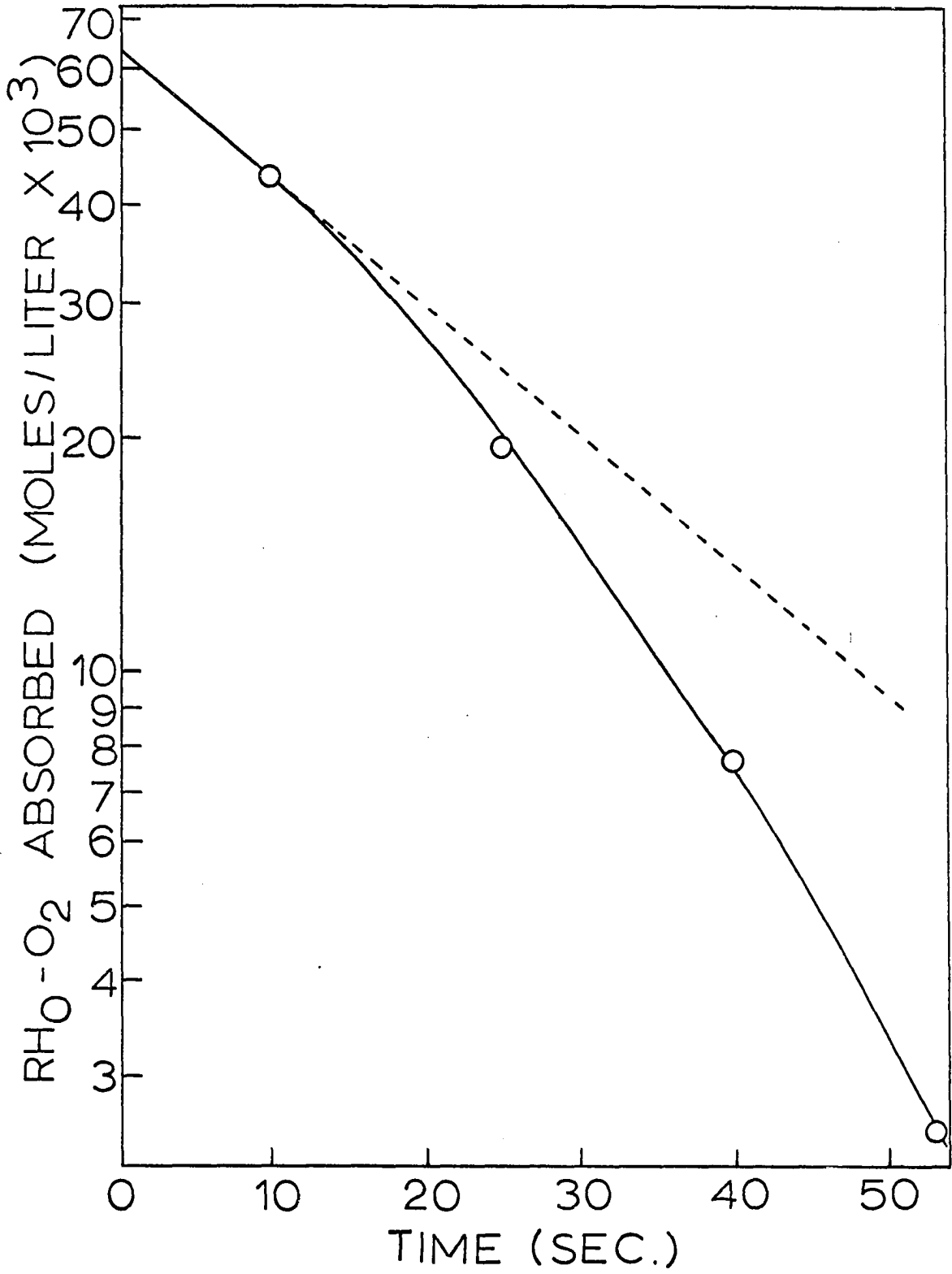
^bMoles/liter.

^cLiter/mole-second.

^dThermostated.

seen since the other points would define the straight line. The average rate constant for the oxidation of diphenylmethane in 80/20 DMSO containing potassium t-butoxide and thermostated at 24.5 was calculated to be $0.085 \pm .015$

Figure 16. Oxidation of diphenylmethane (0.064 M) in dimethyl sulfoxide (80%)-t-butyl alcohol (20%) containing potassium t-butoxide (0.2 M); the ordinate axis is constructed logarithmically; RH_0 = initial concentration of diphenylmethane



liter/mole-second.

Diphenylmethane- α - d_2 was oxidized in 80/20 DMSO, and an experimental rate constant of between 0.02 and 0.015 liter/mole-seconds was obtained. Data from one run of the oxidation of dideutero diphenylmethane in 80/20 DMSO is given in Table 39. The same data are graphed in Figure 17. The

Table 39. The oxidation of diphenylmethane- α - d_2 in dimethyl sulfoxide (80%)-t-butyl alcohol (20%)^a

| Time ^b | RH _o - O ₂ ^c | k _i ^d |
|-------------------|---|-----------------------------|
| 0.0 | 0.1000 | -- |
| 16.8 | 0.0879 | 0.0336 |
| 48 | 0.080 | 0.020 |
| 84 | 0.070 | 0.0198 |
| 120 | 0.0612 | 0.0175 |
| 162 | 0.053 | 0.0168 |
| 290 | 0.0336 | 0.0162 |
| 576 | 0.0134 | 0.0150 |
| 738 | 0.0078 | 0.0148 |
| 890 | 0.004 | 0.0157 |

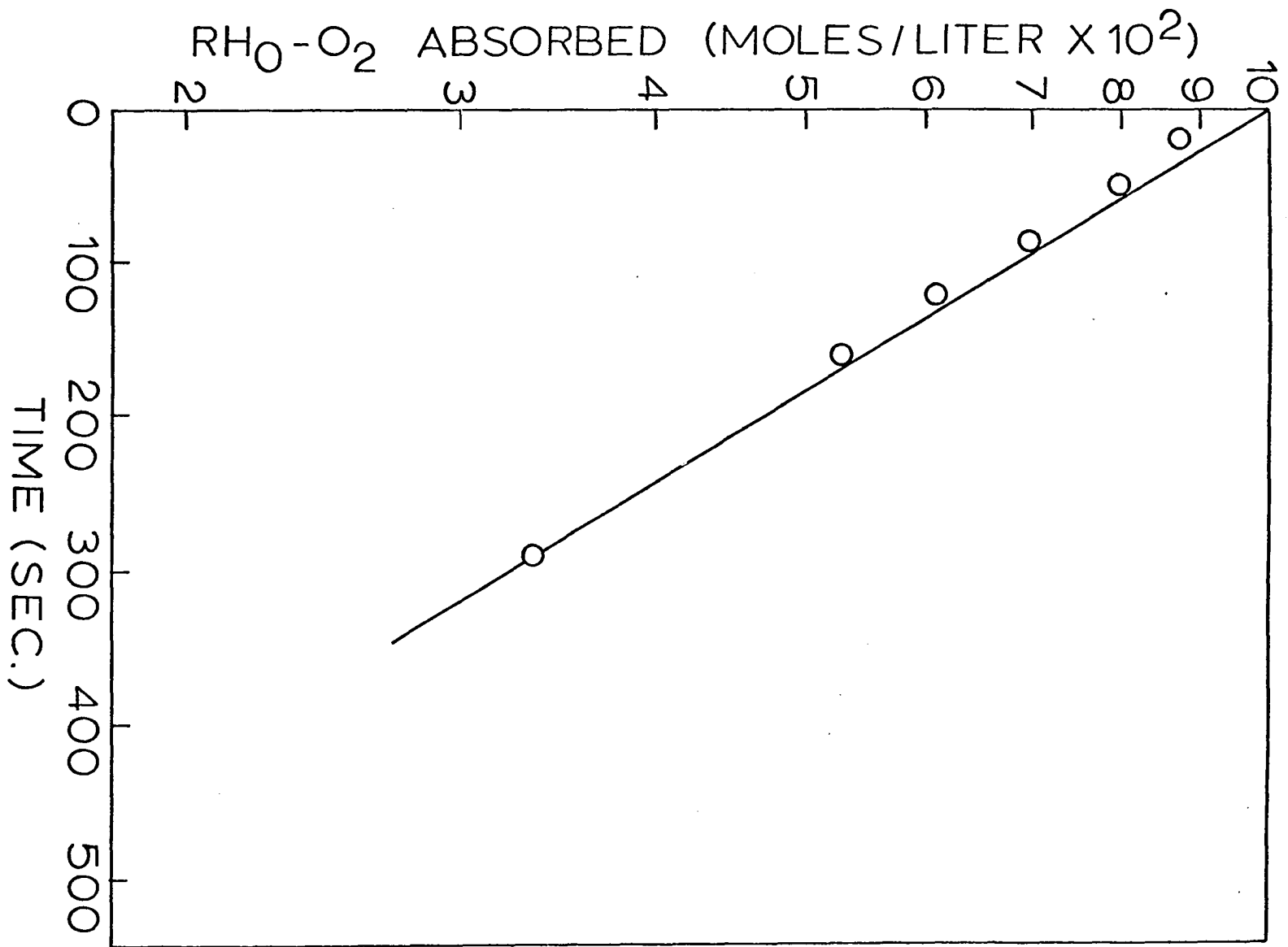
^a25 ml of a vigorously shaken solution, initially 0.1 M substrate, 0.234 M potassium t-butoxide at room temperature and 749 mm of oxygen.

^bSeconds.

^cMoles/liter.

^dLiter/mole-seconds.

Figure 17. Oxidation of diphenylmethane- α -d₂ (0.1 M) in dimethyl sulfoxide (80%)-t-butyl alcohol (20%) containing potassium t-butoxide (0.234 M); the ordinate axis is constructed logarithmically; RH_0 = initial concentration of deuteriodiphenylmethane



starting diphenylmethane was 97% dideuterio by mass spectroscopy. The variation in rate constant with time is due to an initial fast oxidation of the monodeuterio diphenylmethane (2.72%) and undeuterated diphenylmethane (0.4%). Figure 17 should be contrasted with Figure 16, where the rate constant increases with time. In that case, the increase is due to oxidation of benzhydrol, the intermediate. The oxidation of the intermediate from diphenylmethane- α -d₂ is much slower, since benzhydrol- α -d is produced. An oxidation of dideuterio-diphenylmethane was interrupted after 0.96 moles of oxygen per mole of diphenylmethane had been absorbed. The crude product was analyzed by g.l.c. and found to contain only benzhydrol and a trace of diphenylmethane. Although no benzophenone was seen, the DMSO-benzophenone adduct, which readily forms under these conditions when benzophenone is present, can not be detected by this method of analysis. The benzhydrol was isolated and purified (greater than 70% yield) and analyzed for deuterium by mass spectroscopy. This analysis showed the benzhydrol to be 98.5% benzhydrol-d₁. This result is in excellent agreement with the finding reported by Geels (101) that benzhydrol- α -d did not exchange in 80/20 DMSO under the conditions of the oxidation. Geels (101) found the rate of oxidation of benzhydrol- α -d in 80/20 DMSO to be 10.7 times slower than the undeuterated alcohol. The actual rate of oxidation of the deuteriobenzhydrol is 0.0015

moles of oxygen per mole benzhydrol per minute compared to an initial rate of 2.5 moles of oxygen per mole substrate per minute for dideuteriodiphenylmethane. The reasonable interpretation of Table 39 and Figure 17 is that the oxygen uptake in the first few seconds is due in large part to the 3% of the diphenylmethane bearing α -hydrogens, and that oxygen uptake due to benzhydrol (98.5% α -deutero) is unimportant until about 80-90% of the diphenylmethane has been oxidized, when a slow oxidation of the deuteriobenzhydrol begins to contribute enough to the overall oxygen uptake that the apparent rate constant for diphenylmethane begins to increase again. On the basis of this interpretation, the minimum experimental value of the rate constant for diphenylmethane- α -d₂ (0.0148 liter/mole-second) is believed to actually be a maximum value. Probably some benzhydrol oxidation is contributing to this value, and the real rate constant is somewhat smaller. Support for this viewpoint comes from exchange experiments on dideuteriodiphenylmethane, carried out under the usual oxidation conditions, except that nitrogen was used in place of oxygen. From the mass spectroscopic analysis of two exchange experiments, (see Experimental section for crude data) the rate constant for exchange was calculated, $k_{\text{exchange}} = 0.013$ liter/mole-seconds, in fair agreement with $k_{\text{oxidation}} = 0.0148$ liter/mole-seconds. The calculation should be quite small since the concentration of dueterium containing mate-

rial was small. The agreement between the two rate constants indicates that the oxidation of diphenylmethane is ionization rate controlled, confirming the other kinetic data obtained. The oxidation isotope effect is calculated to be $k_H/k_D = 8.1$ from rate constants calculated for oxidations of deuterated and undeuterated diphenylmethane using the same sample of 80/20 DMSO and potassium *t*-butoxide, and run within a few minutes of one another. This isotope effect is nearly identical with that found for triphenylmethane.

The oxidation of α -methylnaphthalene in HMPA (100%) was reasonably slow, so it was felt that it might be ionizing at the same rate it oxidized. Table 40 presents some rates of oxidation of α -methylnaphthalene in HMPA.

Table 40. Oxidation of α -methylnaphthalene in hexamethylphosphoramide^a

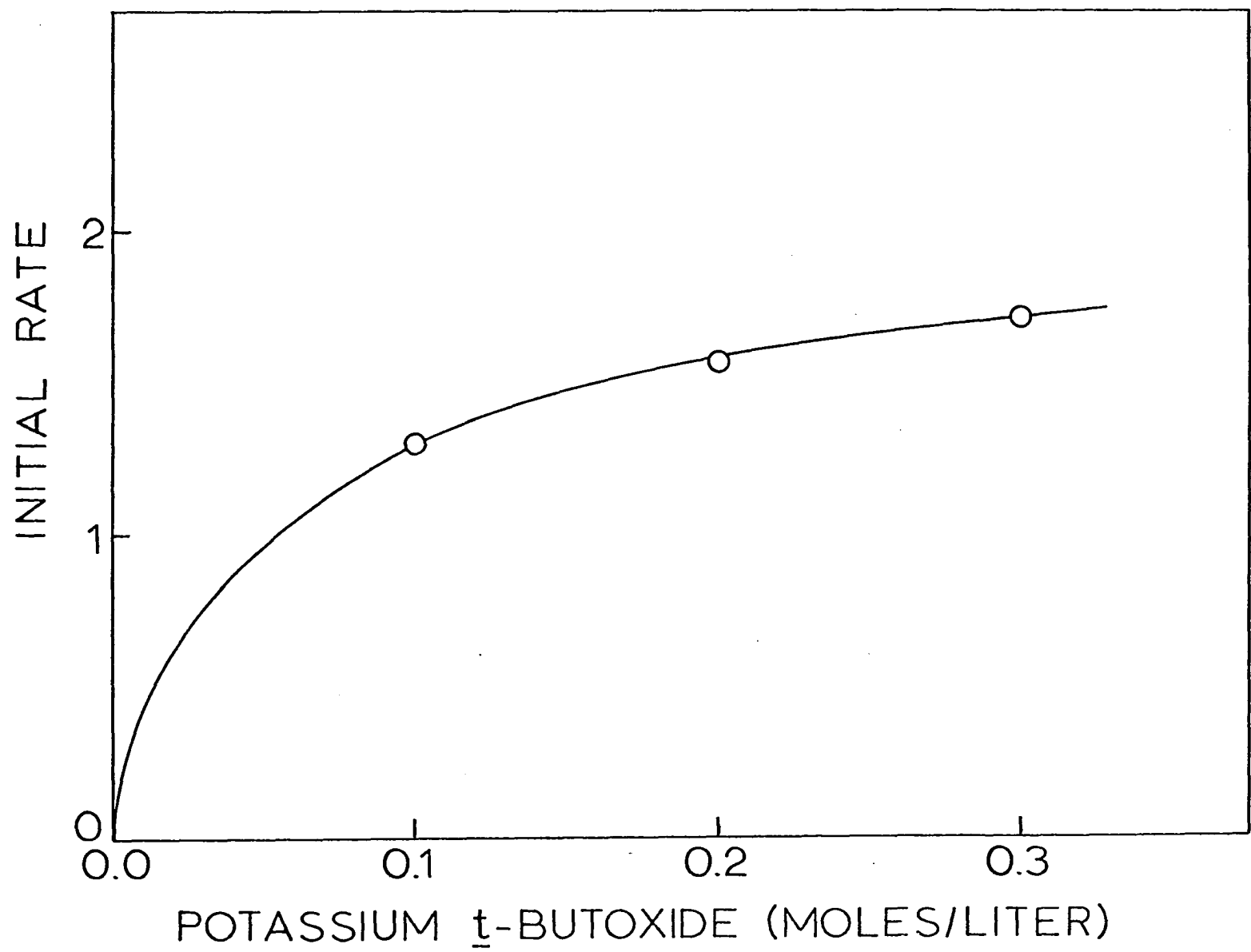
| α -Methylnaphthalene ^b | KOC(CH ₃) ₃ ^b | Initial rate ^c |
|--|---|---------------------------|
| 0.1 | 0.3 | 1.7 |
| 0.1 | 0.2 | 1.56 |
| 0.1 | 0.1 | 1.30 |
| 0.05 | 0.2 | 1.41 |

^a25 ml of a vigorously shaken solution, thermostated at 29.5 and at 749 mm of oxygen.

^bMoles/liter.

^cMoles of oxygen per mole of substrate per minute.

Figure 18. Oxidation of α -methylnapthalene (0.1 M) in hexamethylphosphoramide containing potassium t-butoxide; initial rate in moles of oxygen per mole of α -methylnapthalene per minute



Only a slight variation of rate with base or hydrocarbon concentration is evident in Table 40. The initial rate of oxidation of α -methyl-naphthalene in HMPA is plotted against base concentration in Figure 18. The reaction is obviously not first order in base. A similar plot shows the oxidation is not first order in hydrocarbon either. Although the oxidation may be electron transfer rate controlled, this could not be established since nitrobenzene oxidizes very rapidly in basic HMPA solution. An alternative possibility is that 100% HMPA is similar to 100% DMSO, in that there is a pre-equilibrium of the sort postulated by Cram *et al.* (142).

2. Electron transfer

Many oxidations are obviously not ionization rate controlled. Oxidations which are not ionization rate controlled do not have to be electron transfer rate controlled. If the oxidation is electron transfer rate controlled, catalysis by nitrobenzene is usually observed, and the reaction should be first order in the electron acceptor. Both fluorene and acetophenone in *t*-butyl alcohol oxidize slowly, but are strongly catalyzed by the addition of nitrobenzene and substituted nitrobenzenes. The oxidations in *t*-butyl alcohol containing potassium *t*-butoxide of fluorene (25) and acetophenone (101) were catalyzed by a wide variety of substituted nitrobenzenes. In both cases, an excellent correlation of log oxidation rate against σ was obtained. Separate

electron transfer experiments of these two compounds with the substituted nitrobenzenes under nitrogen, monitored by measuring the rate of formation of nitrobenzene radical anion by e.s.r. were done (25, 101). Graphs of log electron transfer rate against σ gave the identical ρ obtained in the oxidation correlation (25, 101). This is good evidence that the rate of oxidation when catalyzed by nitrobenzene is equal to the rate of electron transfer.

The nitrobenzene or meta-trifluoromethylnitrobenzene (MTB) catalyzed oxidation of fluorene in t-butyl alcohol containing potassium t-butoxide has a stoichiometry of 1 mole of oxygen per mole of fluorene. The stoichiometry is unaffected by the presence or increase in concentration of nitrobenzene. The rate constants for the oxidation of fluorene in t-butyl alcohol over a wide range of nitrobenzene concentrations are presented in Table 41. The oxidations were thermostated at 29.5°. The rate constants were calculated by a simple kinetic treatment, which depends on several assumptions. These assumptions are apparently valid, since the treatment gives good results.

If the rate of oxidation depends on the electron transfer from carbanion to nitrobenzene, the rate expression will have the form:

$$(148) \quad \frac{d[O_2]}{dt} = \frac{-d[RH]}{dt} = k [R^-][Cat.]$$

Table 41. Nitrobenzene catalyzed oxidations of fluorene in t-butyl alcohol^a

| Fluorene ^b | KOC(CH ₃) ₃ ^b | Nitrobenzene ^b | k ₁ ^c | k ₁ ^{c,d} |
|-----------------------|---|---------------------------|-----------------------------|-------------------------------|
| 0.0483 | 0.197 | 0.00 | 0.00241 | 0.00241 |
| 0.0483 | 0.197 | 0.0196 | 0.0169 | 0.0169 |
| 0.0483 | 0.197 | 0.0391 | 0.035 | 0.035 |
| 0.0483 | 0.197 | 0.0783 | 0.0616 | 0.0616 |
| 0.0483 | 0.197 | 0.118 | 0.0905 | 0.0905 |
| 0.0232 | 0.024 | 0.376 | 0.155 | 0.0995 |
| 0.0223 | 0.0231 | 0.725 | 0.328 | 0.166 |
| 0.0215 | 0.0227 | 1.05 | 0.396 | 0.234 |
| 0.0201 | 0.0208 | 1.63 | 0.56 | 0.283 |
| 0.0227 | 0.0236 | 2.73 | 0.852 | 0.321 |

^a25 ml of a vigorously shaken solution, thermostated at 29.5° and at 749 mm of oxygen.

^bMoles/liter.

^cLiter/mole-seconds.

^dCorrected for the oxidation of nitrobenzene.

(where R⁻ stands for the carbanion and Cat. for the catalyst, nitrobenzene in this case).

The concentration of the carbanion is defined by an acidity constant:

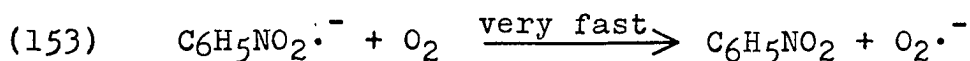
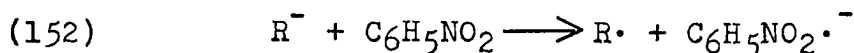
$$(149) \quad K_a = \frac{[R^-][BH]}{[RH][B^-]}$$

$$(150) \quad [R^-] = K_a \frac{[RH][B^-]}{[BH]} = K_a' [RH][B^-]$$

If the conjugate acid of the base (BH, *t*-butyl alcohol in this case) is in large excess, the concentration depends only on the concentration of hydrocarbon and the concentration of base. Substitution of equation 146 into the rate equation (equation 144) gives:

$$(151) \quad \frac{d[O_2]}{dt} = \frac{-d[RH]}{dt} = k K_a [RH][B^-][Cat.]$$

This rate expression can be treated as a pseudo first order equation if two of the three variable concentrations are constant. In the kinetic treatment of the oxidation of triphenylmethane, it was shown that when a large excess of base was present, pseudo first order kinetics were obeyed. Hence one variable can be eliminated by choosing a high enough base concentration. In Section D, it will be shown that the rate of the reaction of nitrobenzene radical anion with oxygen is extremely fast, and is probably diffusion controlled. Thus if the electron transfer from carbanion to nitrobenzene is not extremely fast, the product, nitrobenzene radical anion, will react with oxygen to regenerate nitrobenzene at a rate so fast that an essentially constant concentration of nitrobenzene is always present.



Under these conditions, the kinetics can be treated like those obtained in the triphenylmethane oxidation.

The success of this treatment is illustrated in Figure 19, which graphs the rate constants for the oxidation of fluorene against the concentration of nitrobenzene, up to 0.118 M. A good straight line is obtained, indicating the oxidation is first order in nitrobenzene at low nitrobenzene concentrations. A graph of oxidation rate constant against nitrobenzene concentration, up to 2.7 M, is shown in Figure 20. The plot is apparently not linear in nitrobenzene above 1.0 M, but precise information is not available since, for example, at a concentration of 2 M, nitrobenzene comprises about 23% of the solvent. At this concentration, nitrobenzene may be exerting a considerable solvent effect.

A better electron acceptor is m-trifluoromethylnitrobenzene (MTB) (25). Rate constants for the oxidation of fluorene in t-butyl alcohol containing potassium t-butoxide as a function of MTB concentration are given in Table 42. The rate constants are plotted against MTB concentration in Figure 21. The rate constant for the oxidation of fluorene in t-butyl alcohol is constant (within experimental error) at or above 0.7 M m-trifluoromethylnitrobenzene concentration. The rate leveling is unlikely to be due to a solvent effect at this concentration. Since the rate constant does not change above 0.7 M MTB, the oxidation is no longer dependent on the

Figure 19. Oxidation of fluorene (0.0483 M) in t-butyl alcohol containing potassium t-butoxide (0.197 M) at 29.5° as a function of nitrobenzene concentration; k = rate constant

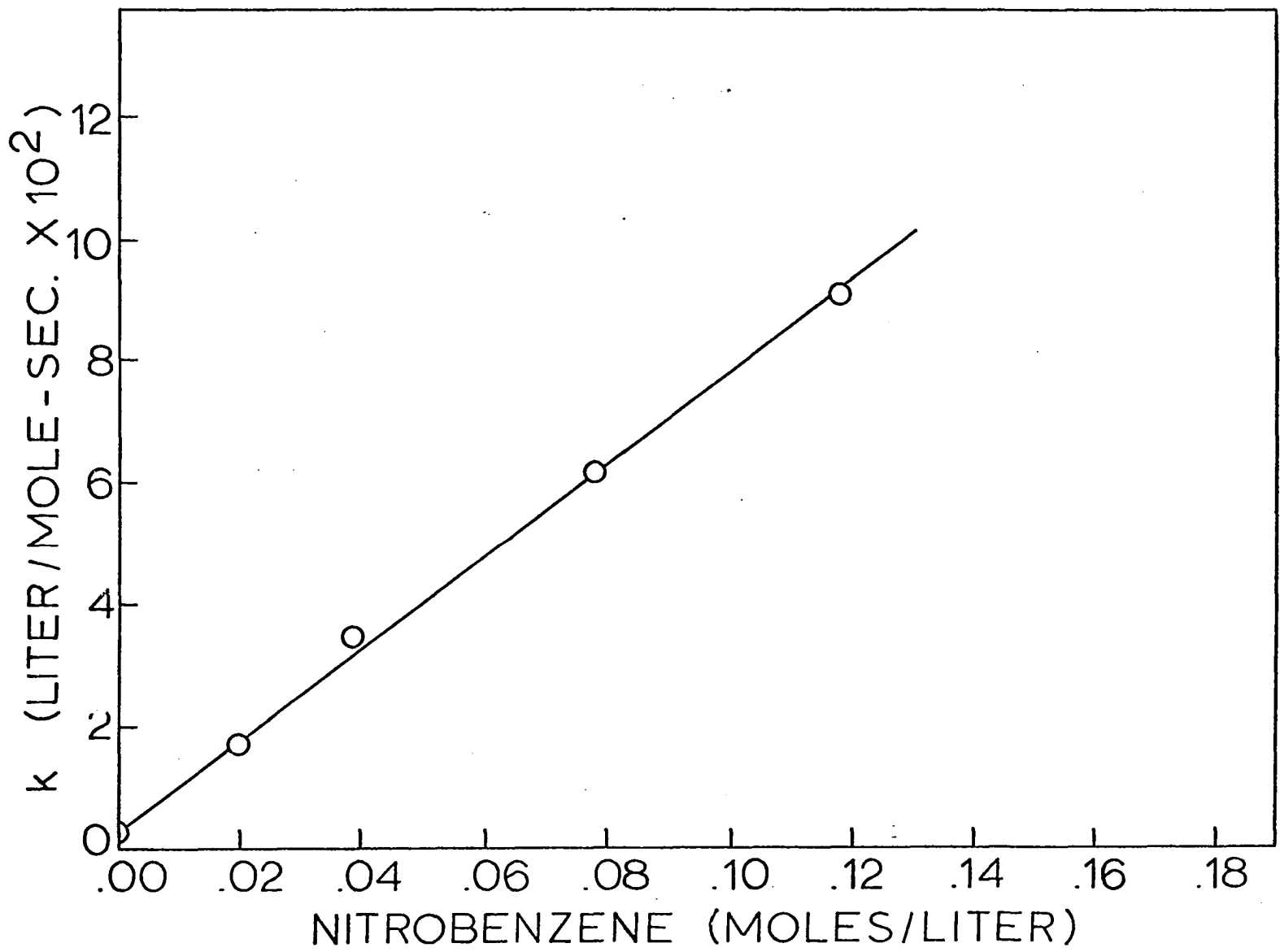


Figure 20. Oxidation of fluorene in t-butyl alcohol containing potassium t-butoxide at 29.5 as a function of nitrobenzene concentration;
 \bar{k} = rate constant

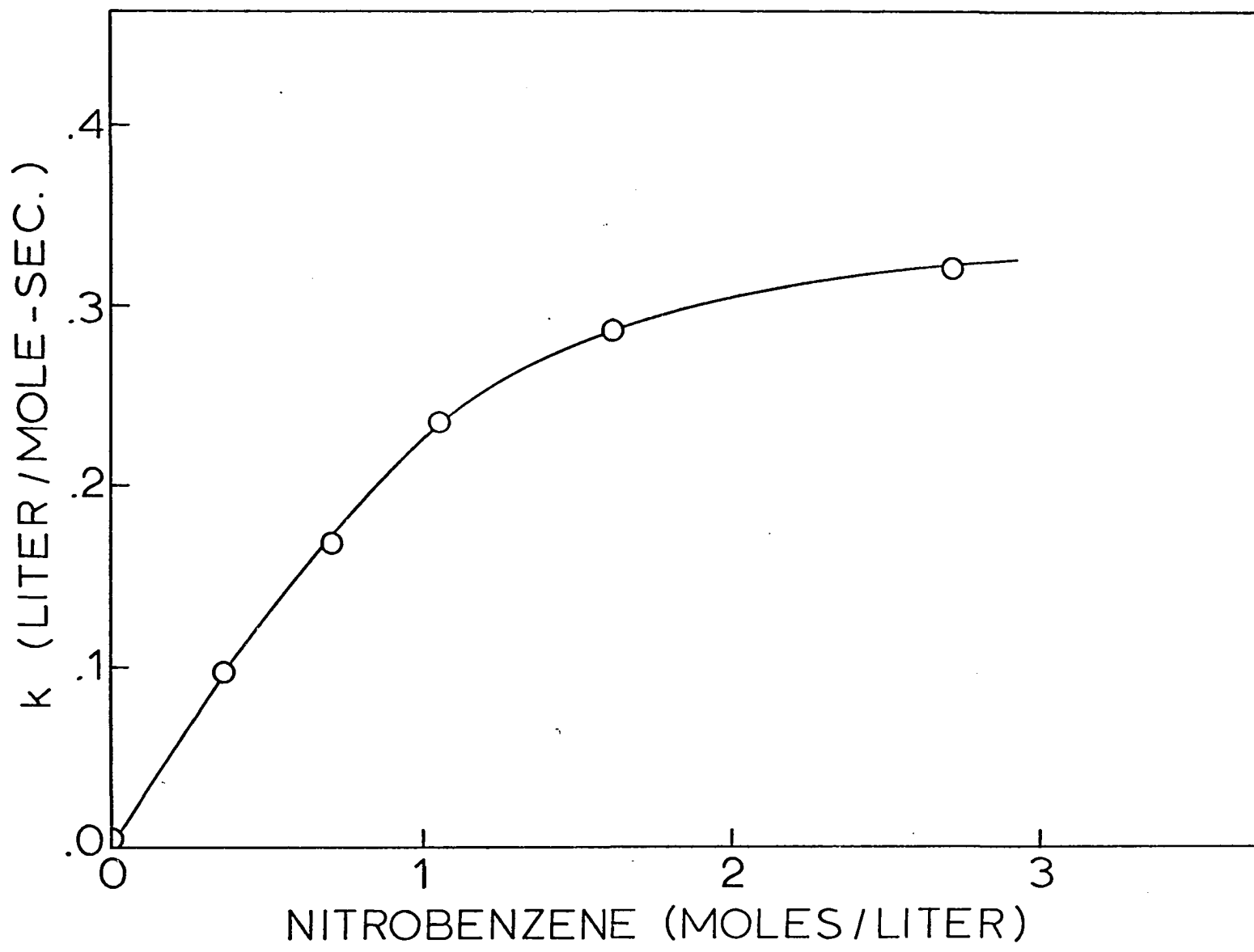


Table 42. m-Trifluoromethylnitrobenzene catalyzed oxidations of fluorene in t-butyl alcohol^a

| Fluorene ^b | KOC(CH ₃) ₃ ^b | MTB ^{b,c} | k ₁ ^d | k ₁ ^{d,e} |
|-----------------------|---|--------------------|-----------------------------|-------------------------------|
| 0.0483 | 0.197 | 0.00 | 0.0024 | 0.0024 |
| 0.0241 | 0.0246 | 0.015 | 0.147 | 0.147 |
| 0.0241 | 0.0246 | 0.03 | 0.376 | 0.34 |
| 0.0237 | 0.0245 | 0.148 | 0.67 | 0.63 |
| 0.0232 | 0.024 | 0.289 | 0.85 | 0.742 |
| 0.0219 | 0.0227 | 0.683 | 1.36 | 1.03 |
| 0.0215 | 0.0223 | 0.805 | 1.38 | 1.05 |
| 0.0201 | 0.0208 | 1.25 | 1.64 | 1.19 |

^a25 ml of a vigorously shaken solution, thermostated at 29.5 and at 749 mm of oxygen.

^bMoles/liter.

^cm-Trifluoromethylnitrobenzene.

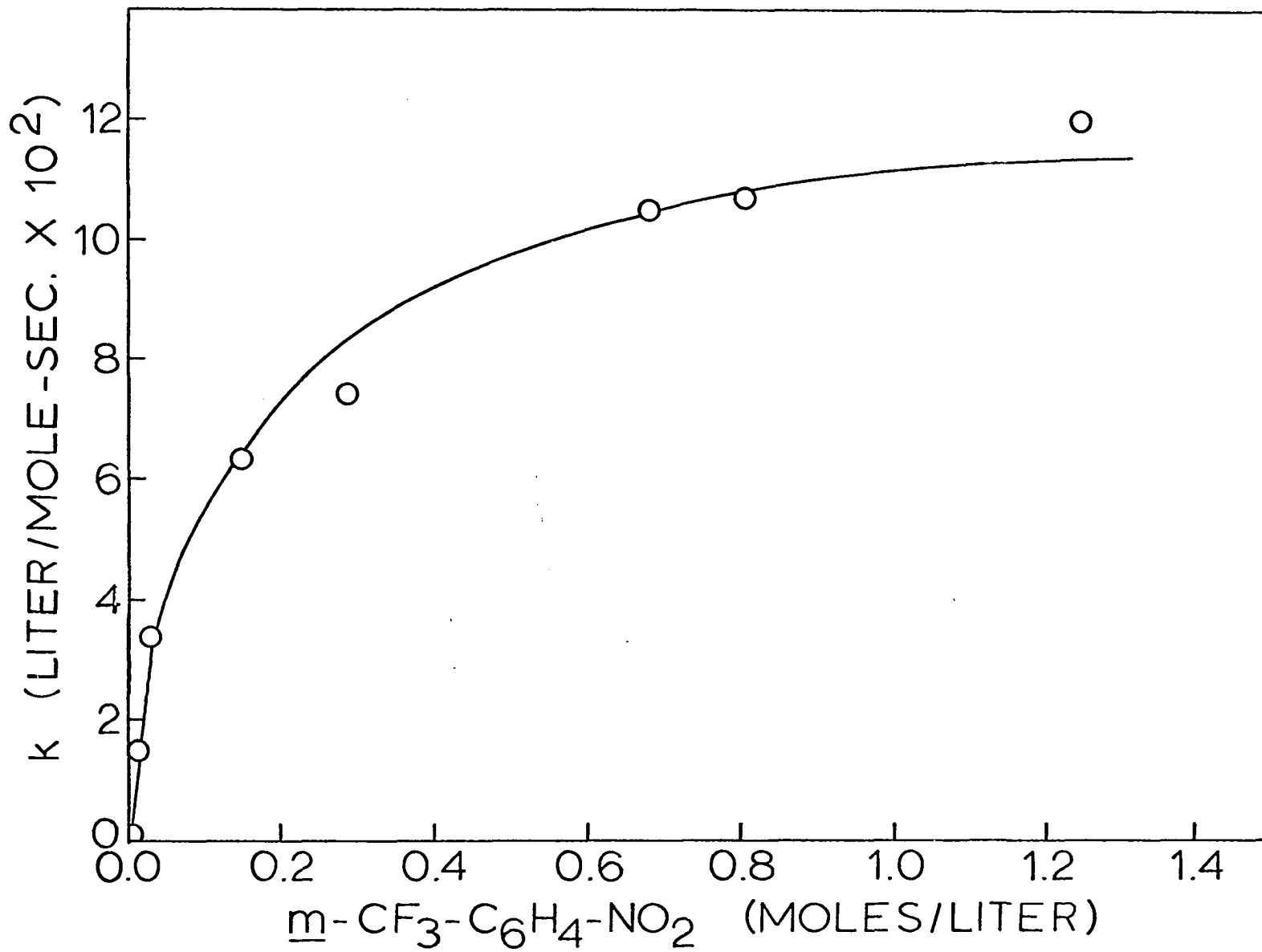
^dLiter/mole-seconds.

^eCorrected for oxidation of catalyst.

concentration of catalyst, and this maximum rate ($k_1 = 1.1 \pm .1$ liter/mole-seconds) is believed to be the rate of ionization of fluorene in t-butyl alcohol.

The lack of an isotope effect in the uncatalyzed oxidation of dideuteriofluorene in t-butyl alcohol is consistent with this data, since the rate constant for ionization (as

Figure 21. Oxidation of fluorene in t-butyl alcohol containing potassium t-butoxide at 29.5° as a function of meta-trifluoromethyl-nitrobenzene concentration; k = rate constant



measured above) is 440 times larger than that for the uncatalyzed oxidation.

Supporting evidence for the validity of measuring the rate constant for ionization in this way was obtained from a study of the rate of exchange of fluorene- α -d₂ in t-butyl alcohol. The exchange was performed in a flow system (described in the Experimental section) and the starting and exchanged fluorene was analyzed for deuterium by mass spectroscopy. Calculation of the rate constant for exchange by the same technique as described for triphenylmethane- α -d or diphenylmethane- α -d₂ gave a rate constant of $k_{\text{exchange}} = 0.12 \pm .01$ liter/mole-seconds for dideuteriofluorene in t-butyl alcohol. Since the ionization of undeuterated fluorene is assigned a rate constant of $k_i = 1.1 \pm .1$ liter/mole-seconds, an isotope effect, $k_H/k_D = 11.0$ can be calculated. This is certainly the magnitude which would be expected, although triphenylmethane and diphenylmethane had isotope effects slightly smaller. The magnitude of error in any of the numbers is basically unknown, but for most oxidations good precision is obtained. Nitrobenzene or MTB in t-butyl alcohol containing potassium t-butoxide absorbs oxygen at a slow rate, and a blank oxidation was run and the rate corrected for each concentration used. There is however, slightly greater imprecision in the catalyzed oxidation rate constants. In most cases, but not always, a good semi-log graph was

obtained for the catalyzed oxidation of fluorene. Figure 22 shows such a graph for a typical m-trifluoromethylnitrobenzene catalyzed fluorene oxidation.

Fluorene- α - d_2 was also exchanged in 80/20 DMSO. A rate constant for exchange of 2.18 liter/mole-seconds was calculated. The oxidation of fluorene in 80/20 DMSO is extremely fast, and difficult to measure volumetrically. A crude calculation gave a rate constant of ca. 1 liter/mole-seconds. This value is definitely a minimum, and could be much higher. It is possible that fluorene is ionization rate controlled in 80/20 DMSO, but an accurate measurement can not be made.

A kinetic investigation of the oxidation of acetophenone in t-butyl alcohol was made. The rate constants for the catalyzed oxidation of acetophenone in t-butyl alcohol were calculated by the same method as used for fluorene. Table 43 gives the rate constants for acetophenone oxidations in t-butyl alcohol containing potassium t-butoxide when nitrobenzene was used as a catalyst. The rate constants obtained are plotted against nitrobenzene concentration in Figure 23. A good straight line is obtained, indicating that the oxidation is first order in nitrobenzene, and that the rate of oxidation is determined by the rate of electron transfer in t-butyl alcohol. Data from the m-trifluoromethylnitrobenzene catalyzed oxidation of acetophenone in t-butyl alcohol is given in Table 44. The rate constants are graphed against

Figure 22. Oxidation of fluorene (0.0237 M) in t-butyl alcohol containing potassium t-butoxide (0.0245 M) at 29.5° and in the presence of meta-trifluoromethylnitrobenzene (0.148 M); the ordinate axis is constructed logarithmically; RH_0 = initial concentration of fluorene

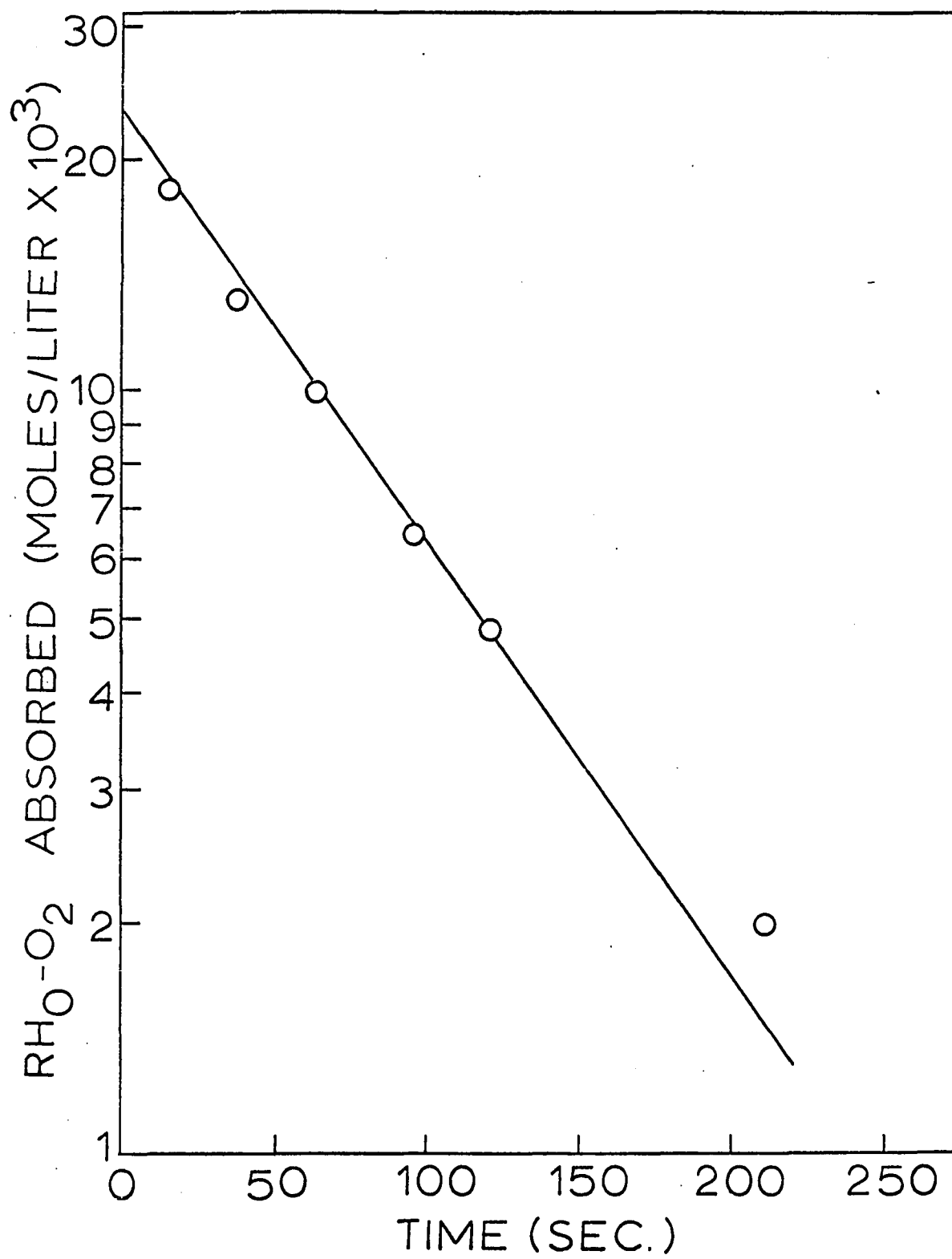


Table 43. Nitrobenzene catalyzed oxidation of acetophenone in t-butyl alcohol^a

| Acetophenone ^b | KOC(CH ₃) ₃ ^b | Nitrobenzene ^b | k ₁ ^c | k _i ^{c,d} |
|---------------------------|---|---------------------------|-----------------------------|-------------------------------|
| 0.102 | 0.197 | 0.00 | 0.000238 | 0.000238 |
| 0.0972 | 0.189 | 0.376 | 0.00321 | 0.00218 |
| 0.0935 | 0.182 | 0.725 | 0.0057 | 0.00377 |
| 0.0913 | 0.176 | 1.05 | 0.0104 | 0.0052 |

^a25 ml of a vigorously shaken solution, thermostated at 29.5° at 749 mm of oxygen.

^bMoles/liter.

^cLiter/mole-seconds.

^dCorrected for small oxidation of catalyst.

MTB concentration in Figure 24. Although the curve begins to flatten, it does not apparently level off at or below 1.25 M m-trifluoromethylnitrobenzene concentration. The logical explanation is that catalysis by MTB is not fast compared to ionization for acetophenone, as it was in the case of fluorene. This is reasonable since the anion derived from acetophenone is a highly stabilized enolate ion, and should donate an electron less readily than a hydrocarbon anion such as fluorene. Confirming this explanation, Dessy et al. (92) report that acetophenone ionizes 100 times more rapidly than fluorene in DMF.

Figure 23. Oxidation of acetophenone in t-butyl alcohol containing potassium t-butoxide at 29.5 \bar{a} s as a function of nitrobenzene concentration; k = rate constant

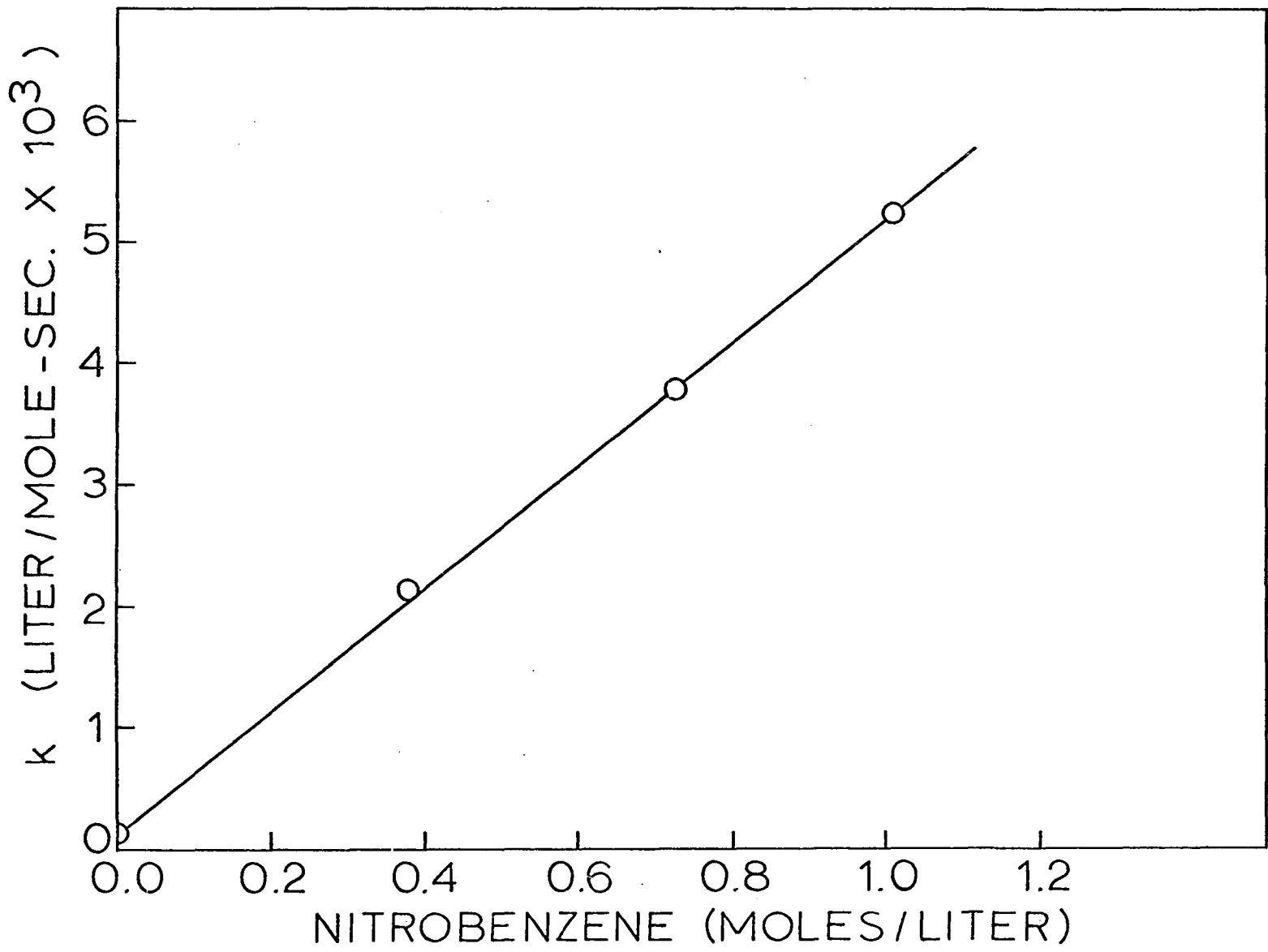


Table 44. m-Trifluoromethylnitrobenzene catalyzed oxidation of acetophenone in t-butyl alcohol^a

| Acetophenone ^b | KOC(CH ₃) ₃ ^b | MTB ^{b,c} | k _i ^d | k _i ^{d,e} |
|---------------------------|---|--------------------|-----------------------------|-------------------------------|
| 0.102 | 0.197 | 0.00 | 0.00024 | 0.00024 |
| 0.102 | 0.197 | 0.0301 | 0.0232 | 0.0227 |
| 0.10 | 0.192 | 0.10 | 0.0622 | 0.0606 |
| 0.098 | 0.189 | 0.202 | 0.102 | 0.099 |
| 0.0972 | 0.189 | 0.289 | 0.119 | 0.113 |
| 0.096 | 0.183 | 0.425 | 0.159 | 0.15 |
| 0.0935 | 0.182 | 0.557 | 0.180 | 0.171 |
| 0.0913 | 0.176 | 0.805 | 0.244 | 0.221 |
| 0.0853 | 0.164 | 1.25 | 0.282 | 0.255 |
| 0.043 | 0.164 | 1.25 | 0.376 | 0.318 |

^a25 ml of a vigorously shaken solution, thermostated at 29.5°, at 749 mm of oxygen.

^bMoles/liter.

^cm-Trifluoromethylnitrobenzene.

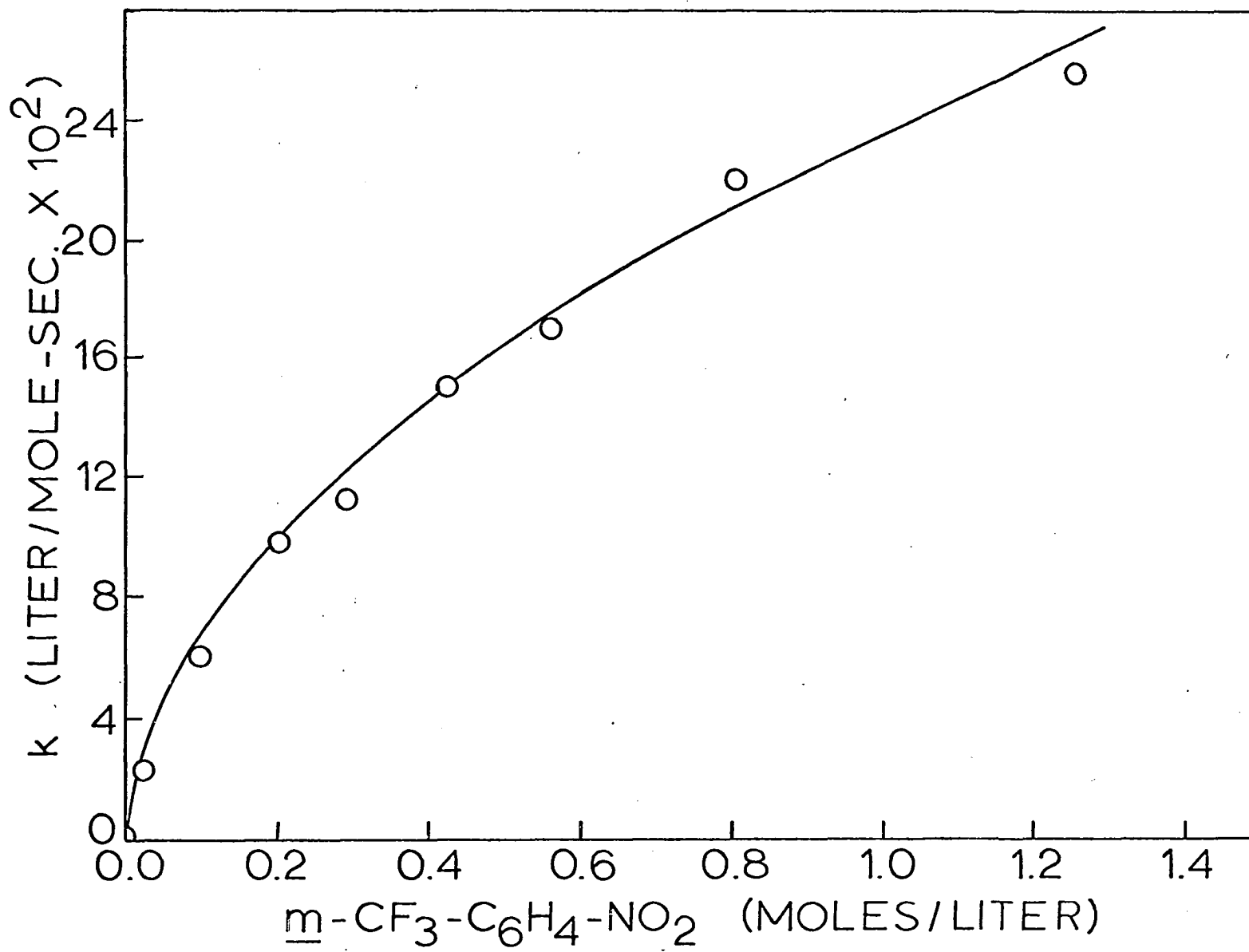
^dLiter/mole-seconds.

^eCorrected for small catalyst oxidation.

The largest rate constant found in the MTB catalyzed oxidation of fluorene is about one-third of the rate constant for ionization of fluorene.

Detailed kinetic studies were not attempted for any

Figure 24. Oxidation of acetophenone in *t*-butyl alcohol containing potassium *t*-butoxide at 29.5° as a function of meta-trifluoromethylnitrobenzene concentration; k = rate constant



other compounds. All of the ketones investigated could be catalyzed, which is reasonable in view of the stability of the enolate anions. Apparently also the rate of oxidation of 9-phenylfluorene and 9-methylfluorene in *t*-butyl alcohol and δ -picoline in 80/20 DMSO are electron transfer rate controlled.

D. Nitrobenzene Radical Anion

The preparation of nitrobenzene radical anion is well known (143) and although it has been characterized only by its e.s.r. spectrum, the well resolved spectrum is an excellent proof of structure. Since nitrobenzene radical anion is a proposed intermediate in nitrobenzene catalyzed oxidations, and has been proven to result from the reaction of nitrobenzene catalyzed oxidations, and has been proved to result from the reaction of nitrobenzene and many carbanions (49), among them the fluorenyl anion, it is of interest to understand something of its reaction with oxygen.

Nitrobenzene radical anion (potassium salt) was readily prepared from nitrobenzene and potassium in tetrahydrofuran under nitrogen. The reaction apparently takes place on the surface of the metal, and the ionic product "flakes" off the metal. This red-brown solid is, however, very finely divided and a slurry of it in tetrahydrofuran can be easily pipetted.

A sample of the slurry of the solid nitrobenzene radical anion in tetrahydrofuran dissolved in DMSO to yield the char-

acteristic purple solution. The e.s.r. spectra of this solution had 54 lines, and was very similar to the reported spectra in 80/20 DMSO (49). The concentration of nitrobenzene radical anion was estimated to be qualitatively of the magnitude required if complete conversion of nitrobenzene had occurred.

The slurry of nitrobenzene radical anion reacted extremely rapidly with oxygen, a minimum rate of 7.5×10^{-2} moles of oxygen/liter-second. The actual rate may be much larger, since this rate is faster than can be accurately measured by the volumetric technique employed. The rate is certainly rapid enough that the reaction of nitrobenzene radical anion with oxygen will prevent any change in kinetics or stoichiometry of most oxidations when nitrobenzene is used as catalyst.

The product from the oxidation was a clear solution with a pale violet color. A yellow solid was present. Analysis by the standard method (108) indicated the presence of a large amount of potassium superoxide. Gas liquid chromatography of the oxidation mixture showed only nitrobenzene and solvent. Table 45 gives the quantitative data for the nitrobenzene radical oxidation and product analysis. These results confirm that the stoichiometry of the reaction of nitrobenzene radical anion with oxygen is 1:1 and the products are superoxide and nitrobenzene.

Table 45. Oxidation of nitrobenzene radical anion

| Process | Substance measured | Moles obtained |
|---------------------|--------------------|----------------------|
| Preparation | Nitrobenzene | 0.00326 ^a |
| Oxidation | Oxygen absorption | 0.00318 |
| Superoxide analysis | Oxygen evolved | 0.00578 |
| | (as superoxide) | 0.00289 ^b |
| G.l.c. | Nitrobenzene | 0.00259 |

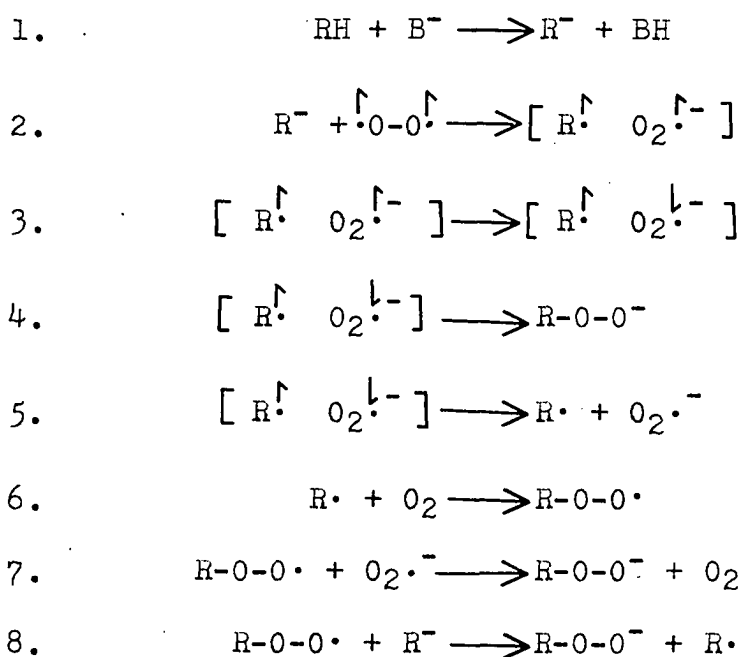
^aAssuming the preparation gave 100% reaction relative to nitrobenzene this would be the concentration of nitrobenzene radical anion prepared.

^b1 Mole of oxygen is evolved for each 2 moles of superoxide present in the method of analysis used.

V. SUMMARY

The reaction of a wide variety of carbanions with oxygen was studied. The rate of oxygen absorption, stoichiometry, and products of this reaction were determined. The effect of solvent on the rate of oxygen absorption was measured for representative types of molecules.

Evidence was presented which makes the following mechanism for the base catalyzed oxidation of hydrocarbons attractive.



The existence of steps 3 and 4 was not demonstrated, but can not be discounted. At least some evidence was presented in favor of all the other steps postulated.

The isolation of alcohols, rather than hydroperoxides from the oxidation of tertiary carbanions in dimethyl sulfox-

ide containing solution was shown to be due to the reduction of the hydroperoxide by DMSO.

Kinetic evidence was presented to show that the slowest step, and hence the rate controlling step in the oxidation of triphenylmethane, diphenyl- α -naphthylmethane, and diphenylmethane in dimethylsulfoxide (80%)-t-butyl alcohol (20%) was the initial ionization. Deuterium isotope effects of 8.1 and 7.2 were found in the oxidation of diphenylmethane and triphenylmethane, respectively. The rates of exchange of deuterated diphenylmethane and triphenylmethane were found to be equal to the respective rates of oxidation in 80/20 DMSO.

The base-catalyzed oxidations of fluorene and acetophenone in t-butyl alcohol are readily catalyzed by nitrobenzene and m-trifluoromethylnitrobenzene. The rate of ionization of fluorene in t-butyl alcohol was obtained by measuring the rate of oxidation in the presence of an excess of electron transfer catalyst, m-trifluoromethylnitrobenzene, which insured that the rate of electron transfer was more rapid than the rate of ionization. Measurement of the rate of exchange of deuterated fluorene supported the value of the rate constant for ionization obtained by the excess electron transfer catalyst method.

The rate of electron transfer of acetophenone in t-butyl alcohol was slower than the rate of ionization for all concentrations of electron transfer catalyst used.

The preparation and reaction with oxygen of the potassium salt of nitrobenzene radical anion was accomplished. Potassium superoxide and nitrobenzene were the products from the very rapid reaction of nitrobenzene radical anion with oxygen.

The results obtained demonstrate the utility of the reaction of carbanions with oxygen for preparing oxygenated or unsaturated compounds, or for measuring rates of ionization or rates of electron transfer. The measurement of the rate of oxygen absorption is an excellent and experimentally uncomplicated method of obtaining ionization rate constants.

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