# THE AUTOXIDATION OF SOME LIQUID BENZYL ETHERS

By

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# INTRODUCTION

As defined by Waters (95) autoxidations are those "comparatively slow oxidations which can be effected by free oxygen (e.g., by air) at moderate temperatures." It is not surprising, therefore, considering the broad scope of this definition, to find that autoxidations are among the most widespread of all reactions. Encompassing such diverse phenomena as the slow oxidation of sulfite to sulfate, the deterioration of natural and synthetic polymers, and the hardening of drying oils, the field has undergone extensive investigation for over a century. Early work on the isolation and identification of unstable compounds has been supplemented and almost supplanted by newer analytical tools, like polarography and infrared spectrophotometry. The previously perplexing problems of inhibition and activation by traces of impurities now are recognized as natural consequences of the free-radical initiation of the reaction.

Notwithstanding the great progress which has been made, it is still difficult to predict with any degree of accuracy and even more difficult to control the course of an autoxidation. The deficiency, of course, lies in an inadequate understanding of the reaction mechanisms. One of the most successful methods used in elucidating oxidation mechanisms has been the application of kinetics, especially that branch involving the steady-state approximations.

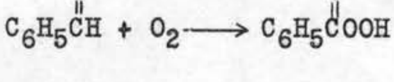
Autoxidation research over the past two decades has been directed primarily toward three technically important types of materials: liquid hydrocarbons, rubber, and drying oils. Alcohols, aldehydes, ketones, esters, ethers, and amines--all of which autoxidize--have by comparison been largely neglected. It is indeed surprising to find ethers thus slighted, for it is possible that some of the early interest in this field arose from the spectacular results obtained from distillations of peroxide-containing ethers. This present study was undertaken to alleviate partially the neglect suffered by ether autoxidation.

# HISTORICAL

## Structure of Ether Peroxides

Much of the history of ether oxidation has been centered around diethyl ether, because of its widespread use both as a solvent and as an anesthetic. As early as 1851, Schönbein (199) reported the formation of an oxidizing substance in ether which had been exposed to air and light and noted its similarity to the product obtained from treating ether with ozone. During the next seventy-five years, the many explosions which occurred during distillations of ether were attributed to these peroxides, whose compositions had become a matter of some interest. Berthelot (23), who also considered ether peroxide to be identical to the one he obtained from the treatment of ether with ozone, assigned it the formula $(C_2H_5OC_2H_5)_2O$. Nef (158), however, believed that the peroxide was acetyl peroxide.

In 1922, Clover (44) reported the first results of his researches in ether autoxidation. From ether which had been allowed to stand exposed to light and air for five to six months, he obtained an oil which he believed was the $\alpha$-hydroperoxide, $CH_3CH(OOH)OCH_2CH_3$, formed in a manner analogous to that proposed by Baeyer and Villiger (8) for benzaldehyde oxidation:



$$C_6H_5\overset{\overset{O}{\|}}{C}H + O_2 \longrightarrow C_6H_5\overset{\overset{O}{\|}}{C}OOH$$

Clover's conclusion was based on the following findings: the active-oxygen content was approximately that required by the hydroperoxide formula; the peroxide was formed directly by the action of oxygen on ether; the peroxide was volatile; the thermal decomposition products included acetaldehyde, ethyl alcohol, methane, and carbon dioxide; the ether peroxide was acidic; and the products of the acid hydrolysis were hydrogen peroxide, ethyl alcohol, and acetaldehyde. Since no peracetic acid was found, the possibility of the formation of acetyl peroxide was discounted. Although hydrogen peroxide was found in the crude ether to the extent of several per cent of the total peroxide concentration, Clover believed it to be a product of the hydroperoxide hydrolysis.

Other ethers whose peroxides were isolated by Clover included n-propyl, isopropyl, n-butyl, isoamyl, and diethoxymethane (45). Benzyl, benzyl methyl, and benzyl ethyl ether all formed peroxides; but, owing to the difficulties involved in removing the excess ether, these could not be isolated. While the peroxides in most cases appeared to be simple $\alpha$-hydroperoxides, the one obtained from isopropyl ether was shown to be identical with the product in the reaction of acetone with hydrogen peroxide, presumably $(CH_3)_2C(OH)OOH$. In a more qualitative way, he also found that allyl ethers peroxidize more rapidly than saturated ethers to give peroxides which decompose to give resins, and that anisole and phenetole do not peroxidize.

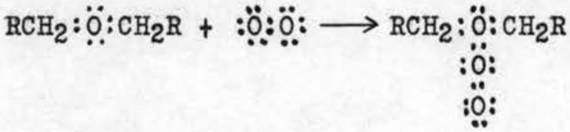
Wieland and Wingler (236) proposed the theory that the ether was first dehydrogenated to give vinyl ethyl ether:

$$CH_3CH_2OCH_2CH_3 + O_2 \longrightarrow CH_2{=}CHOCH_2CH_3 + H_2O_2$$

Hydrolysis of the vinyl ethyl ether would then result in acetaldehyde and ethyl alcohol. To explain the formation of an organic peroxide, they assumed a reaction between acetaldehyde and hydrogen peroxide to give

1-hydroxyethyl hydroperoxide, $CH_3CH(OH)OOH$, followed by its intermolecular loss of hydrogen peroxide to give 1,1'-dihydroxydiethyl peroxide, $CH_3CH(OH)OOCH(OH)CH_3$. The principal support for this hypothesis came from the fact that vinyl ethyl ether was found in a sample of peroxidized ether. It is now known, however, that commercial ether frequently contains this compound (181). King (126) showed that the peroxide first formed resembled Clover's product but that after reacting further with acetaldehyde, it resembled Wieland and Wingler's.

In disputing Clover's claim, Milas (148) went so far as to say that true autoxidation proceeded only by the addition of molecular oxygen to an ether to form a "dative peroxide":

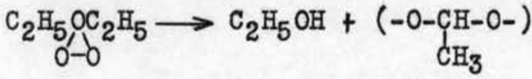


$$\mathrm{RCH_2{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}{:}CH_2R} + \mathrm{{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}{:}} \longrightarrow \begin{array}{c}\mathrm{RCH_2{:}\overset{\cdot\cdot}{O}{:}CH_2R}\\ \mathrm{{:}\overset{\cdot\cdot}{O}{:}}\\ \mathrm{{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}{:}}\end{array}$$

In support of his theory, Milas claimed that peroxides are formed by such ethers as diphenyl ether (147). In view of the fact that the diphenyl ether he used was a commercial ether not otherwise purified, the claim seems unjustified.

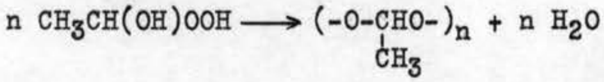
The danger of explosions resulting from ether distillations was then and still is a definite hazard to be considered carefully by anyone working with ether solvents (57, 62, 104, 107, 127, 157, 168, 192, 211, 213, 237, 242). The extreme violence of the detonation is not generally known, however; for example, one worker experienced a serious explosion while attempting to run carbon and hydrogen determinations on a four-milligram sample of residue (232). Moreover, the peroxides need not be isolated to be hazardous; especially in the case of diisopropyl ether, explosions have occurred when a bottle or can of the peroxidized ether was moved (105, 154).

Although both Clover (44) and Wieland and Wingler (236) had shown that the compounds they had isolated detonated when heated, Rieche (184) did not believe that such simple peroxides could be stable enough to account for a dangerous accumulation in residues. He proposed that the peroxide first formed decomposes to give polyethylidene peroxide. Although at first he showed the reaction as proceeding from a dative peroxide,



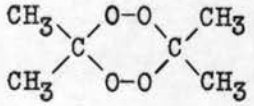
$$\underset{O-O}{C_2H_5OC_2H_5} \longrightarrow C_2H_5OH + (-O-\underset{CH_3}{\underset{|}{C}}H-O-)_n$$

later (185, 186), after he had accepted the hydroperoxide structure, he indicated a two-step reaction in which the hydroperoxide is first hydrolyzed to 1-hydroxyethyl hydroperoxide, which then polymerizes:

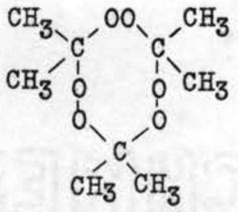


$$n\ CH_3CH(OH)OOH \longrightarrow (-O-\underset{CH_3}{\underset{|}{C}}HO-)_n + n\ H_2O$$

He believed polyethylidene peroxide was the compound primarily responsible for the explosions, although he had found earlier (187) that the α-hydroperoxide which he prepared synthetically also exploded when heated rapidly. When warmed to 70° at 20 mm., it changed into a viscous mass having the properties of polyethylidene peroxide. The polymeric substances obtained by treating 1-hydroxyethyl hydroperoxide with $P_2O_5$, by warming butylene ozonide, and by autoxidizing dry diethyl ether were identical (188). In each case, the oily product first obtained underwent further reaction in air to produce a polymer even more highly explosive. Sulfur may accelerate the polymerization (213). The theory of the polymeric nature of the peroxide was especially useful in explaining why isopropyl ether accumulated dangerous amounts of peroxides after it had been established by Rieche and Koch (186) that acetone peroxide was one of the principal products. They were successful in isolating both the dimer and trimer, which are cyclic:

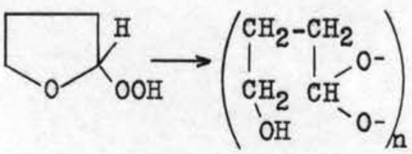


dimer



trimer

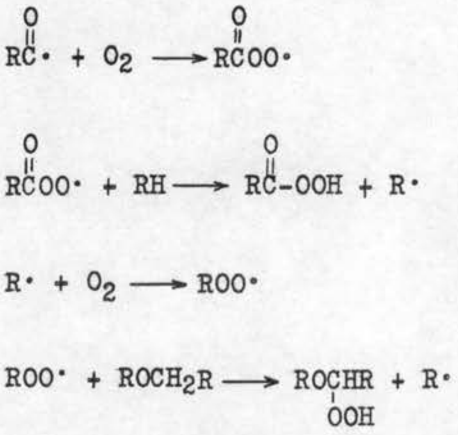
A marked similarity between the ultraviolet spectra for these two compounds and butylene ozonide was noted. These structures were further supported by molecular-weight determinations. The trimer has also been isolated from autoxidized isopropyl ether and identified by other workers (2, 122), and resinous products have been reported by one (178). Since very little isopropyl alcohol is found in peroxidized isopropyl ether, Rieche and Koch (186) proposed that the polymer developed from a "bis-hydroperoxydiisopropyl ether." Quite significantly, Ivanov and co-workers (116) have reported that this compound is the main product in isopropyl ether autoxidation. More recently, the formation of a polymeric peroxide has been used to explain explosions of aged tetrahydrofuran upon distillation. Robertson (193) had prepared tetrahydrofuran α-hydroperoxide, which he found to decompose without detonation even when heated rapidly to 100°. Rein (183), however, experienced a serious explosion while attempting to distill tetrahydrofuran. Criegee (50), who apparently had prepared the hydroperoxide earlier and had worked with it extensively, reported that he had found the compound to be harmless when treated with due care. The explosions, he believed, were caused by the polymeric peroxide which was formed from the hydroperoxide:



Free-Radical Mechanisms

Although early workers had frequently compared ether oxidation to aldehyde (more especially benzaldehyde) oxidation, later workers were reluctant to carry the analogy further after Backström (7), in 1927, employing the theories developed by Christiansen (42) in his studies of photochemical reactions, demonstrated that benzaldehyde oxidation is a chain reaction. Milas (147) suggested that such studies in ether oxidation might be fruitful, but he did not undertake them. Although Backström had in mind an energy-chain oxidation, Haber and Willstatter (100) four years later showed that the chain carriers are radicals.

It was not until 1942 that a chain mechanism was formulated for ether oxidation. This mechanism was proposed by Rieche and Koch (186) and, as usual, was directed toward ethyl ether:



$$R\overset{\overset{O}{\|}}{C}\cdot + O_2 \longrightarrow R\overset{\overset{O}{\|}}{C}OO\cdot$$

$$R\overset{\overset{O}{\|}}{C}OO\cdot + RH \longrightarrow R\overset{\overset{O}{\|}}{C}\text{-}OOH + R\cdot$$

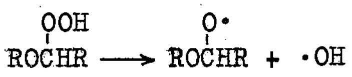
$$R\cdot + O_2 \longrightarrow ROO\cdot$$

$$ROO\cdot + ROCH_2R \longrightarrow RO\underset{\underset{OOH}{|}}{C}HR + R\cdot$$

In this scheme, acetaldehyde is given the role of an accelerator. It is assumed that "RH" was intended to represent an ether molecule and that "R·" is the 1-alkoxyalkyl radical.

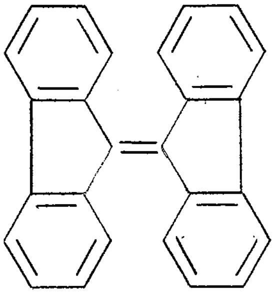
Reimers (179, 180, 182) also believed the reaction to be a free-radical chain reaction in which the initially formed radical reacts first with oxygen and then with an ether molecule to form the peroxide, but he did not attempt to show a mechanism, primarily because he did not believe the structure of the peroxide was as yet known. His opinion was based on polarographic differences between ether peroxide and those prepared synthetically by either Wieland and Wingler (236) or Rieche and Meister (187). Not enough is known concerning the manner in which these comparisons were made to draw any significant conclusion. In the light of present knowledge, it seems doubtful that the α-hydroperoxide is not one of the most important types of peroxides found in ethers. For example, there is now abundant evidence to show that a free-radical attack upon an ether molecule is indeed an attack upon the α-hydrogen atom. In the case of diethyl ether, this has been observed with the following free radicals: benzoyl (15, 37, 38), lauroyl (39), n-propyl (71), methyl (124), isopropyl (71), phenyl (74, 97, 101, 206, 225), and p-chlorophenyl (24). The β-hydrogen atoms may be attacked to a much lesser extent (71, 74). In the case of other ethers, the following reactions have also indicated an α-hydrogen attack: n-butyl ether with methyl (73) and benzoyl (15); diethyl cellosolve with benzoyl (38); and dioxane with benzoyl (38). It will be shown later that the radical thus produced will react with oxygen to produce a peroxyl radical which then reacts with hydrogen donors to form the hydroperoxide.

In view of the great advances which have been made toward furthering the understanding of autoxidations of other materials, notably hydrocarbons, it is worthwhile to apply the same sort of reasoning to ether autoxidation in search of a plausible free-radical mechanism. For example, initiation in hydrocarbon autoxidation is frequently given as proceeding from the homolytic decomposition of a hydroperoxide (21, 195, 223). A similar chain-starting reaction for ethers (142) is



$$\mathrm{RO\overset{OOH}{C}HR} \longrightarrow \mathrm{RO\overset{O\cdot}{C}HR} + \cdot\mathrm{OH}$$

In agreement with this is Robertson, who found that tetrahydrofuran $\alpha$-hydroperoxide is an active catalyst for the polymerization of styrene and methyl methacrylate (193). Various patents have also suggested the use of peroxides from tetrahydrofuran (214), 1,4-dioxane, 1,3-dioxolane, and derivatives of the last two (215, 216) as polymerization catalysts. Moreover, it has been shown that dibiphenyleneëthylene (see formula)



in the presence of autoxidizing ethers is itself oxidized to fluorenone, probably by hydroxyl radical addition to the ethylenic bond (239, 240). The value of the dissociation energy for the -O-O- bond in hydrogen peroxide has been reported by Pauling (170) as 34.9 kcal. and by Walsh (221) as about 56 kcal.; in other peroxides it is more or less, depending upon the exact structure. In view of Eastwood and Hinshelwood's observation (61) that the -O-O- bond in ether peroxides is very weak, the lower value obtained by Pauling may more nearly apply; and indeed reasoning like that of Walsh (222) suggests that an electron-withdrawing group like alkoxyl must weaken the electron-deficient peroxide link. From this, and from the additional observation that the ether hydroperoxides are less stable than many of those obtained from hydrocarbons (as evidenced by the much greater difficulty in isolating the former), it may be concluded that -O-O- bond fission does occur.

The radicals produced may then either recombine or react with solvent molecules. According to the Franck-Rabinowitsch principle (81), the recombination of radicals in solution has a probability greater than that expected from mass action alone. It is supposed that the solvent acts as a "cage" in which the two radicals, after losing their initially high kinetic energy to solvent molecules, are held in close proximity. The recombining radicals may regenerate the initial compound, in which case the reaction is kinetically indistinguishable from a slower forward reaction; or they may undergo dismutation to form a new compound if the activation energy for that reaction is low (141). It must be emphasized here that the Franck-Rabinowitsch principle was proposed primarily to explain why there should be a combination in dilute solutions. It does not satisfactorily account for the formation of large amounts of these products.

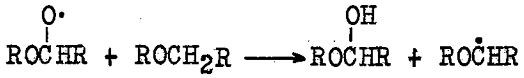
It has been observed that solvents which easily yield free radicals accelerate the decomposition of such substances as tetralin hydroperoxide (195, 196), cumene hydroperoxide (204), and even lauroyl and benzoyl peroxides (13, 15, 37, 38, 39, 167). For hydroperoxides, the reaction is believed to be the following (195, 196):

$$R_2CHOOH + \cdot OH \longrightarrow R_2\dot{C}OOH + HOH$$

$$R_2\dot{C}OOH \longrightarrow R_2C{=}O + \cdot OH$$

Likewise, the formation of an ester from an ether hydroperoxide could be explained.

The greatest probability is that radicals of such high intrinsic energy will react almost immediately with the solvent (228). As indicated previously, the most probable reaction of a radical with an ether molecule is α-hydrogen abstraction:



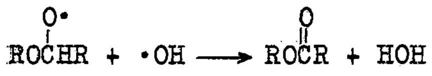
$$RO\overset{O\cdot}{C}HR + ROCH_2R \longrightarrow RO\overset{OH}{C}HR + RO\dot{C}HR$$

$$\cdot OH + ROCH_2R \longrightarrow HOH + RO\dot{C}HR$$

In the first reaction there are formed a hemiacetal and a 1-alkoxyalkyl radical. In the second, water and the same radical are formed. These reactions give a reasonable explanation for the formation of aldehydes, alcohols, and water, all known products of the oxidation, and show why water is among the first products formed in the oxidation of a very dry ether (147).

The possibility of an interaction of radicals, while less probable than the radical-solvent interaction, should not be completely disregarded. It is known, for example, that primary and secondary hydroperoxides of many different types of hydrocarbons form aldehydes and ketones upon decomposition (18, 19, 110, 111, 151, 210). The formation of these products rather than the regeneration of the hydroperoxide is reasonable from a consideration of the dipole moments of the radicals (231).

An analogous interaction of radicals in an ether hydroperoxide decomposition should give esters:



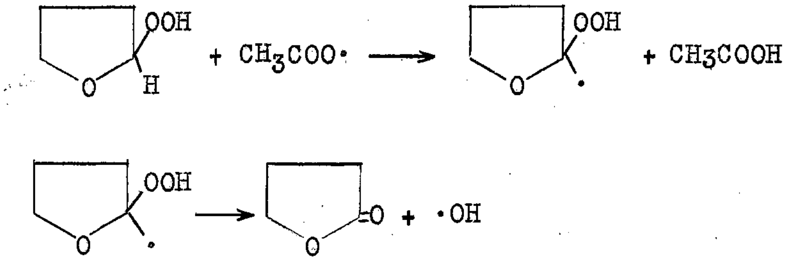
$$RO\overset{O\cdot}{C}HR + \cdot OH \longrightarrow RO\overset{O}{\overset{\|}{C}}R + HOH$$

Robertson (180) showed that this was true in the case of tetrahydrofuran, the hydroperoxide of which decomposes to give γ-butyrolactone. Similarly, Clover (45) found that the hydroperoxide of ethyl benzyl ether decomposes to give almost exclusively ethyl benzoate. In addition he found that *n*-propyl and *n*-butyl ether after prolonged exposure to light and air contain respectively *n*-propyl propionate and *n*-butyl butyrate. Bremner and Jones (32) obtained γ-butyrolactone and δ-valerolactone from tetrahydrofuran and tetrahydropyran respectively by air oxidation at 140° and under pressure. Benzyl benzoate has been obtained in the extended air oxidation of benzyl ether in the temperature range 150-250° (64, 65).

From such reasoning, it would be expected that the hydroperoxides of allyl ethers, $ROCH(OOH)CH{=}CH_2$, should undergo homolytic decomposition to give alkyl acrylates. Whether by this method or another, alkyl acrylates and polyacrylates do occur during oxidation of allyl ethers (98).

As further evidence for this behavior, Fischer (77) found that the action of dry ozonized oxygen on ethyl, butyl, isoamyl, ethyl isoamyl, and benzyl ether gives ethyl acetate, butyl butyrate, isoamyl isovalerate, ethyl isovalerate, and benzyl benzoate, respectively. Since it had been shown in the autoxidation of other substances that ozone acts merely as a catalyst (33, 75), it is not improper to include these reactions here.

Another possible source of these compounds is the reaction of radicals with the molecular hydroperoxide. Criegee (51) has shown that lead tetraacetate oxidizes alkyl hydroperoxides to carbonyl compounds in high yields. In the case of tetrahydrofuran hydroperoxide, γ-butyrolactone is formed (50) in a reaction which may follow the course



The reaction of the hydroperoxide with a radical gives a mechanism much simpler than the one proposed recently by Hawkins (102) for the formation of γ-butyrolactone. He suggested that the hydroperoxide decomposition proceeds through γ-hydroxybutyraldehyde to γ-hydroxybutyric acid, which then forms the lactone by esterification.

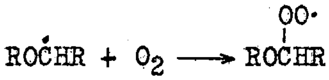
Nothing has yet been said about what happens to the ether radical formed from an α-hydrogen abstraction. The radical produced may dissociate to form an aldehyde and a hydrocarbon radical:

$$RO\dot{C}HR \longrightarrow RCHO + R\cdot$$

This type of behavior is postulated to account for the production of acetaldehyde in the reaction of phenyl radicals (74, 101), methyl radicals (72), and benzoyl radicals (15) with ethyl ether; ethylene in the reaction of methyl radicals with ether (72, 124); and butane, butenes, and butyraldehyde in the reaction of methyl radicals (14) and benzoyl radicals with n-butyl ether (15). The thermal dissociation of benzyl ether into benzaldehyde and toluene probably occurs by a similar route (64, 65, 118, 243).

Reactions which appear to be examples of other C-O bond fissions of this type--notably the reaction of the methyl radical with ethyl ether to give methyl ethyl ether (124) and the reaction of n-butyryl and isobutyryl radicals with ethyl ether to give ethyl n-butyrate and ethyl isobutyrate respectively (123)--may actually result from an attack of a free radical upon molecular ether (124).

This tendency of the ether radical to dissociate is for the most part offset by a tendency to become resonance-stabilized. Of the two possible structures, $R-\ddot{\underset{\cdot\cdot}{O}}-\dot{C}HR$ and $R-\overset{+}{\underset{\cdot\cdot}{O}}-\overset{-}{\ddot{C}}HR$, the first contributes more to the resonance hybrid (15, 146). The radical is likely to be destroyed by reacting with excess ether as solvent; but, in so doing, it regenerates the same type of radical: *the species is continued*. In the presence of oxygen, a more significant reaction takes place:



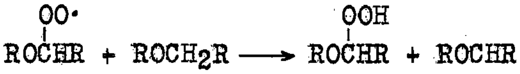
$$RO\dot{C}HR + O_2 \longrightarrow RO\overset{OO\cdot}{\overset{|}{C}}HR$$

Even in the case of a highly stabilized radical like triphenylmethyl the reaction with oxygen occurs readily. The fact that oxygen inhibits the decomposition of benzoyl peroxide in ether can be explained most satisfactorily by assuming that the ether radicals, which ordinarily accelerate the decomposition, react with oxygen:

$$R\cdot + O_2 \longrightarrow ROO\cdot \xrightarrow{RH} ROOH + R\cdot$$

The radical, $R\cdot$, was shown to be of the type $RO\dot{C}HR$ by isolation and identification of products (37, 38, 39).

The peroxyl radical formed as indicated previously may then abstract hydrogen from the solvent:



$$RO\overset{OO\cdot}{\overset{|}{C}}HR + ROCH_2R \longrightarrow RO\overset{OOH}{\overset{|}{C}}HR + RO\dot{C}HR$$

An ether radical has thus been regenerated and may react with another molecule of oxygen. This oxygen-uptake cycle can continue until it is broken by a termination reaction.

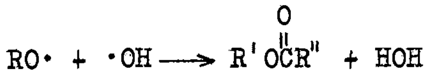
Chain termination may result from some sort of interaction of a radical with a surface or from a combination of two radicals. Letting $R'O\dot{C}HR''$ be represented simply by $R^{\circ}$, the most probably termination reactions by combination of radicals are:

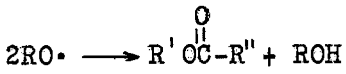
(a) $2R\cdot \longrightarrow R\text{-}R$

(b) $R\cdot + \cdot OH \longrightarrow ROH$

(c) $R\cdot + \cdot OR \longrightarrow ROR$

(d) $RO\cdot + \cdot OH \longrightarrow ROOH$

(e) 
$RO\cdot + \cdot OH \longrightarrow R'O\overset{O}{\overset{\|}{C}}R'' + HOH$

(f) 
$2RO\cdot \longrightarrow R'O\overset{O}{\overset{\|}{C}}\text{-}R'' + ROH$

(g) $2RO\cdot \longrightarrow ROOR$

(h) $ROO\cdot + R\cdot \longrightarrow ROOR$

(i) $ROO\cdot + \cdot OH \longrightarrow ROH + O_2$

(j) $ROO\cdot + \cdot OR \longrightarrow ROR + O_2$

(k) $2ROO\cdot \longrightarrow ROOR + O_2$

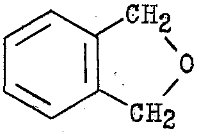
(l) $2\cdot OH \longrightarrow H_2O + \frac{1}{2}O_2$

The dimerization given in reaction (a) would proceed if the energy of the radicals is low and the concentration of oxygen is low. As pointed out by Waters (228), the direct combination of radicals can occur in the liquid phase, but substitution reactions occur so easily in most cases that radicals of high intrinsic energy interact almost immediately with the solvent. Radicals of low energy, such as triphenylmethyl, do not react with most solvents but tend to combine with other free radicals. The more important restriction, however, is that of oxygen concentration. It has been shown for hydrocarbons that the concentration of R· is so small compared to ROO· at ordinary oxygen pressures that termination reactions involving R· are negligible (16, 21, 28, 224). For similar reasons, reactions (b), (c), and (h) may be eliminated. Reactions (d) and (e) have been treated previously and shown likely to occur only at relatively high concentrations of ROOH. Because it requires the interaction of radicals from the decompositions of two molecules of hydroperoxide, reaction (f) is less likely to occur than reaction (e). Furthermore, in discussing the formation of α-cumyl peroxide from cumyl hydroperoxide, Kharasch (121) states that all the evidence thus far obtained indicates that free RO· radicals do not dimerize. Reaction (g), therefore, is also doubtful. Waters (224) believes that the reaction of ROO· with ·OH--reaction (i)--is more important than R· + ·OH, and with this most authors would heartily concur. In *aqueous media*, reaction (i) may be important because of the longer life of the hydroxyl radical (228). Certain catalyzed reaction chains in which the concentration of ·OH remains high are also believed to terminate by this reaction (195). Reaction (j) would not seem much less likely to occur, but it has not been suggested. Reaction (k) is the most frequently proposed chain termination reaction (16, 17, 28). It has been shown by Bell and others (21) that the decomposition of *tert*-butyl hydroperoxide in chlorobenzene gives almost a quantitative yield of oxygen according to the equation

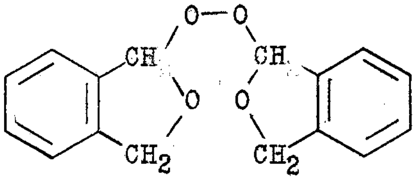
$$2ROO\cdot \longrightarrow 2RO\cdot + O_2$$

The decomposition of tetralin hydroperoxide has also been shown by Robertson and Waters (195) to produce some oxygen. Although they interpreted the reaction as reaction (i), since some tetralol was formed, the oxygen formation can also be explained on the basis of the dimerization of ROO°, in which the product ROOR is not stable but dissociates into 2RO· as given above. These reactions, which are not chain-termination reactions, but rather chain-branching steps, would be expected to be most important in the vapor phase, where ROOR has low stability. Eastwood and Hinshelwood (61) found this to be true in the vapor-phase oxidation of ethers.

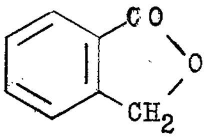
In the liquid phase, the ether peroxides are surprisingly stable. Rieche and Meister (187), in attempting to prepare the α-hydroperoxide of benzyl ether, obtained its peroxide, $C_6H_5CH(OCH_2C_6H_5)OOCH(OCH_2C_6H_5)C_6H_5$, which is a white crystalline compound having a definite melting point, 119°. Entel et al. (67) found that exposure of thin films of phthalan



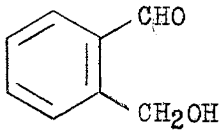
on a watchglass to light and air causes a "complete" conversion to phthalan peroxide,



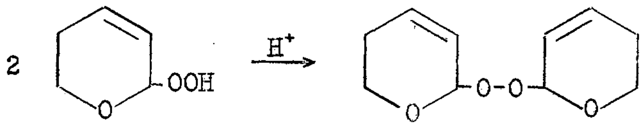
a white, crystalline compound, mp 137.5-139.5°. Since phthalide,



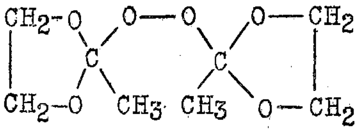
and o-hydroxymethylbenzaldehyde,



two of the products expected from a hydroperoxide decomposition, did not occur, it is possible that the large surface area altered the normal course of the reaction. Another example of peroxide formation is the decomposition of 2-(5,6-dihydro-2H-pyranyl) hydroperoxide (198) in the presence of a trace of acid:

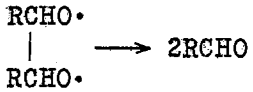


The hydroperoxide is formed by the oxidation of 5,6-dihydro-2H-pyran. Again, 2-methyl-1,3-dioxolane upon autoxidation gives not the hydroperoxide but a crystalline peroxide,



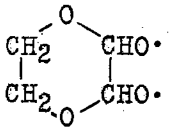
m.p. 68° (133).

Reaction (1), the dimerization of hydroxyl radicals, could occur if their concentration were unusually high or if the hydroxyl radicals had a long life, as in an aqueous medium. Their interaction would not, nevertheless, produce hydrogen peroxide, for it has been shown (231) that their dipole moments favor the formation of water and oxygen. An explanation for the occurrence of hydrogen peroxide in oxidized ethers--up to 24% of the total peroxide content has been so reported for at least one ether (10)--should be based on the observation that hydrogen peroxide is produced in the hydrolysis of an ether hydroperoxide (187). One other case of chain termination, which was not listed with the other reactions partly because of its specificity and partly because it had not been previously suggested by anyone, is that of intramolecular termination. It has been suggested (95) that the lead tetraacetate oxidation of glycols to aldehydes proceeds by way of the biradical:

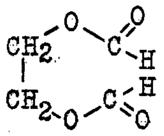


$$\begin{array}{c} RCHO\cdot \\ | \\ RCHO\cdot \end{array} \longrightarrow 2RCHO$$

which may or may not be held in a loose complex with lead. In an analogous case, a biradical such as



which conceivably could be derived from 1,4-dioxane 2,3-dihydroperoxide, could undergo -C-C- bond fission to give ethylene diformate,



A dihydroperoxide was shown to be the primary autoxidation product of isopropyl ether (see p. 7), and is, therefore, possible in the case of dioxane.

The formation of ethylene formate has been the subject of a patent by Fleming (79), who found that air oxidation of dioxane in cyclopentane gives significant yields of the ester. Wibaut and Strang (234) observed that a glycol biradical will undergo chain-branching if the solvent has no easily removable hydrogen atoms. It is possible, of course, to postulate a chain-branching reaction from which termination is excluded; and this may be the main course. The oxidations of tetrahydrofuran, 2-methyltetrahydrofuran, and 2,5-dimethyltetrahydrofuran to give 4-hydroxybutanal, 5-hydroxy-2-pentanone, and 5-hydroxy-2-hexanone could possibly follow the latter course.

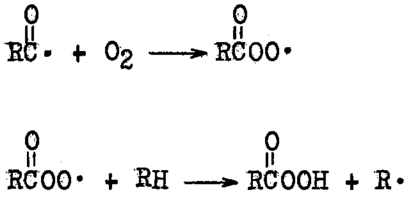
## Initiation

Initiation of the free-radical chain reaction was given as proceeding from a homolytic hydroperoxide decomposition. An explanation is now required for the formation of the hydroperoxide in ethers originally free of this initiator.

Waters (230) holds the opinion that the initiation of the autoxidation of all reasonably well-purified organic substances may be ascribed to residual traces of catalytically active impurities in the substance itself or on the walls of the reaction vessel. Hilditch (108) was able to show that methyl oleate which has been carefully purified to remove all diene compounds is resistant toward oxidation even under the influence of ultraviolet irradiation. Wibaut and Strang (234) found that very pure _n_-nonane does not oxidize at 110° even in the presence of cobalt stearate.

In the case of ethers, Hess and Frahm (106) found that 1,4-dioxane which has been purified by distillation over sodium followed by repeated freezing out until a constant melting point, 11.80°, is reached contains very little peroxide at the end of two weeks compared to a sample of the same product on which recrystallizations have been carried out only until the melting point is 11.71°. Eigenberger (66) similarly found the pure compound to resist oxidation.

The especially reactive impurity in ethers may be the aldehyde. Clover (44) was able to show that in ethyl ether containing acetaldehyde but no peroxides oxidation occurs rapidly; furthermore, ether samples which are oxidizing rapidly are stopped in this behavior by distilling out low-boiling components. Rieche (186) postulated that *acceleration* by aldehydes follows the sequence



$$R\overset{O}{\overset{\|}{C}}\cdot + O_2 \longrightarrow R\overset{O}{\overset{\|}{C}}OO\cdot$$

$$R\overset{O}{\overset{\|}{C}}OO\cdot + RH \longrightarrow R\overset{O}{\overset{\|}{C}}OOH + R\cdot$$

although *initiation* is accomplished by traces of metallic impurities. It has been shown (6) that aldehyde- and peroxide-free ethers also undergo slow autoxidation, however. Neu, who found that traces of iron compounds act as catalysts in ether autoxidation (161, 162), demonstrated that even ether which contains neither iron nor aldehydes still oxidizes (163).

The question now is one of whether or not an absolutely pure compound would undergo autoxidation. Bolland and Gee (26) believe that, in the liquid-phase uncatalyzed oxidation of pure ethyl linoleate in the temperature range 35-55°, the reaction

$$RH + O_2 \longrightarrow \text{free radicals}$$

does occur. They have suggested that the energy of activation of this reaction should not be much different from that of the homolytic hydroperoxide decomposition.

The apparent reluctance of most kineticists to accept this initiation reaction for liquid-phase oxidations is not encountered in dealing with vapor-phase oxidations, where the direct reaction of oxygen with the oxidizable substance is considered an important initiation step. McDowell and Thomas (143) proposed this type of initiation in the vapor-phase oxidation of acetaldehyde:

$$CH_3CHO + O_2 \longrightarrow CH_3CO\cdot + HOO\cdot$$

The existence of HOO· was confirmed by mass-spectrometer data. For the vapor-phase oxidation of ethers in the temperature range, 150-200°, Eastwood and Hinshelwood (61) propose a similar initiation step. It is possible that initiation in the liquid phase follows a similar course, since it has been shown that vapor-phase oxidations of ethers resemble liquid-phase oxidations (52).

In contrast to this, for example, George and Robertson (91) believe that the formation of a hydroperoxide in tetralin arises from an energy chain according to the following scheme:

$$RH \longrightarrow RH^*$$

$$RH^* + O_2 \longrightarrow P^*$$

$$P^* + RH \longrightarrow ROOH + RH^*$$

$$P^* \longrightarrow \text{inactive molecule}$$

In this scheme, a hydrocarbon molecule becomes thermally activated (indicated by the asterisk) and combines with oxygen to form P*, which may be either a vibrationally excited ROOH molecule or an "activated complex" of the hydrocarbon with oxygen. The loss of energy resulting from a collision of P* with RH permits the formation of a stable hydroperoxide and at the same time activates another hydrocarbon molecule. Bolland (27) objected to this energy chain reaction on the grounds that only slight reaction would occur in a system depending upon vibrational energy transfer. But, if the reaction occurs even to a slight extent, the formation of the hydroperoxide free-radical initiator has been satisfactorily explained. Acceleration may be caused in an energy-chain reaction by the presence of a compound capable of becoming easily activated. Lindgren (136) suggests that the rapid oxidation of ether in glass bottles must be due to the presence of impurities such as acetaldehyde which absorb light of wave lengths longer than ether can absorb.

## Inhibition and Retardation

While in the oxidation of hydrocarbons and related materials catalysis has received the most attention, in ether autoxidation inhibition has played the most prominent role. The reason for this is simply that the ether oxidation products are almost without exception detrimental to the intended uses. True inhibition, according to Waters (228), is brought about only by a union of two radicals or the chemisorption of radicals on surfaces. In some cases, the "inhibitor" is actually a chain-transfer agent, which substitutes a series of slow reactions for a series of fast ones, and should more properly be called a "retarder." An example is the retardation of butyraldehyde oxidation by a small amount of *p*-cresol.

Waters and Wickham-Jones (230) have shown that under these conditions the slow oxidation converts over 90% of the aldehyde to butyric acid leaving over 60% of the p-cresol unchanged. Although the ArO· radical produced from p-cresol is relatively stable because of resonance, it is still capable of dehydrogenating the substrate. The radicals derived from 1,2- or 1,4-dihydric phenols are too stable to attack the substrate, so that there exists effectively inhibition, despite its non-conformity to Waters' definition. Robertson and Waters (196) pointed out that, since phenolic inhibitors have no inhibitory effect upon tetralin oxidation after the "steady state" has been reached, the inhibitors must be considered as destroyers of the peroxide radicals and not of hydroperoxide molecules. From this Waters (223) concluded that inhibitors are "invariably easily oxidizable compounds," such as phenols, thiols, amines, and alcohols. That the ability of phenols to act as antioxidants increases with decreasing oxidation-reduction potentials, that is, increasing oxidizability, was shown by Bolland and ten Have (29) in the oxidation of ethyl linoleate. Phenol itself has an oxidation-reduction potential low enough to react with molecular oxygen. These workers conclude, as did Waters, that the reaction

$$ROO\cdot + ArOH \longrightarrow ROOH + ArO\cdot$$

is the most important "terminating" step.

Compounds of this type which have been used as other antioxidants are p-aminophenol (69, 178, 179), aniline (207), benzyl-p-aminophenol (49), catechol (155, 207), p-cresol (31, 68, 178), diphenylamine (69, 76, 136, 237), hydroquinone (113, 119, 135, 155, 166, 207, 237), 1-naphthol (159, 237), 2-naphthol (68, 113, 155, 159, 237), 1-nitroso-2-naphthol (68), m-phenylenediamine (69), p-phenylenediamine (69, 177), phloroglucinol (68), picric acid (147, 207), propyl gallate (25), pyrocatechol (119, 159), pyrogallol (68, 155, 207), resorcinol (68, 119), and salicylic acid (69, 237). Of these, Boehm and Williams (25) report that propyl gallate is extremely effective. In a concentration of 0.0002%, it prevented the formation of peroxides in diethyl ether for over four months.

An indication of some of the confusion in this field is the conflicting report that some of the above antioxidants cause an acceleration of oxidation (159, 177), a statement incompatible with the theory presented. On the other hand, the report that salicylic acid is an effective antioxidant for most ethers but not for isopropyl ether (237) may be an example of the "selective inhibition" discovered by Milas (149).

Since it was suggested that reactions of radicals with simple phenols could more properly be labeled "chain-transfer" reactions, it is well to consider here other reactions of that type. The retardation of ether autoxidation by alcohols and water has been frequently observed (113, 135, 146, 147, 159, 177). Merz and Waters (145) who have studied extensively radical-transfer reactions involving hydroxyl radicals, state that in alcohols the two principal reactions are

$$RCH_2OH + \cdot OH \longrightarrow RCH_2O\cdot + HOH$$

and

$$RCH_2OH + \cdot OH \longrightarrow R\dot{C}HOH + HOH$$

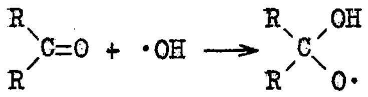
The first reaction is considered more important in the splitting of glycols by Fenton's reagent; but the second, because of the relative strengths of the C-H and O-H bonds, is predominant.

The fact that the monoethyl ether of ethylene glycol oxidizes much more slowly than that of diethylene glycol (212) is reasonable from a consideration of the concentration of hydroxyl groups. The reason for retardation by water is similar:

$$HOH + \cdot OH \longrightarrow HO\cdot + HOH$$

but, since the radical is changed only in identity and not in species, there is no change in radical reactivity. In aqueous acidic solutions of diethyl ether, tetrahydrofuran, and tetrahydropyran, in concentrations from 0.01 to 0.02 M, the autoxidations have been shown to be chain reactions (35). The addition of a dehydrating agent like calcium chloride to ethyl ether promotes peroxidation* (232), perhaps by decreasing radical transfers with water.

Ethanolamine and triethanolamine, which are used in stabilizing chloroacetals (22, 41), and acetaldehyde-ammonia, which stabilizes simple ethers (69), are probably also retarders of this class. Acetone and methyl ethyl ketone have been similarly used as stabilizers (69), but their activity has been attributed to an addition rather than a simple transfer (146):



$$R_2C{=}O + \cdot OH \longrightarrow R_2C(OH)O\cdot$$

A hydroperoxide could participate in radical transfer by the reaction (196):

$$ROOH + \cdot OH \longrightarrow ROO\cdot + HOH$$

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* The use of the term "peroxidation" in preference to "autoxidation" for this and other cases to follow is meant to emphasize the formation of peroxides.

Although this has been proved to occur in the vapor phase (201), the reaction could not generally be considered retardation because the new radical has no appreciably diminished activity.

Utilizing primarily the equations

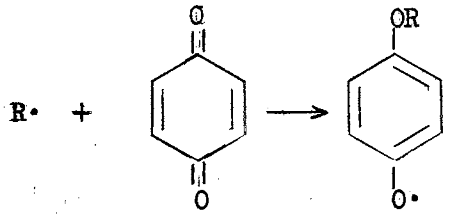
$$Fe^{++} + \cdot OH \xrightarrow{ka} Fe^{+++} + OH^-$$

and

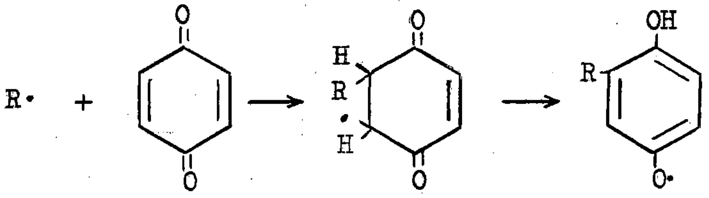
$$XOH + \cdot OH \xrightarrow{k_2} XO\cdot + HOH$$

(where X may be an acyl or other type radical), but also considering additional reactions of the $\cdot OH$ and $\cdot OX$ radicals with the substrate, Merz and Waters (146) evaluated $ka/k_2$, the "transfer coefficient," for a number of substances. They found that large free radicals, such as the acetoxyl radical, are less capable of attacking a C-H bond than free hydroxyl. Maleic and fumaric acids give radical transfer to the exclusion of the anticipated addition of the hydroxyl radical.

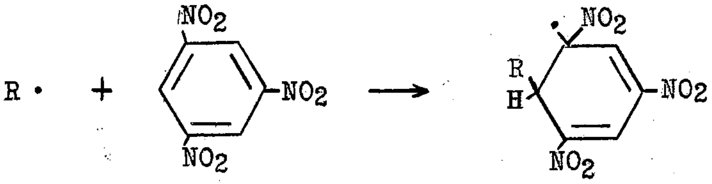
A significant group of inhibitors, although they have been used very little in stabilizing ethers, does depend for its action primarily on radical addition: the quinones. Bickel and Waters (24) showed that a radical like $\cdot C(CH_3)_2CN$ obtained from $\alpha,\alpha'$-azoisobutyronitrile adds to p-benzoquinone by the reaction



while more reactive radicals, like methyl and phenyl, attack the nucleus. The inhibition of vinyl polymerizations by quinones is likewise believed due to the addition of radicals to the nucleus (175):



In the polymerization of allyl acetate and vinyl acetate, it was found that both simple quinones and tetra-substituted quinones are inhibitors, showing that both C- and O-alkylation occurs (14). The products formed with benzoquinone were identified and found to be both substituted quinones and hydroquinone ethers. Benzoquinone is apparently the only quinone which has been used as an inhibitor in ethers (147). sym-Trinitrobenzene, which undergoes similar reactions in polymerizations (175),



has also received little attention as an ether stabilizer.

In ether autoxidation, the most confusion lies in the use of metals and compounds of metals as inhibitors. In contrast to the prevalent use of metallic iron and copper as catalysts for the oxidation of hydrocarbons (for example, see (30)), metallic iron has frequently been used as an inhibitor for ethyl ether oxidation (94, 113, 140, 179). It has been reported that ethyl ether stored over powdered iron can be kept free of peroxides for two to three years (94), and that several tons of this ether stored in steel tanks vented to the atmosphere developed no peroxides over the same length of time (113). On the other hand, Neu (163) reports that colloidal iron accelerates the oxidation of ethyl ether. Man'kov and Larionov (140) found that, although iron filings in the dark retard the formation of peroxides, they accelerate the formation of aldehydes; moreover, in the light, iron filings and especially powdered iron from reduced iron oxide considerably accelerate the oxidation. Iron filings show definite inhibitory action only in the absence of decomposition products.

The value of metallic iron as an inhibitor for use in other ethers is questionable; it has been found ineffective in both isopropyl ether (113) and glycol ethers (207).

When chemists in India were faced with the problem of keeping diethyl ether free of peroxides in a tropical climate, they found that the addition of copper wire was successful (138). In fact, some samples five years old still had not developed peroxides. Comparing the effectiveness of amber-glass bottles, ordinary tin cans, and copper-plated tin cans, Van Derripe *et al.* (217) found that only in the copper-plated containers were there neither peroxides nor aldehydes formed. Reimers (179) similarly recommended copper. In agreement that ordinary tin cans are ineffective inhibitors, Neu (163) reported that they actually accelerate oxidation, with the formation of acetic acid and ethyl acetate. Contrary to the favorable results found by others for copper, Bailey and Roy (9) found that copper, copper amalgam, and the zinc-copper couple are poor inhibitors for use in diethyl ether. The zinc-copper couple has also been found poor for glycol ethers (207).

Metallic copper and the zinc-copper couple (powder) have been recommended for freeing diethyl ether of peroxides (76, 164). It has been shown that the peroxide decomposition is accompanied by the appearance of decomposition products, notably acids, and the disappearance of dissolved oxygen (165). Ether peroxides are also decomposed by sodium (130, 160), sodium amalgam (9), mercury (154), and aluminum amalgam (150). Aluminum, however, promotes the formation of peroxides in glycol ethers (207) and has no inhibitory effect on isopropyl ether oxidation (113). Milas (147) reported that mercury is a catalyst in benzyl ether autoxidation, but Burroughs (36) was unable to confirm his results. Considering that photosensitized mercury is capable of dehydrogenating ethyl ether (53) and even cyclopentane (3) and <u>n</u>-decane (173) without itself undergoing chemical change, it is entirely possible that mercury actually is a catalyst in an illuminated system. Moreover, in the presence of water, metals such as silver and mercury are able to reduce molecular oxygen to hydrogen peroxide, presumably by way of an $\cdot$OOH intermediate (84, 85).

Metals may, therefore, according to Waters (227), be regarded as both chain-promoters and chain-breakers, a dual action which is explicable in terms of the electrochemical properties of metallic surfaces. In the reversible system

$$\text{metal (electron source)} + O_2 \longrightarrow (\text{metal}{:}O\text{-}O\cdot)$$

electron donation, equivalent to chain-initiation, is a cathodic process; and electron abstraction, equivalent to chain-breaking, is an anodic process. The potential difference between the two in a given system will determine whether initiation or termination reactions will predominate.

With the exception of strong bases like sodium hydroxide (130, 207) and reducing agents like ferrous and stannous salts (78, 160, 237), most of the other materials which have been tested as inhibitors are metallic oxides. Of these, only lead oxide and lead dioxide have been recommended as inhibitors (40, 56, 78). The dioxide has been used to remove peroxides from dioxane, ethyl ether, isopropyl ether, and isopentyl ether (78, 160). Manganese dioxide and silver oxide cause the decomposition of ether peroxides with evolution of oxygen (44). The catalytic activity of metallic silver in the commercial vapor-phase oxidation of isopropyl ether to acetone (35) may be related to the activity of its oxide. Alumina, which removes peroxides from glycol ethers and acts as an inhibitor (207), was shown to adsorb, without destroying, peroxides in ethyl ether, dioxane, and n-butyl ether (54). In isopropyl ether, copper oxide and ferric oxide have little effect on peroxidation (113). In glycol ethers, calcium oxide and barium oxide in a similar way exhibit almost no effect; sodium carbonate, however, increases the formation of peroxides (207). In ethyl ether, zinc sulfate promotes peroxidation (56).

Most of these effects seem to be intimately related to surface area. Barium sulfate, which was used in studying the effects of surface area on tetralin oxidation, appears to have about the same activity as glass wool (89). Both activation and termination are assumed to occur on the surface, the reactions proposed being, for activation,

$$\underline{S}(\text{surface}) + O_2 \longrightarrow \underline{S}{-}{-}{-}O_2$$

$$\underline{S}{-}{-}{-}O_2 + RH \longrightarrow \underline{S} + R\cdot + \cdot OOH$$

and, for termination,

$$ROO\cdot + S \longrightarrow ROO{-}{-}{-}S$$

Henderson (103) proposed a similar chain-termination mechanism for ethylbenzene oxidation:

$$R\cdot + \text{wall} \longrightarrow R^{-}\text{wall}^{+}$$

That Pyrex wool can both initiate and terminate chains in the oxidation of dioxane is indicated by the work of Burroughs (36). According to Stephens (205), the rate of oxygen absorption by cyclohexene is increased by Pyrex wool and decreased by quartz fibers. This, too, may be interpreted as illustrating the relative chain-initiating and -terminating efficiencies of two materials.

After investigating the effects of charcoal and silica gel on ethyl ether oxidation, Demougin and Landon (56) reported that charcoal of all types accelerates both the formation and destruction of peroxides. Silica gel brings about the decomposition of peroxides but also causes the formation of hydrogen peroxide. The accelerated oxidation resulting from charcoal was confirmed by Neu (163).

It may be concluded from the discussion thus far that inhibition is a complex phenomenon which may involve removal of peroxide molecules by destruction or adsorption, capture of radical carriers to form resonance-stabilized systems, and possibly electron abstraction by metallic surfaces. Since activation frequently accompanies inhibition, the relative efficiency of the two processes will determine whether the resulting effect is catalytic or inhibitory. Some substances which have been recommended as inhibitors are in reality catalysts which accelerate oxidation by promoting initiator decomposition.

## Catalysis

Catalysis of ether autoxidations is becoming increasingly important as industry is faced with the growing problem of utilizing ether by-products. Controlled autoxidation offers promise in elevating many ethers from their subservient roles as solvents to more respectable roles as highly valued intermediates in the production of alcohols, acids, aldehydes, and esters. The oxidations of dioxane to ethylene diformate (79), allyl ethers to acrylates (98), and tetrahydrofuran to $\gamma$-butyrolactone (32) and $\gamma$-hydroxybutyraldehyde (139) represent almost all of the patented processes in this field. Bancroft (11) once stated, in referring to catalytic reactions involving hydrogen peroxide, that it was "a hopeless subject for the phenomenological, or Baconian, experimenter, because the misleading experiment is everywhere." His statement could have been applied equally to catalysis of autoxidation. Yet, because of the potential utility of catalyzed ether oxidations, some sort of attempt should be made to coordinate the available data.

Catalytic activity in free-radical reactions can arise principally from three types of reactions: the catalyst can accelerate the decomposition of an initiator; it can activate a molecule of reactant by adding to it; and it can initiate chains by attacking the substrate.

In 1934, Haber and Weiss (99) proposed this set of reactions to explain the ferrous-ion catalyzed decomposition of hydrogen peroxide (in the so-called "Fenton's reaction"):

$$Fe^{++} + HOOH \longrightarrow Fe^{+++} + OH^{-} + \cdot OH$$

$$HO\cdot + HOOH \longrightarrow HOH + HOO\cdot$$

$$HOO\cdot + HOOH \longrightarrow O_2 + H_2O + \cdot OH$$

$$Fe^{++} + \cdot OH \longrightarrow Fe^{+++} + OH^-$$

$$Fe^{+++} + HOO^- \longrightarrow Fe^{++} + HOO\cdot$$

The hydroperoxide ion in the last step would result either from the ionization of hydrogen peroxide or from the equilibrium

$$HOOH + OH^- \rightleftharpoons HOO^- + HOH$$

Utilizing these equations, Robertson and Waters (196) suggested that the metal-catalyzed decomposition of organic hydroperoxides can proceed by a similar path, the two main steps being decomposition

$$ROOH + M^+ \longrightarrow RO^- + \cdot OH + M^{++}$$

followed by catalyst regeneration

$$RO^- + ROOH \rightleftharpoons ROH + ROO^-$$

$$ROO^- + M^{++} \longrightarrow ROO\cdot + M^+$$

Support for this mechanism came first from the observation that the products obtained in hydroxyl radical oxidations are essentially those expected in catalyzed autoxidations (146). Later, Robertson and Waters showed that in the cobalt naphthenate-catalyzed decomposition of tetralin hydroperoxide (in chlorobenzene and a nitrogen atmosphere), considerable oxygen is evolved. Since they had already found that a little oxygen is produced in the non-catalyzed reaction, presumably by

$$ROO\cdot + \cdot OH \longrightarrow ROH + O_2$$

they expected the catalytic effect to result in an increase in the hydroxyl radical concentration. However, attempts to prove the presence of the hydroxyl radical by hydroxylation of aromatic solvents were unsuccessful (195).

Recently, Barb *et al.* (12) have re-examined the hydrogen peroxide decomposition and have arrived at the conclusion that the important catalyst regeneration step is

$$Fe^{+++} + HOO\cdot \longrightarrow Fe^{++} + O_2 + H^+$$

An analogous reaction for organic peroxyl radicals is unlikely.

Fordham and Williams (80) believe that the cumene hydroperoxide-ferrous ion interaction is quite different from the hydrogen peroxide reaction. The decomposition reaction is

$$ROOH + Fe^{++} \longrightarrow RO\cdot + OH^- + Fe^{+++}$$

the significant difference being the formation of an alkoxyl radical instead of a hydroxyl radical. They did not give any reactions for catalyst regeneration. Kharasch, Fono, and Nudenberg (121) verified this mode of cumene hydroperoxide decomposition by showing that the resulting alkoxyl radical will add to olefins. The reaction differs from the tetralin hydroperoxide decomposition in that only a small amount of oxygen is evolved. In similar reactions, it was shown that the alkoxyl radicals from either *tert*-butyl hydroperoxide or cumene hydroperoxide will add to butadiene, isoprene, alkenes, and allyl alcohol (125). No catalyst regeneration steps were proposed.

In their study of cobalt-catalyzed reactions, Woodward and Mesrobian (241) for tetralin oxidation, and Bawn, Pennington, and Tipper (19) for trimethylethylene oxidation have shown that the hydroperoxide decompositions follow similar paths:

$$ROOH + Co^{++} \longrightarrow RO\cdot + OH^{-} + Co^{+++}$$

In both studies, the regeneration step was believed to be

$$ROOH + Co^{+++} \longrightarrow ROO\cdot + H^{+} + Co^{++}$$

That the cobaltic ion is also a catalyst was shown by adding cobaltic acetate prepared immediately before use by an electrolytic oxidation. There was observed a very strong immediate catalytic effect gradually diminishing to that obtained from cobaltous acetate alone (19). A result similar to this electrolytic "activation" was obtained in ether oxidation by adding acetaldehyde to the cobalt acetate catalyst before use (112). Wibaut and Strang (234) agreed with the decomposition reaction in the oxidation of alkanes; they were able to show both that the cobaltous ion is oxidized to cobaltic by hydroperoxides and that the alkoxyl rather than the hydroxyl radical is produced. For the catalyst regeneration step, they preferred the reaction

$$ROOH \rightleftharpoons ROO^{-} + H^{+}$$

$$ROO^{-} + Co^{+++} \longrightarrow Co^{++} + ROO\cdot$$

It has been reported that the reaction

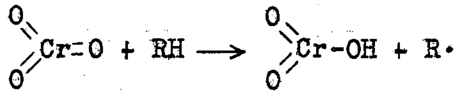
$$RH + Co^{+++} \longrightarrow R\cdot + H^{+} + Co^{++}$$

occurs readily at room temperature for trimethylethylene (19), and it has been suggested for the initiation of tetralin oxidation (241).

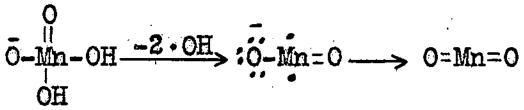
Although a peroxide-free n-nonane could not be oxidized even at 110° and in the presence of cobalt stearate (234), copper stearate has been reported as a good chain-initiation catalyst for lubricating oils (34). The nature of the radical carrier was questioned by Anderson and Nylen (4), who suggested that the radical carriers in methyl linoleate oxidations are metal-methyl linoleate adducts.

The violent oxidation of ethyl ether by chromic anhydride, which was noticed as early as 1915 (115), was shown by Waters (226) in 1946 to be accompanied by oxygen absorption but only while the chromic anhydride was being reduced. Since the ease of oxidation for a group of alcohols, ethers, and esters did not follow the ease of proton removal, he assumed that a hydrogen atom was removed. The oxidation of cyclohexene to 2-cyclohexenone by chromic anhydride in acetic acid had been shown several years earlier to occur by an attack on the α-hydrogen atom (233); Farmer (75) indicated that hydrogen abstraction from an α-methylene group is a general reaction for this reagent.

Waters (229) proposed the free-radical mechanism



and so on until $Cr(OH)_3$ is formed. The permanganate ion could act similarly to give $Mn(OH)_3$ and OH , although an alternative reaction, after two molecules of substrate have been dehydrogenated, is hydroxyl radical expulsion:



$$\bar{O}-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{Mn}}-OH \xrightarrow{-2\cdot OH} :\bar{\ddot{O}}-\dot{Mn}=O \longrightarrow O=Mn=O$$

Dehydrogenations of organic compounds, according to Waters, can occur only if the oxidizing agent contains a double covalent bond:

$$H\cdot + O{=}M^{n} \longrightarrow H{-}O{-}M^{n-1}$$

A coordinate compound, $M^{+}O^{-}$, has no tendency to pick up electrically neutral hydrogen.

In the light of this discussion, it is interesting to note that both chromic anhydride and potassium permanganate have been recommended for purifying isopropyl ether (109, 154).

Discussing early research on fluorescence of solutions, Rieche (200) concluded that in photosensitized oxidations the oxygen molecule becomes activated and adds to a sensitizer, which is then capable of hydrogen abstraction. That this actually occurs in this manner is debatable, of course; but there are some who believe that oxygen does add to catalysts, forming loose complexes (90, 203).

George and Robertson (92) suggest the reactions

$$M + O_2 \longrightarrow MOO\cdot$$

$$MOO\cdot + RH \longrightarrow M + R\cdot + HOO\cdot$$

Since they observed that copper, iron, and cobalt stearates are able to terminate chains, they proposed

$$M + ROO\cdot \longrightarrow MOOR$$

as a termination reaction. In tetralin, copper has a greater chain-terminating ability than cobalt or iron; but cobalt stearate inhibits the oxidation of heptanal.

In 1924, Robinson (197) mentioned that hemoglobin, methemoglobin, and hemin act as catalysts in the autoxidation of linseed oil, presumably owing to the iron content. Gebauer-Fuelnegg and Konopatsch (86) found, a few years later, that many cobalt complexes similarly catalyse the drying of oils. These complexes include those of acetaldoxime, $\alpha$-nitrosoacetophenone, 2-nitroso-1-naphthol pyridine, and $\alpha$-acetylacetophenone dipyridine. Cobalt-acetophenone and cobalt-2-nitroso-1-naphthol complexes had practically no drying action. Compounds of the iron phthalocyanine type were shown by Cook (47) to catalyze the decomposition of tetralin hydroperoxide, the oxidation of benzaldehyde, and the oxidation of diphenylmethane. In the last instance, the catalysts promoted both peroxide decomposition and ketone formation.

In discussing the properties of elements which are good autoxidation catalysts, George, Rideal, and Robertson (90) asserted that the transition elements are best although they could not decide whether the ease of valency change or the ease of complex formation is more important. They were inclined toward the latter on the basis of their findings that the rates of catalyzed reactions are dependent upon oxygen pressure and that the complexes of the transition-metal ions have structures similar to those of the known oxygen carriers, such as hemoglobin.

The combination of a metal catalyst with oxygen

$$M + O_2 \longrightarrow MOO\cdot$$

would have the effect of converting a relatively inactive biradical (oxygen) into an active monoradical and would be expected to produce an increase in paramagnetism. Pauling and Coryell (171) discovered to the contrary that ferrohemoglobin (hemoglobin itself) and oxygen, both of which are paramagnetic, combine to form diamagnetic oxyhemoglobin. Ferrohemoglobin has sixteen unpaired electrons and the bonds to iron are ionic, while oxyhemoglobin has no unpaired electrons and the bonds are covalent. A recent review (88) of the reactions of oxygen with hemoglobin has indicated that oxygen activation in oxyhemoglobin is a result of an alteration of the oxygen-iron link by an acid.

A cobalt complex, disalicylethylenediimine cobalt, is like hemoglobin in its ability to absorb and release oxygen. Like hemoglobin, it, too, is paramagnetic, becoming diamagnetic upon oxygen absorption (59). It has not been tried as an autoxidation catalyst.

Chlorophyll has been used as an autoxidation catalyst for oleic acid (120). The activity, which is noticeable in both the light and the dark, is interesting in view of the fact that the central ion, magnesium, has almost no activity by itself.

Another type of compounds which have been used to promote tetralin autoxidation is the "positive halogen" type (194). Compounds such as _N_-bromosuccinimide, _N_-bromophthalimide, chloropicrin, and even benzyl chloride are reportedly immediate catalysts for tetralin autoxidation at the comparatively low temperature of 76°. The activity is believed due to the reaction

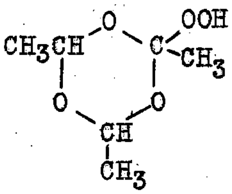
$$RX \longrightarrow R\cdot + \cdot X$$

It may be concluded, by way of restatement and summary, that a catalyst for autoxidation can work in a variety of ways: it may attack the substrate, react with molecular oxygen, or accelerate hydroperoxide decomposition. By its chain-terminating ability it may also act as an inhibitor. The final rate of a catalyzed reaction will thus depend upon the direction and magnitude of the resultant of a large number of factors.

Structural Effects

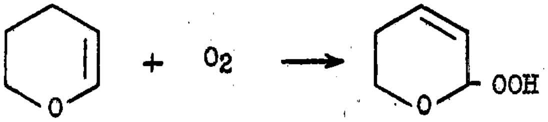
The rate-controlling factors which have been considered thus far are inhibition and catalysis. Little has yet been said about the most important consideration--the effect of the structure of the ether itself.

Burroughs (36) has indicated that the general rates of autoxidation follow the order: acetals > benzyl ethers > acyclic and heterocyclic ethers > aromatic ethers. So pronounced is this difference in some cases that 3-ethoxy-5,7,7-trimethyloctanal diethyl acetal, $(CH_3)_3CCH_2CH(CH_3)CH_2CH(OC_2H_5)CH_2CH(OC_2H_5)_2$, is oxidized entirely at the acetal group to produce the respective octanoic acid (144). In the case of aldehyde trimers, there may be some question as to whether the structure undergoing oxidation should be regarded as an aldehyde instead of a type of ether. Criegee (51) has resolved this in favor of the ether structure by showing that paraldehyde forms the hydroperoxide,

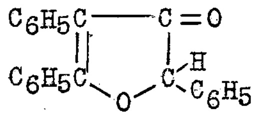


Criegee also believed that 2-methyl-1,3-dioxolane forms the hydroperoxide, but more recent evidence indicates that the compound found is actually the peroxide (see p. 19). Although they made no comparisons with other types of ethers, Legault and Lewis (135) showed that the oxygen absorption rates are extremely high for 1,3-dioxolane and its 2-methyl homolog, the latter oxidizing faster. The hydroperoxides of these compounds are decomposed during distillation. Chloroacetals are known to peroxidize (22, 41), but no rate data, even qualitative, are available. Diethoxymethane, which forms a volatile peroxidation product, may be attacked in either the alkyl or the methylene group (45).

Although Burroughs did not study them, allyl ethers probably should precede benzyl ethers but follow acetals in their oxidation rates. Clover (45) observed that allyl ethers autoxidize much more rapidly than saturated ethers to give peroxides which decompose causing resin formation. Dimethallyl ether forms peroxides faster than any other ether studied by Williams (237), including several tert-butyl alkyl ethers; but the ether can be freed of peroxides by heating. Oxidations of allyl alkyl ethers, in which the allyl group has an opportunity to compete with an alkyl group, show that the allylic group is preferentially attacked (98). In the competition in orientation between the benzyl group and the allyl group in 5-phenyl-2-pentene autoxidation, the attack is on the 4-position, the allylic methylene group, exclusively (151). That the oxygen linkage in an allyl ether exerts a great accelerating influence is shown by the fact that 5,6-dihydro-4H-pyran is attacked not in the 4-position but in the 2-position although a double bond shift is required (198):



The order of reactivity toward oxygen in the ethers studied by Milas (147) was shown to be tert-butyl benzyl> dibenzyl> sec-butyl ethyl> tert-butyl ethyl> n-butyl ethyl> tert-butyl propyl> di-n-butyl> (dioxane and tert-butyl methyl)> ethyl phenyl> methyl phenyl> diphenyl. Burroughs (36) showed the rate of oxidation of several benzyl ethers is in the order dibenzyl> benzyl ethyl> benzyl methyl> benzyl n-butyl. The ability of benzyl ethers to autoxidize was noted also by Olson et al. (169), who determined the physical properties of a number of ethers. Waters (226) stated that benzyl methyl ether undergoes autoxidation with a "marked" absorption of oxygen, faster than either isopropyl ether or n-butyl ether. β-Hydroxytriphenylfuran, which in its keto form is actually a benzyl ether,



very easily undergoes oxidation (128) to form the α-hydroperoxide (51). The oxidation of phthalan, another benzyl-type ether, has been mentioned previously (p. 18).

An indication of the relative reactivities of some of the aliphatic ethers has already been shown from the work of Milas. In addition, Burroughs (36) found that 2,2'-dichlorodiethyl ether absorbs oxygen faster than simple aliphatic ethers and that tetrahydrofuran absorbs oxygen faster than 1,4-dioxane.

Anisole and phenetole have generally been found quite inert to oxygen (36, 45, 226, 240); but Milas (147) states that oxidation does occur not only in both anisole and phenetole but also in diphenyl ether. His results are not elsewhere substantiated.

## Experimental Determinations of Reaction Mechanisms

It should have become clear from the discussion this far that, while reaction product studies are indispensable, the most progress toward a complete understanding of the autoxidation mechanism has come from kinetic studies. That this is true is not surprising because, as Frost and

Pearson (83) emphasize, "kinetics provides the most general method of determining the mechanism of reaction." Although it has been demonstrated here that the theories proposed for the autoxidation of other compounds may be profitably applied to ethers, it is perhaps impossible and certainly unwise to try to formulate a mechanism for autoxidation of ethers without making similar kinetic studies on the ethers themselves.

Such studies have been reported for only one liquid ether--isopropyl ether (152). In addition, there are two related investigations which deal with the vapor-phase oxidation of aliphatic ethers (40, 61). An insight into the reasons for the apparent disdain of a kinetic approach to ether autoxidation may be acquired by reviewing what Gee (87) puts forth as a _sine_ _qua_ _non_. He states that, before kinetic methods can be usefully employed, it is necessary to find conditions under which the rate of a single reaction or chain sequence can be studied experimentally. Tetralin and a few olefins have been extensively investigated because they can be made to yield the pure hydroperoxides. Under these conditions, the rate of oxygen absorption as a function of the hydrocarbon, peroxide, and catalyst concentration provides useful kinetic data. Even then it is generally impossible to decide unequivocally the course of a reaction.

From this it may be concluded that probably the greatest impediment toward the use of kinetics as a tool in ether autoxidation studies has been the seeming complexity of the reactions. At the beginning of this present work, the author believed that the two main conditions which would make kinetics impracticable would be the unattainability of the "steady-state" and the irreproducibility of data. As it shall now be shown, neither of these fears materialized.

# EXPERIMENTAL

## Apparatus

The most common types of apparatus used for studying oxygen absorption may be classified broadly as follows: the first brings the sample into contact with oxygen by shaking in a flask; the second circulates oxygen through the sample. Mostly because of mechanical difficulties, the first method is limited to the use of relatively small samples. The 10-g. samples used by Milas (147) in his comparison of oxidation rates illustrate this point. Making the system leak-proof--always a problem in this type of work--is a difficulty increased by the use of a shaking apparatus (although it may be partially offset by fewer joints). Usually the rate of pressure decrease is determined. Since changes in pressure may affect rates of oxidation, the validity of data based on such measurements is always subject to question, especially where large pressure changes have occurred. Opposed to these objections is the very real advantage of having generally available a commercial instrument--the Warburg apparatus--which permits studying simultaneously several samples (ten to twenty in some instruments). The inability of Burroughs (36) to obtain reproducible data using this apparatus was due to the fact that he was comparing the total volumes of oxygen absorbed instead of the rates of absorption. Although experimental details of their work were not available, Molodovskii and Neiman (152) apparently used a similar apparatus for studying the liquid-phase oxidation of isopropyl ether--the only kinetic study of ether autoxidation.

The second method, that of circulating oxygen through the sample, had not been applied to ethers in spite of its successful application to other materials. Most of the present forms of the apparatus are modifications of the one first described in 1936 by Dornte (60) in his study of white oil oxidation. Although his method was not entirely original, he was the first to provide sufficient details to enable others to construct similar types of apparatus. Subsequent modifications have been concerned largely with increasing the sample size (10 to 15 g. were used by Dornte) and with making the apparatus fully automatic. The versatility of the apparatus is shown by the different types of compounds which have been investigated in this way. A few examples are GR-S type hydrocarbons (132), aliphatic and aromatic hydrocarbons (30, 131), fats (55), and diester lubricating fluids (156).

The Dornte-type apparatus is commonly used as a constant-pressure method for measuring absorption of oxygen. Frequently the term "constant-pressure" is misused to apply to those measurements in which the volume of oxygen necessary to restore the pressure of the system to atmospheric is fed in intermittently.

It was decided for this work that a constant-pressure method capable of using 100- to 200-g. samples was desirable; consequently, a Dornte-type apparatus seemed the most promising.

The apparatus (Figure 1) may be depicted as fundamentally a circulatory system in which oxygen was circulated through the ether sample held at a constant temperature in an electrically heated bath. Circulation was accomplished by means of a piston acting on mercury in a 28-mm. glass U-shaped tube (A). Two mercury valves (B) gave unidirectional flow to the oxygen as it was alternately compressed and expanded by the rise and fall

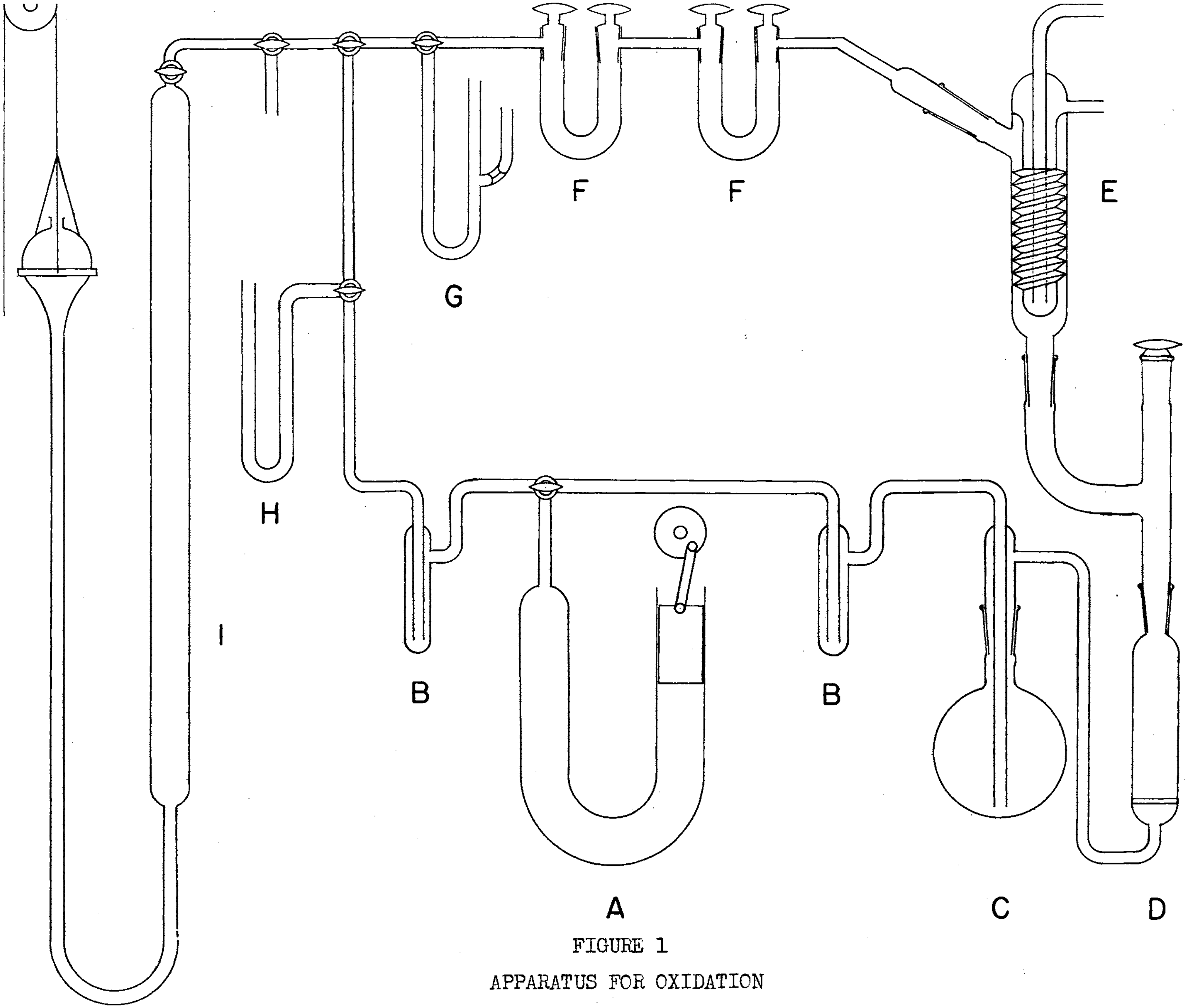


FIGURE 1

APPARATUS FOR OXIDATION

of the mercury in the U-tube--a Toepler pump. The piston was operated by a gear train which reduced the speed of a 1/6 H.P. 1725 rpm. motor to 90 rpm. From the pump, the oxygen passed through a one-liter round-bottom flask (C) which served as a surge tank and also as a preheater since the flask was in the thermostatted bath with the reaction tube. The reaction tube (D) was a 40-mm. glass tube having at the bottom a fritted disc through which oxygen entered from the liter flask and at the top a ₮ 29/42 outer joint. The capacity of the reaction tube was 180 ml. During the first few runs, the reaction tube was also provided, by means of other standard-taper joints, with a sampling device and a condenser. The sampling device was similar to that used by Sharp, Patton, and Whitcomb (202) and consisted of a 20-mm. tube attached to a 7-mm. tube with the 7-mm. tube reaching nearly to the bottom of the reaction tube. A sample could be drawn into the sampling device by reducing pressure in it by means of an aspirator. A stopcock shut off the reaction tube from the sampling device when it was not in use. After the first few runs, this device was replaced by a three-way connecting tube with a parallel side arm as shown in the diagram. The side arm led to a Friedrichs condenser (E). By means of a pipette, samples could be withdrawn through the vertical part of the connecting tube; the top was glass-stoppered except during sampling. Oxygen passed from the reaction tube through the condenser to U-tubes (F) containing Drierite and Ascarite to absorb water and carbon dioxide. Oxygen from these tubes returned to the pump. It was shown that the rate of oxygen circulation was about 35 l./hr. through the uncharged reactor. This is higher than is usual in experiments of this kind and guaranteed saturation of the reactor contents with oxygen at all times.

Connected to this system were a mercury manostat (G), a manometer (H), and a constant-pressure burette (I). The constant-pressure burette consisted of a 100-ml. gas burette with a leveling bulb which could be raised by a pulley attached to a 1/4 H.P. 1725-rpm. motor geared down to about 8 rpm. by means of a Boston gear reductor (Boston Gear Works, Quincy, Mass.). A safety switch was provided to prevent raising the bulb too far. Under continuous operation, the leveling bulb displaced less than one milliliter per second of oxygen in the burette. The motor was actuated by the mercury switch operating through a Cenco-Gilson electronic relay. When pressure in the system dropped, the motor was turned on momentarily to restore the pressure to the predetermined value. Pressure fluctuations in the system existed primarily because of the pump action but amounted to only ±5 mm. at most. The constant-pressure device maintained the pressure within these limits easily.

All connections not made of glass were made of Tygon tubing coated with "Sealit" (Fisher Scientific Co.). Ground-glass seals were lubricated with a silicone stopcock lubricant (Dow-Corning Corp.). To test the suitability of these substances, oxygen absorption measurements on the system alone were made; these showed negligible volume changes over a three-day period.

The volume of the train exposed to variations in room temperature was determined from the ideal gas law by taking the burette reading, $V_n$, at several pressures, $P_n$. The volume of the system, $V_s$, was then found:

$$P_1(V_1 + V_s) = P_2(V_2 + V_s)$$

$$V_s = \frac{P_2V_2 - P_1V_1}{P_1 - P_2}$$

The volume exposed to temperature variation after subtracting the volumes of the surge tank, reaction tube, and condenser was found to be 60 ± 5 ml. exclusive of the burette reading. All readings were corrected to millimoles of oxygen absorbed per mole of ether.

The thermostatted bath was stirred by a Sargent cone-drive motor and heated by two 250-watt knife heaters operated by a Cenco electronic relay, which was actuated by a sensitive mercury switch. The bath temperature remained constant to about $\pm 0.1^{\circ}$ at lower temperatures and about $\pm 0.2^{\circ}$ at $70^{\circ}$. Surrounding the bath was a jacket made of Masonite; this, together with a lid of the same material, served to keep out light and thus eliminated the photocatalysis reported for ether autoxidation by many workers (for example, see references 45 and 147).

## Procedure

In carrying out a run, the system was thoroughly flushed with oxygen before adding the ether (usually 100 to 150 g.). After several minutes, the pump was started and the "zero" reading was taken. Since there was in almost every case an induction period extending over an hour or more, the establishment of a zero time was not found to be critical. The first reading was usually taken within five minutes after starting the pump, however. Normally, the apparatus was operated at pressures a few millimeters below atmospheric; consequently, to take burette readings, the pressure in the system had to be equalized to that of the atmosphere. When samples were to be removed, the burette reading was taken, the pump was stopped, and the sample was withdrawn and placed in a 10-ml. flask for weighing. The pump was started again and a second reading was taken. (It was necessary to take the second reading because sometimes a difference as great as ±0.5 ml. between readings would occur.) The whole operation required not more than thirty seconds.

## Analyses

The peroxide method was essentially that of Wagner, Smith, and Peters (219). It was chosen because of both its simplicity and its ready adaptability to the analysis of discolored solutions by a potentiometric dead-stop method (1). (This technique was not required, however.) Into a 250-ml. soil-digestion flask (an Erlenmeyer flask with a ₮ 24/40 outer joint) were introduced 25 ml. of the solvent (made by mixing 950 ml. of isopropyl alcohol with 50 ml. of glacial acetic acid), about 2 g. of the sample, and 2 ml. of sodium iodide solution (made by dissolving 20 g. of sodium iodide in 150 ml. of hot isopropyl alcohol). The mixture was refluxed for five minutes and then without appreciable cooling titrated with 0.05 to 0.1 N sodium thiosulfate to the disappearance of the yellow color. New sodium iodide solution was prepared whenever the blank was greater than 0.1 ml. Benzoyl peroxide by this method consistently analyzed about 99%.

The carbonyl method was a modification of the one employed by Dermer *et al.* (58). To the sample were added 20 ml. of 0.5 N hydroxylamine hydrochloride in methanol (70 g. of hydroxylamine hydrochloride and 0.1 g. of butter yellow in two liters of methanol, adjusted to neutral with sodium methoxide solution). The solution was refluxed twenty minutes and then titrated with 0.05 to 0.1 N sodium methoxide in methanol (prepared by dissolving sodium in a little dry methanol, and diluting to two liters; standardized against potassium hydrogen phthalate using a phenolphthalein indicator). The method was tested on salicylaldehyde, which happened to be the only pure aldehyde available at the time. Without refluxing or standing, the aldehyde assayed 85%. Standing sixteen hours raised the titer to 98.5% and 98.6% for two samples. Similar results were obtained by varying the reflux time from five to thirty minutes. Fifteen minutes reflux was barely sufficient, but twenty minutes gave consistent results.

Determinations of acidity were made by titrating a mixture of the sample and water with the standard sodium methoxide in methanol, using a phenolphthalein indicator.

## Materials

A list of the ethers investigated is given in Table I. Unless otherwise specified, the ethers were prepared in this laboratory. The most general preparative method for the benzyl ethers was found to be the Williamson synthesis as modified by Olson *et al*. (169). In this method, sodium hydroxide (1 mole) was refluxed with the respective alcohol (4 moles) for thirty minutes. The benzyl chloride (1 mole) was then added at a rate just fast enough to promote a smooth reaction as indicated by gentle refluxing. After all of the benzyl chloride had been added, the reaction mixture was refluxed for eight hours and freed of most of the excess alcohol by distillation and the precipitated sodium chloride by filtration. The filtrate was then washed repeatedly with water, dried over sodium sulfate, and finally distilled. Yields ranged from 60 to 90%. All the benzyl ethers prepared except benzyl *tert*.-butyl ether and benzyl phenyl ether were made in this way.

In the preparation of benzyl *tert*.-butyl ether, it was necessary to modify the procedure by substituting sodium for sodium hydroxide on account of the low solubility of the latter in *tert*.-butyl alcohol.

## TABLE I

## PHYSICAL CONSTANTS OF ETHERS

| Ether | Boiling point, °C | | | Refractive index, $n_D^t$ | | |
|---|---|---|---|---|---|---|
| | found | lit. | ref. | found | lit. | ref. |
| Anisole* | $153.6^{740}$ | $153.9^{760}$ | (20) | | | |
| Benzaldehyde diethyl acetal | $105\text{-}107^{15}$ | $92\text{-}93^{10}$ | (129) | $1.4780^{22}$ | | |
| Benzyl methyl | $167.5\text{-}168.0^{740}$ | $170.5^{760}$ | (169) | $1.5001^{22}$ | $1.5022^{20}$ | (169) |
| Benzyl ethyl | $184.0\text{-}184.5^{743}$ | $184^{744}$ | (20) | $1.4953^{20}$ | | |
| Benzyl *n*-propyl | $72\text{-}73^{22}$ | $96^{24}$ | (153) | $1.4949^{22}$ | $1.4905^{20}$ | (153) |
| Benzyl isopropyl | $100\text{-}101^{36}$ | $83.0^{16}$ | (169) | $1.4868^{20}$ | $1.4859^{22}$ | (169) |
| Benzyl *n*-butyl** | $86^{6}$ | $220.5^{744}$ | (20) | $1.4872^{20}$ | | |
| Benzyl *tert.*-butyl | $107^{36}$ | $82\text{-}83^{8}$ | (70) | $1.5150^{20}$ | | |
| Benzyl phenyl | $133\text{-}134^{6}$ | $178\text{-}179^{35}$ | (20) | | | |
| Bis-(α-methylbenzyl)*** | $141^{11}$ | $286.3^{760}$ | (174) | | | |
| *p*-Chlorobenzyl methyl | $83^{4}$ | | | $1.5207^{22}$ | | |
| Dibenzyl* | $185^{30}$ | $184^{28}$ | (20) | $1.5635^{18}$ | | |
| Dioxane* | $100^{740}$ | $101.3^{760}$ | (106) | | | |
| *p*-Methoxybenzyl methyl | $81\text{-}83^{4}$ | $225.5^{758}$ | (20) | $1.5317^{20}$ | | |
| *p*-Methylbenzyl methyl | $75^{5}$ | | | $1.5013^{20}$ | | |
| *p*-Nitrobenzyl methyl | m.p. 27 | 26-27 | (20) | $1.5604^{20}$ | | |
| Styrene oxide**** | $126\text{-}127^{100}$ | $126.8^{100}$ | (208) | | | |

* The Matheson Co.; ** Eastman Kodak Co.; *** Carbide and Carbon Chem. Co.; **** Dow Chem. Co.

Benzyl phenyl ether was prepared by a modification of the procedure given by Huston and Eldridge (114) in their synthesis of benzyl 2,6-dichlorophenyl ether. Small pieces of sodium (3 moles) were allowed to react with methyl alcohol (one liter) until all the metal had been consumed. Phenol (2.5 moles) was next added, and the solution was refluxed for thirty minutes. Benzyl chloride (3 moles) was added to the cooled solution with vigorous stirring. After standing overnight followed by refluxing for four hours, the mixture was filtered and the excess methyl alcohol was distilled from the filtrate at atmospheric pressure. The remaining liquid was distilled at reduced pressure, whereupon the product distilling at 133-134° at 6 mm. immediately crystallized in the receiver (m.p., 39°). The yield was relatively low--about 60%. The pure ether had a very slight aromatic odor which gradually was replaced by a phenolic odor after storage for several months.

Benzyl chloride or a substituted benzyl chloride was used in every case except the preparation of p-methylbenzyl methyl ether, for which p-methylbenzyl bromide (Eastman Kodak Co. reagent) was used. p-Methoxybenzyl chloride was obtained from the chloromethylation of anisole by the procedure of Quelet and Allard (176). A mixture of anisole (400 g.) and formalin (350 g.) was saturated with hydrogen chloride at 0° in less than two hours, treated with ice, water, and cold 10% sodium carbonate solution in that order, and finally washed repeatedly with cold water. After drying briefly over sodium sulfate, the p-methoxybenzyl chloride was used without separation from the anisole or by-products.

Benzaldehyde diethyl acetal was prepared by a modification of the method of Claisen (43). Benzaldehyde (330 g.), absolute ethyl alcohol

(385 g.), ethyl orthoformate (500 g.) and ammonium chloride (7 g.) were mixed together and refluxed for ten minutes. Since the odor of benzaldehyde was still strong at the end of this time, a drop of concentrated hydrochloric acid was added. After standing two hours, the solution was neutralized with potassium hydroxide and extracted with water and sodium carbonate solution. After drying over sodium carbonate, the solution was distilled and the product collected in the range 105 to 107° at 15 mm. The yield was about 45%, less than half of that reported by Claisen.

The purification method generally applicable was the following: peroxide- and aldehyde-containing ethers were treated with strong potassium iodide solution repeatedly until the aqueous layer was no longer discolored, then with cold sodium bisulfite solution, and finally 10% sodium carbonate solution. The ether was dried overnight over sodium carbonate before distilling.

Dioxane, because of its complete miscibility with water, could not be purified in this way; instead, it was allowed to stand over activated alumina, which removed most of the peroxides and aldehydes. (Activated alumina was likewise found capable of removing all the hydroperoxides and 90% of the aldehydes from a sample of benzyl methyl ether containing originally 0.03 mole of each.) The dioxane from the alumina treatment was then refluxed with metallic sodium, a procedure similarly used for anisole and later even bis-($\alpha$-methylbenzyl) ether.

Except in the case of styrene oxide, which was purified only by distillation, those ethers which were not purified by these methods were used as received from the syntheses outlined previously. Distillations through a simple Claisen head were found to suffice and in fact to be preferable to distillations through the Todd column, especially for the less stable ethers, which underwent partial decomposition upon prolonged heating. The use of a nitrogen atmosphere was found to be unnecessary for those ethers which had been sufficiently purified before the distillation.

## Results

The procedure for running the oxidations has already been given. To test the apparatus, the first ether examined was dibenzyl ether, which was run at 30°, using 0.01 mole % benzoyl peroxide as initiator. From this, it was found that the acid content remained very low and practically constant, that neither the aldehyde nor the peroxide content was directly proportional to the oxygen absorption, and that the rate of oxidation at 30° was too low for purposes of comparing dibenzyl ether with other ethers. Only the beginning of the steady state was reached. The initial rate seemed sufficiently constant to suggest that this stage of the oxidation could be handled by kinetics if the data were reproducible. A second run using dibenzyl ether showed essentially the same results, indicating that a kinetic approach at least was not formidable. For the present, it was decided to test the apparatus on dioxane, another ether known to peroxidize readily.

The results obtained with dioxane, *n*-butyl ether, and especially paraldehyde indicated that the apparatus could not be satisfactorily applied to low-boiling ethers without further modifications, consisting at least of devising means for removing ether vapors from the cycling oxygen, perhaps by using a cold trap or possibly by simply slowing the operation of the pump. Similar difficulties of "screening" volatile materials from oxygen led Cooper and Melville (48) to use decanal instead of lower-boiling aldehydes in their study of aldehyde autoxidation. That the presence of these vapors was deleterious was shown vividly by the blackened appearance of mercury in the pump, valves, manometers, and burette. Although the oxygen absorption data were thus invalidated, the peroxide and carbonyl data obtained in the dioxane oxidation were useful in showing an apparent maximum in the carbonyl content (Figure 2). A maximum was not found with other ethers.

Now that the apparatus had been shown to be applicable primarily to compounds having low vapor pressures, the benzyl ethers seemed admirably suited to this investigation. For a kinetic study, dibenzyl ether seemed especially good not only because its oxidation products were well known but also because the point of probable oxidative attack was limited to the $\alpha$-hydrogen atoms. The removal of the hydrogen atom from this position had been assumed, for a working hypothesis, to be the rate-controlling step. To test this, the best mode of attack seemed to be to determine the effect of structure on the oxidation rate by comparing the oxidation rates for a number of these compounds. For the purposes of these comparisons, the ethers were oxidized at 50° in the presence of 0.01% benzoyl peroxide initiator.

The effects of changing the alkyl groups in benzyl alkyl ethers are shown in Figure 3 (straight-chain) and Figure 4 (branched-chain). In the latter, benzyl ethyl ether is included for comparison. These data are summarized in Table II. In general, the hypothesis was supported as evidenced by an increased oxidation rate for compounds in which there was an increased electron density on the $\alpha$-carbon.

Another method of varying the electron density on the $\alpha$-carbon is by the use of ring substituents. Ideally suited to this purpose seemed to be the derivatives of benzyl phenyl ether. When the parent compound,

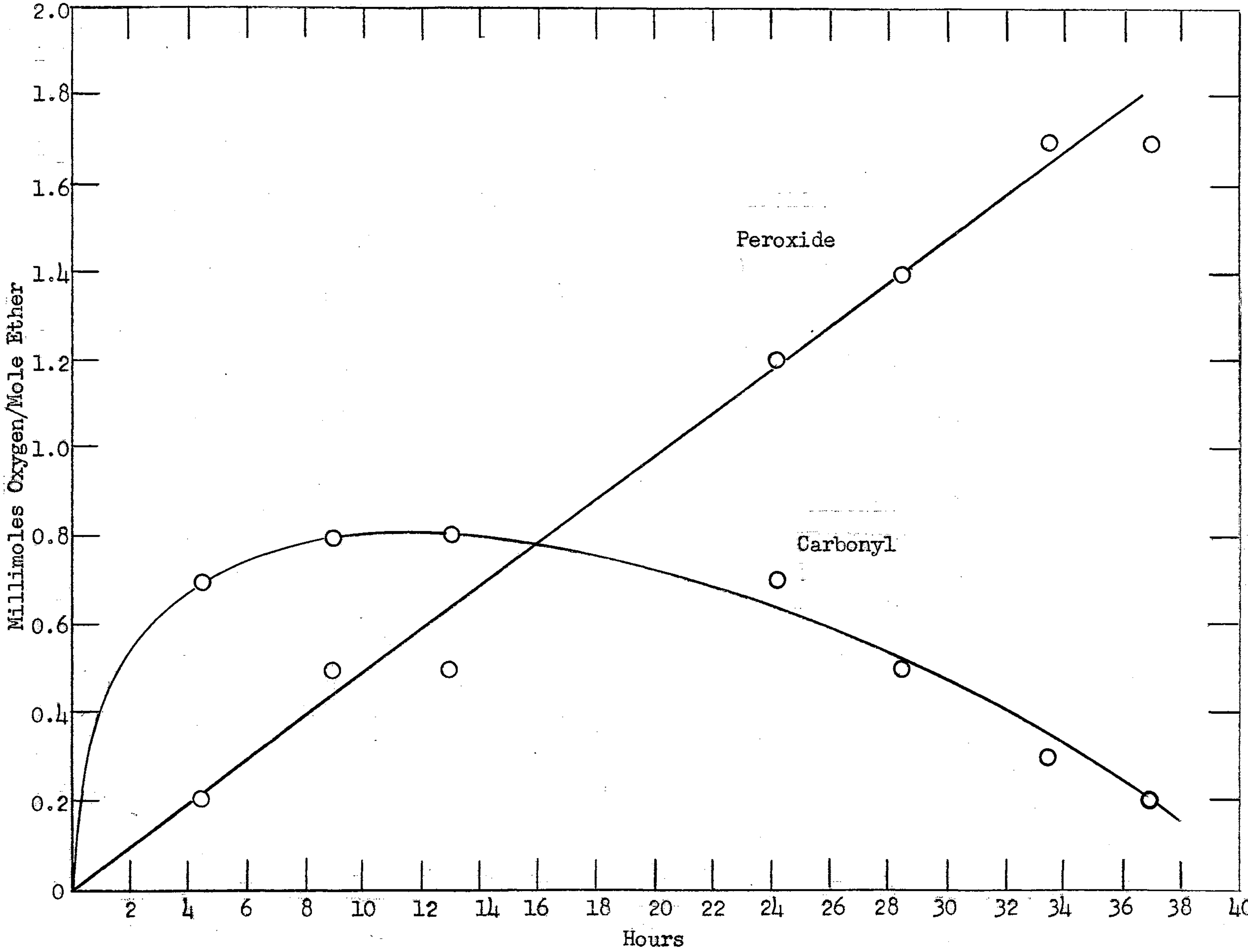


FIGURE 2

AUTOXIDATION OF DIOXANE

FIGURE 3

AUTOXIDATION OF STRAIGHT-CHAIN ALKYL BENZYL ETHERS

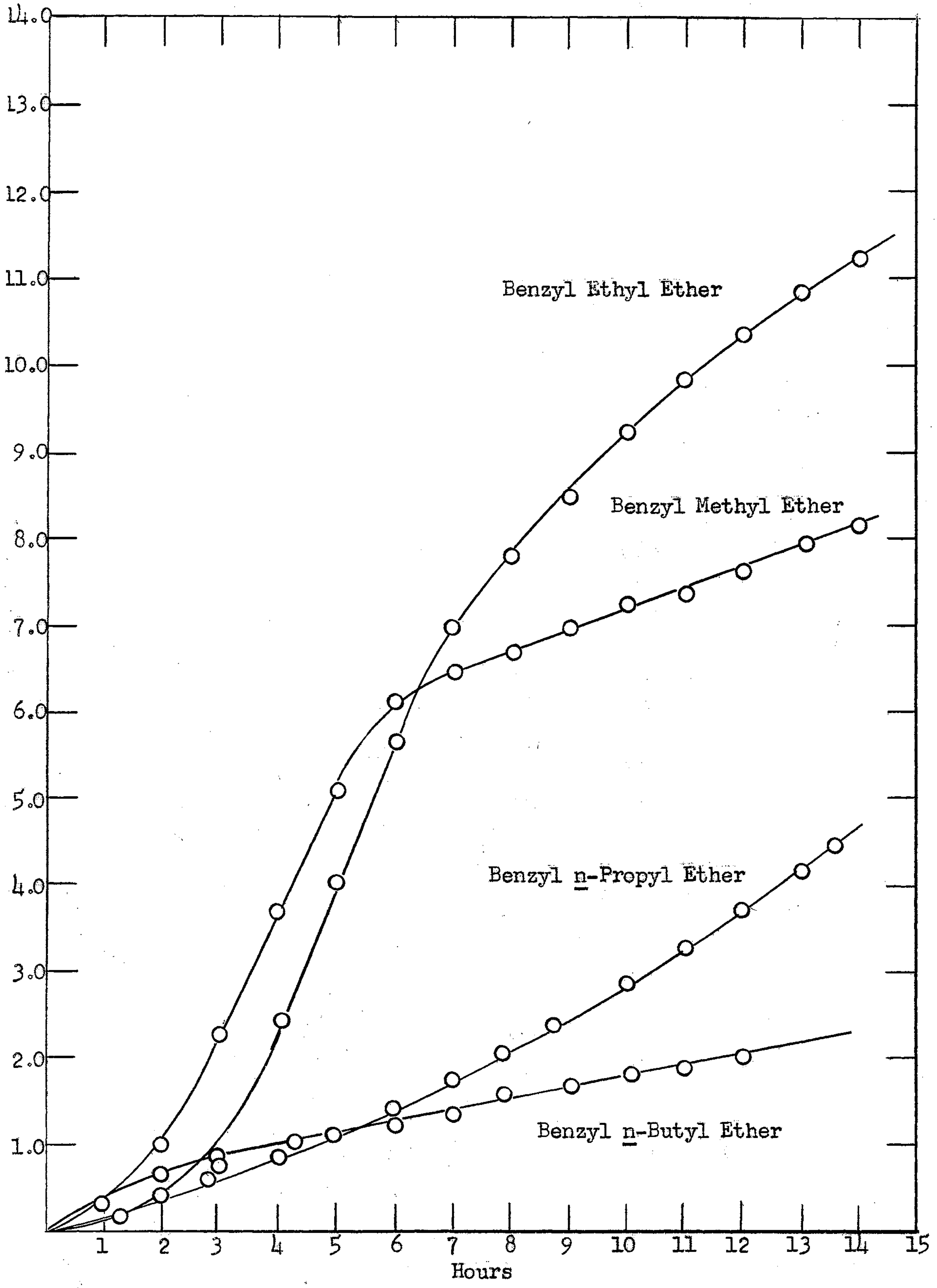
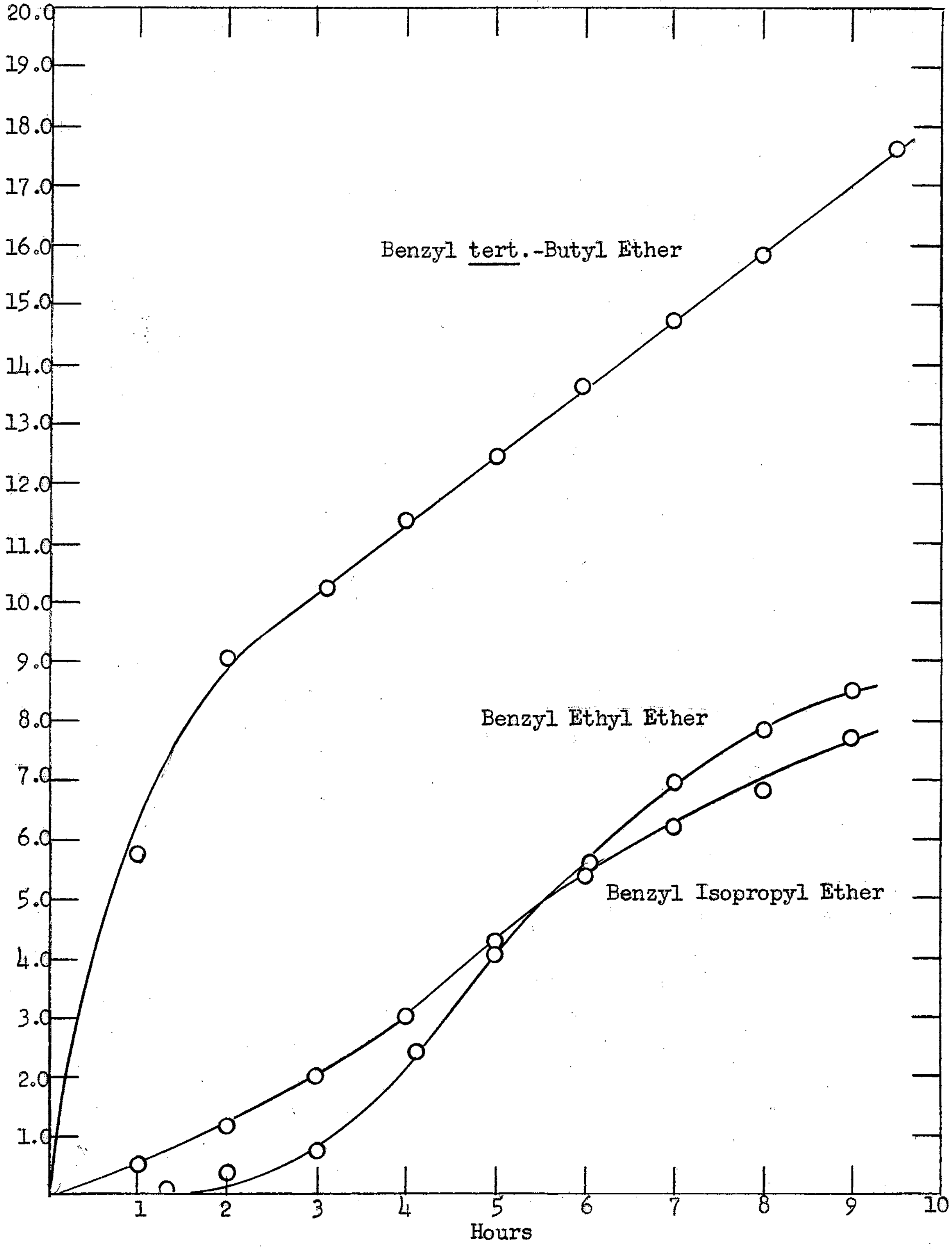


FIGURE 4

AUTOXIDATION OF BRANCHED-CHAIN ALKYL BENZYL ETHERS



## TABLE II

## OXIDATION RATES OF ALKYL BENZYL ETHERS AT 50°

| Alkyl Benzyl Ether | Steady rate x $10^7$ (moles $O_2$/mole ether/sec.) |
|---|---|
| Methyl | 3.92 |
| Ethyl | 4.58 |
| _n_-Propyl | 1.2 |
| _iso_-Propyl | 3.31 |
| _n_-Butyl | 0.372 |
| _tert_-Butyl | 16* |

* The last 90% of the run proceeded at a constant rate of 2.34.

benzyl phenyl ether, could not be induced to oxidize, this course of attack was abandoned in favor of para-substituted benzyl methyl ethers. Figure 5 and Table III present the results of these experiments. For every substituted ether, the steady rate was lower than for the unsubstituted ether. This phenomenon is discussed in more detail later (see "Discussion").

Most of the rates for these and subsequent tables were determined by the "least squares" method, which finds the most probable slope of a straight line through a set of points. If the data plotted on an oversize graph were found not to approximate a straight line, a reasonable straight line was drawn through the points, and its slope was determined from the graph.

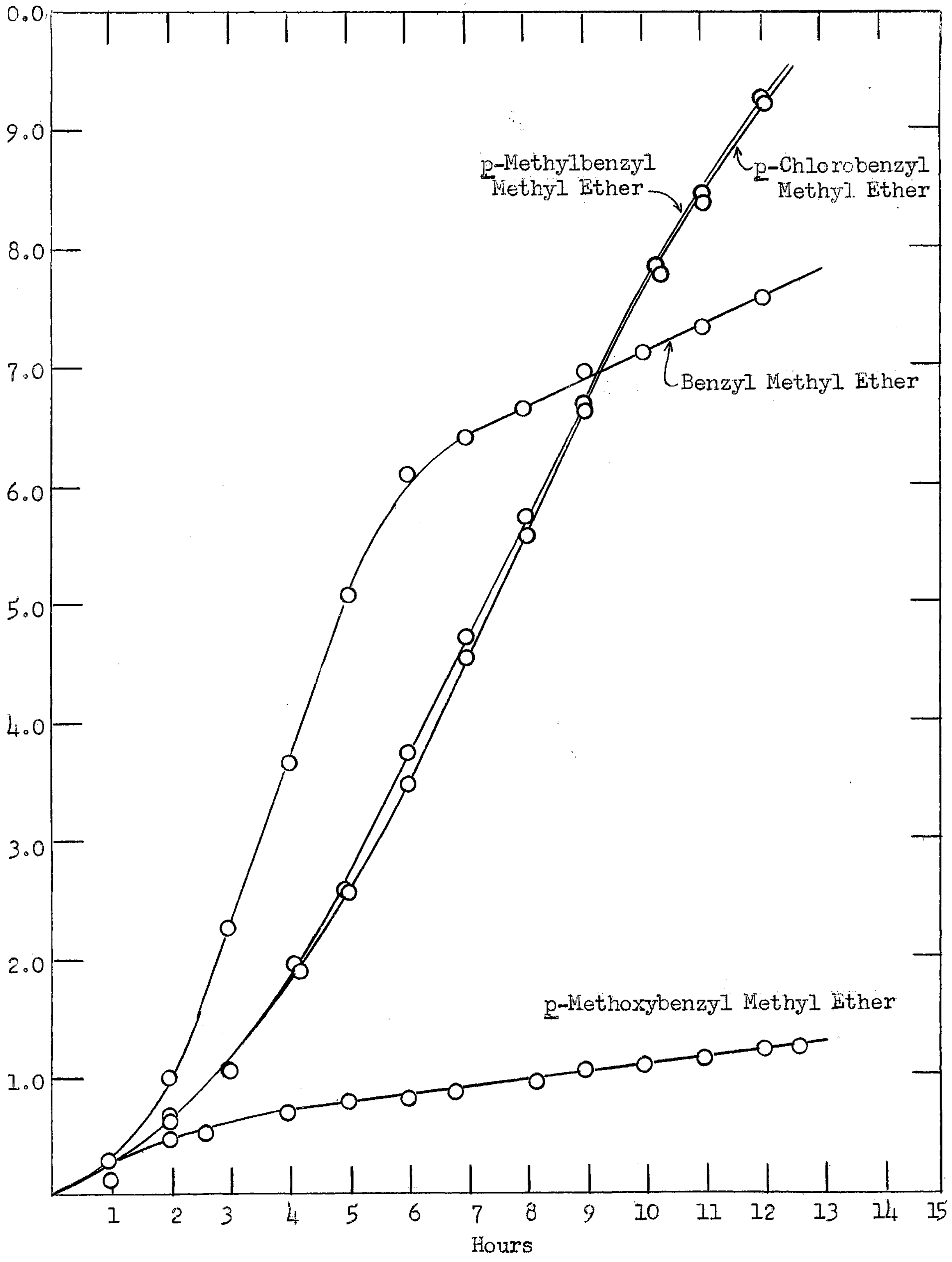
The effects of α-substituents were investigated using two compounds: bis-(α-methylbenzyl) ether and benzaldehyde diethyl acetal. The expectations that the former would oxidize rapidly owing to the high electron density did not materialize. In fact, bis-(α-methylbenzyl) ether could not be induced to oxidize at all. Under more drastic conditions, 100°, decomposition occurred without the formation of peroxides or appreciable carbonyl compounds. A more rigorous purification, including distilling over sodium, still produced an ether which would not oxidize.

The slow oxidation of benzaldehyde diethyl acetal may be due to the retardation effected by ethyl alcohol, one of the reaction products. The freshly distilled compound had a pleasant odor not at all resembling benzaldehyde; but, soon after the oxidation had begun, the aldehyde odor was apparent.

The study of styrene oxide oxidation was undertaken not so much from an electronic consideration of this special type of benzyl ether as from

FIGURE 5

AUTOXIDATION OF PARA-SUBSTITUTED BENZYL METHYL ETHERS



## TABLE III

## OXIDATION RATES OF PARA-SUBSTITUTED BENZYL METHYL ETHERS AT 50°

| *para* Substituent | Steady rate x $10^7$ (moles $O_2$/mole ether/sec.) |
|---|---|
| Hydrogen | 3.92 |
| Methoxy | 1.89 |
| Chloro | 2.94 |
| Methyl | 2.83 |
| Nitro | 0 |

a desire to see how epoxides behaved. No rate data were available in the literature. Although both the peroxide and carbonyl methods were inapplicable, the oxygen absorption curve was satisfactory. This curve together with that of benzaldehyde diethyl acetal is shown in Figure 6. Tetralin and dibenzyl ether are included for comparison. These data also appear in Table IV.

Unfortunately, tetralin did not serve well for comparison; under the rather mild conditions used for ether oxidation, tetralin oxidized very slowly and did not reach the "steady state." Even the steady-state rates are apparently not easily duplicated by different investigators. For example, Woodward and Mesrobian (241) found the rate at 50° to be 4.09 moles $O_2$/liter/sec. x $10^{-6}$ (or about 5.6 moles $O_2$/mole hydrocarbon/sec. x $10^{-7}$); Bamford and Dewar (10), however, found the rate at 45° to be 5.97 moles $O_2$/liter/sec. x $10^{-7}$ (about 0.81 moles $O_2$/mole hydrocarbon/sec. x $10^{-7}$). The temperature difference of $5^{\circ}$ cannot possibly be responsible for such a difference in observed rates.

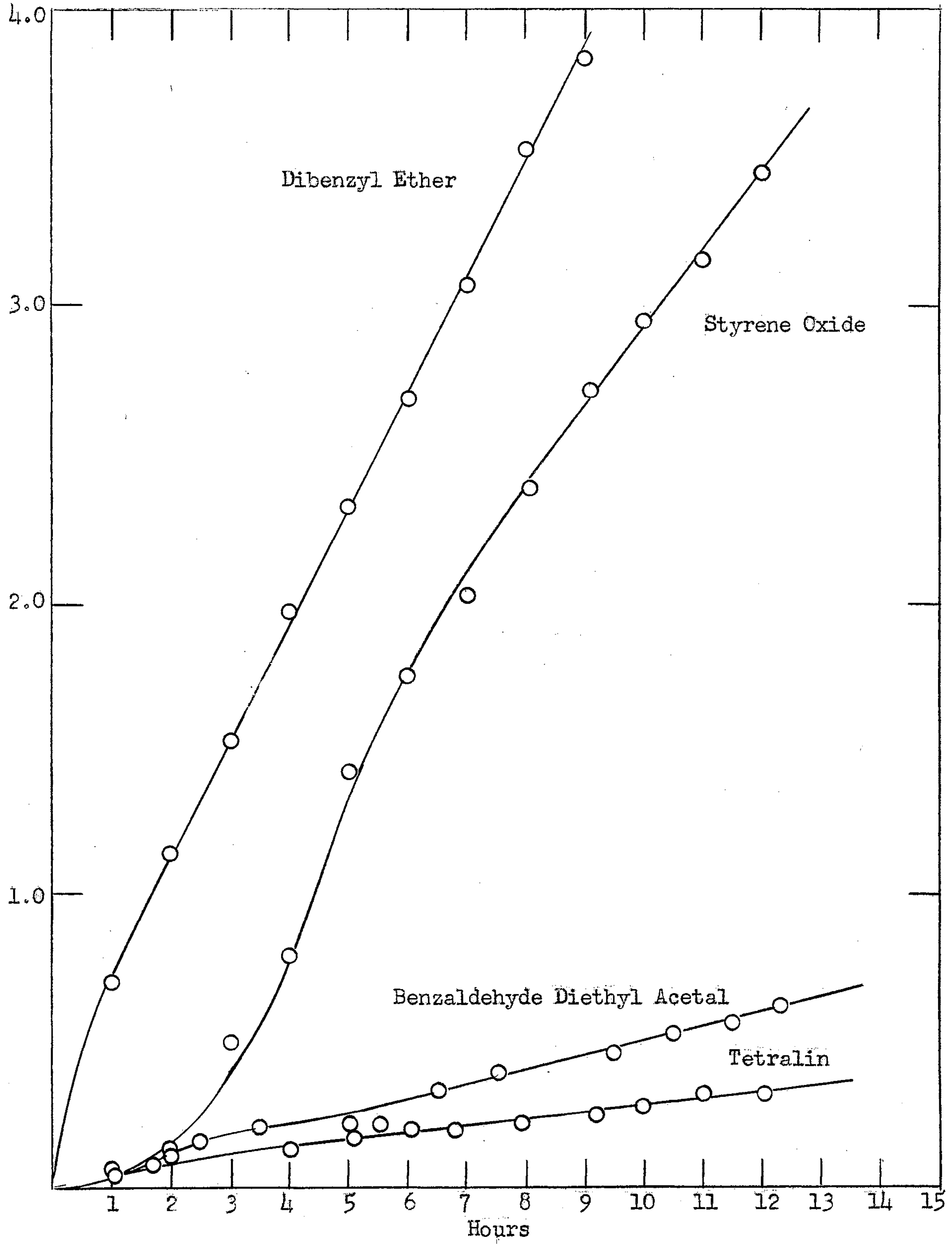
For the reasons cited previously, the ether most extensively studied was dibenzyl ether. First, in order to determine the activation energy, the oxidations were run at several temperatures. Figure 7 and Table V summarize these data. As evident from Figure 8, plotting log rate versus $\frac{1}{T} \times 10^3$ gave a straight line, as it should according to the equation

$$\log k = -\frac{\Delta E}{2.30R}\left(\frac{1}{T} \times 10^3\right) + I$$

which is a logarithmic form of the Arrhenius equation. The use of rates instead of rate constants is justifiable so long as the concentrations of oxygen and ether remain essentially constant. Using the least squares

FIGURE 6

AUTOXIDATION OF COMPOUNDS RELATED TO BENZYL ETHERS



## TABLE IV

## OXIDATION RATES OF COMPOUNDS RELATED TO BENZYL ETHERS AT 50°

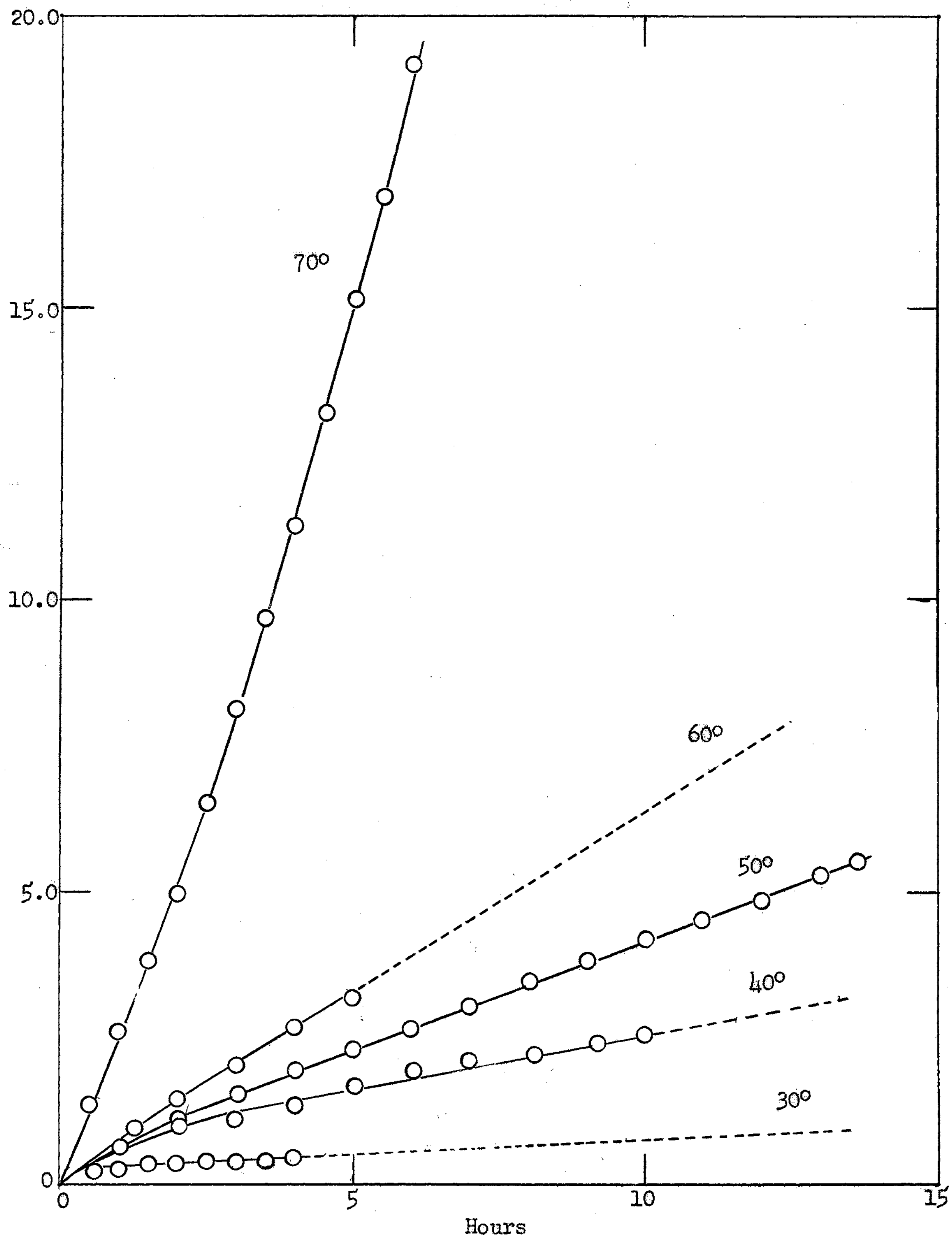
| Compound | Initial rate x $10^7$ (moles $O_2$/mole ether/sec.) |
|---|---|
| Bis-($\alpha$-methylbenzyl) ether | 0 |
| Benzaldehyde diethyl acetal | 0.13 |
| Styrene oxide | 1.3* |
| Tetralin** | 0.164 |

* Steady rate

** For comparison

FIGURE 7

AUTOXIDATION OF DIBENZYL ETHER



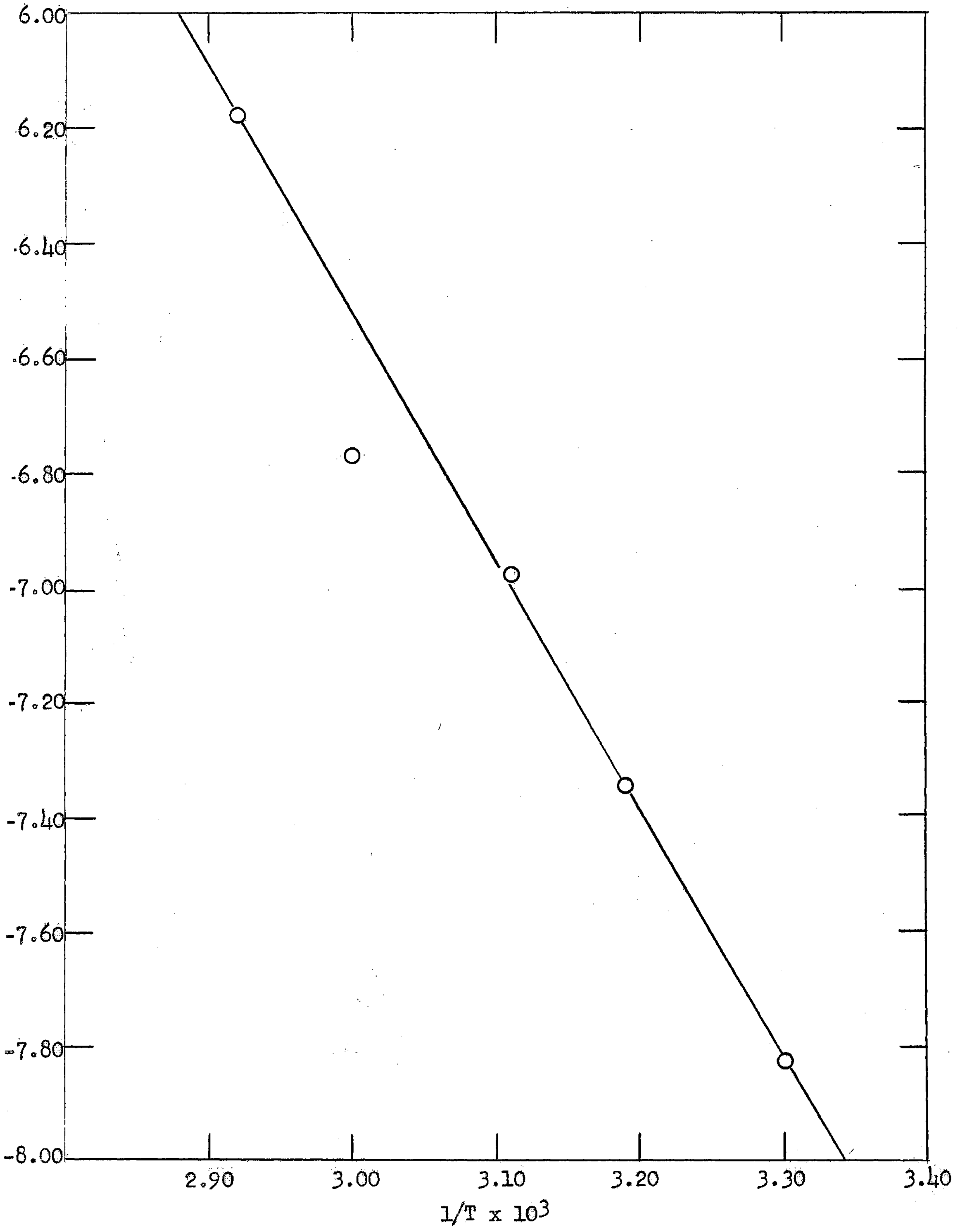
## TABLE V

## OXIDATION RATES OF DIBENZYL ETHER

| Temperature, °C | Initial rate x $10^7$ (moles $O_2$/mole ether/sec.) |
|---|---|
| 30 | 0.150 |
| 40 | 0.453 |
| 50 | 1.05 |
| 60 | 1.70 |
| 70 | 6.70 |

FIGURE 8

DIBENZYL ETHER. ARRHENIUS EQUATION.



method (and omitting the rate at 60°), the slope was found to be -4.06. From this,

$$\text{slope of line} = -\frac{\Delta E}{2.303R} = -4.06$$

$$\text{Energy of activation} = (4.06)(2.30)(R)$$

$$= 17.8 \text{ kcal./mole}$$

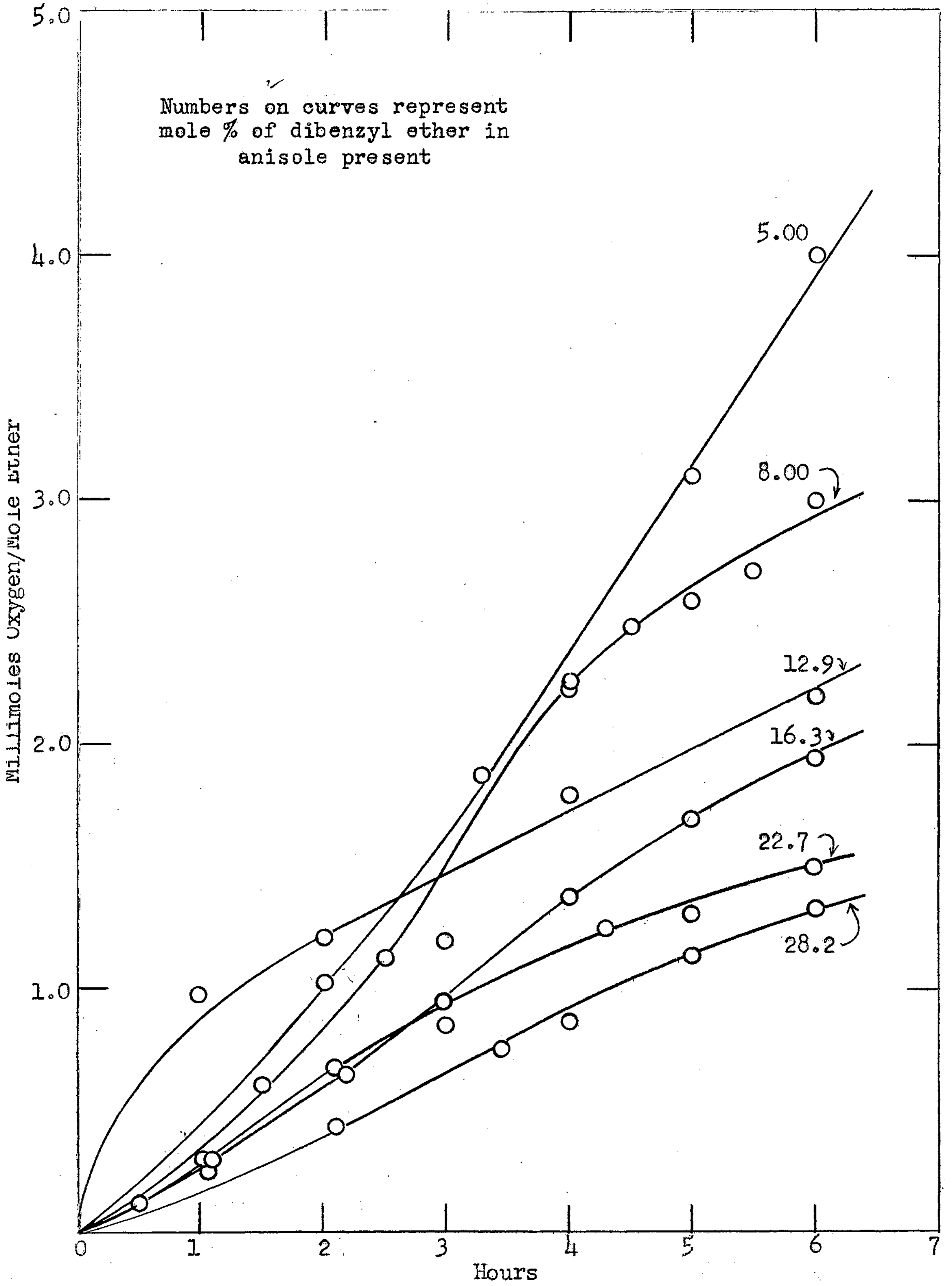
In the discussion which follows this experimental section, it will be shown that the various possible mechanisms when treated by kinetics yield mathematical expressions differing principally in powers of the ether concentration, i.e. $(RH)^n$. To study the effects of concentration, the first problem was one of finding a suitable solvent. Gisser (96, 190), in his study of the autoxidation of saturated aliphatic diesters, used diethyl adipate, which oxidized slowly compared to the branched-chain esters studied. For this present work, however, it seemed preferable to use a solvent which did not itself undergo oxidation; the number of extraneous reactions thus could be held to a minimum.

Three solvents were investigated--anisole, nitrobenzene, and acetic acid--none of which absorbs oxygen under the experimental conditions. Nitrobenzene, which had not previously been used as a solvent in autoxidation reactions, was shown to retard the reaction somewhat but not enough to make the oxygen absorption immeasurable. Acetic acid exerted a slight acceleratory effect. The most promising solvent was anisole, which Gibbs (93) found to be inert even to ozone. Bartlett and Nozaki (15) showed that anisole acted like "normal" aromatic compounds in the benzoyl peroxide decomposition. That anisole did not retard isopropyl ether oxidation was reported by Katsuno (119). Anisole, of course, shares these properties with many other phenyl ethers; but a final consideration leading to its adoption as the solvent for this work was the ease of purification: refluxing with sodium followed by a facile distillation at atmospheric pressure sufficed. To insure easily measurable rates of oxygen absorption, the solutions of dibenzyl ether in anisole were run at 70°. The absorption curves are given in Figure 9. Rate data are listed in Table VI. The two plots of data which most nearly gave a straight line are shown in Figures 10 and 11. While the first treats the hydroperoxide concentration as a constant and the second does not, both plots indicate that the termination is accomplished by the interaction of peroxyl and ether radicals. The mathematical details are given in the "Discussion."

The relative increase in rate with dilution (observe the negative slopes in Figures 10 and 11) indicated an increasing chain length, suggesting in turn the possibility of a wall-termination step. To investigate this wall effect further, the dibenzyl ether oxidations were run in the presence of Pyrex glass wool and silica gel. The Pyrex wool was cleaned with acetone, washed thoroughly with water, treated next with dilute nitric acid, and finally washed repeatedly with distilled water. After it had been dried at 110° for two days, the Pyrex wool showed a marked alkaline reaction when placed in water containing a little phenolphthalein. In spite of this, a run was made using 15 g. of the Pyrex wool for a mole of the ether. Table VII shows that the rate of this oxidation was quite low. To make certain that the effect was definitely due to the surface extent and not to the basic nature of the surface, a

FIGURE 9

AUTOXIDATION OF DIBENZYL ETHER IN ANISOLE



## TABLE VI

## OXIDATION RATES OF DIBENZYL ETHER IN ANISOLE AT 70°

| Mole Fraction of Dibenzyl Ether | Steady rate x $10^7$ (moles $O_2$/mole ether/sec.) |
|---|---|
| 0.0498 | 2.50 |
| 0.0800 | 2.1 |
| 0.163 | 1.17 |
| 0.227 | 1.0 |
| 0.282 | 0.678 |

## FIGURE 10

## AUTOXIDATION OF DIBENZYL ETHER IN ANISOLE

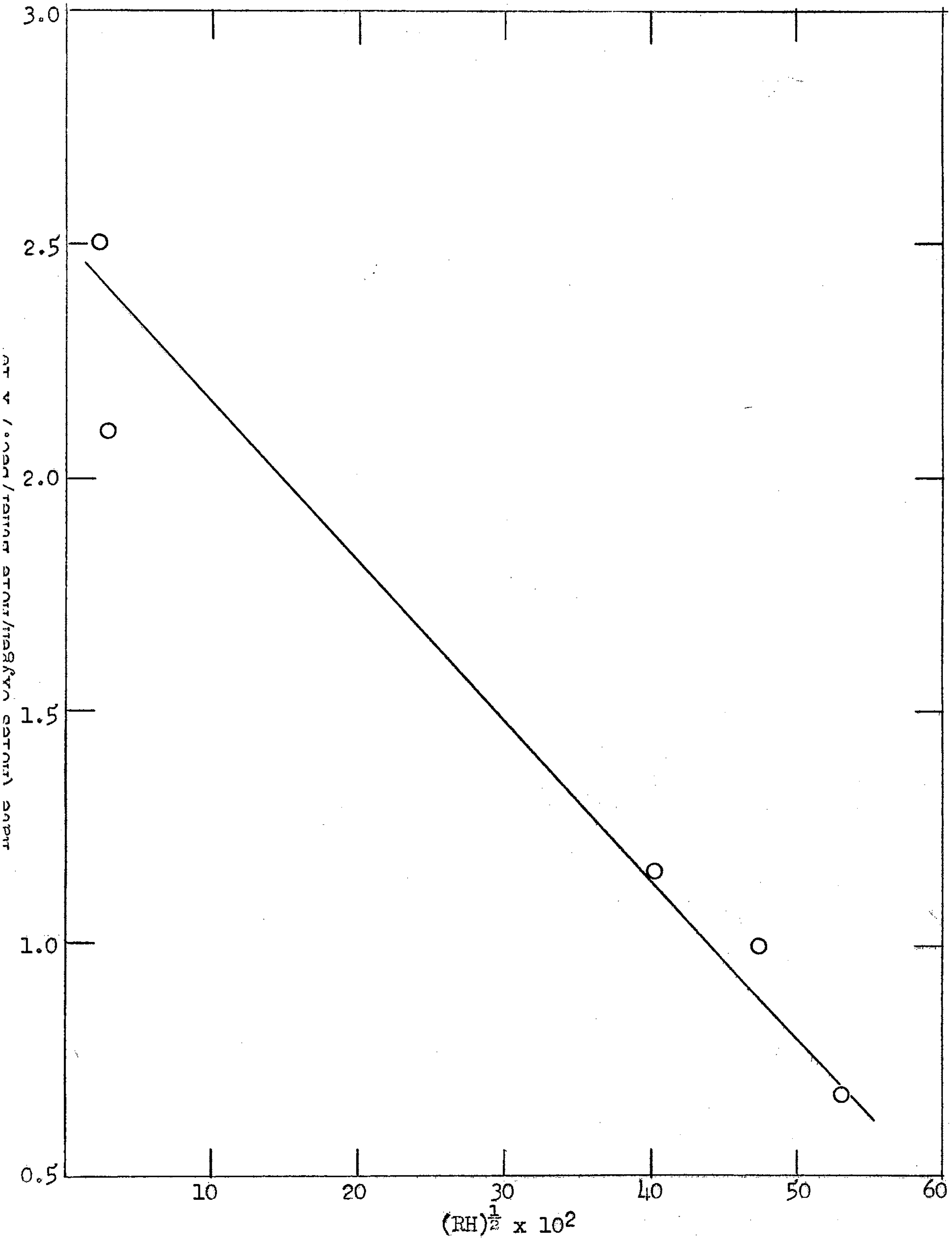
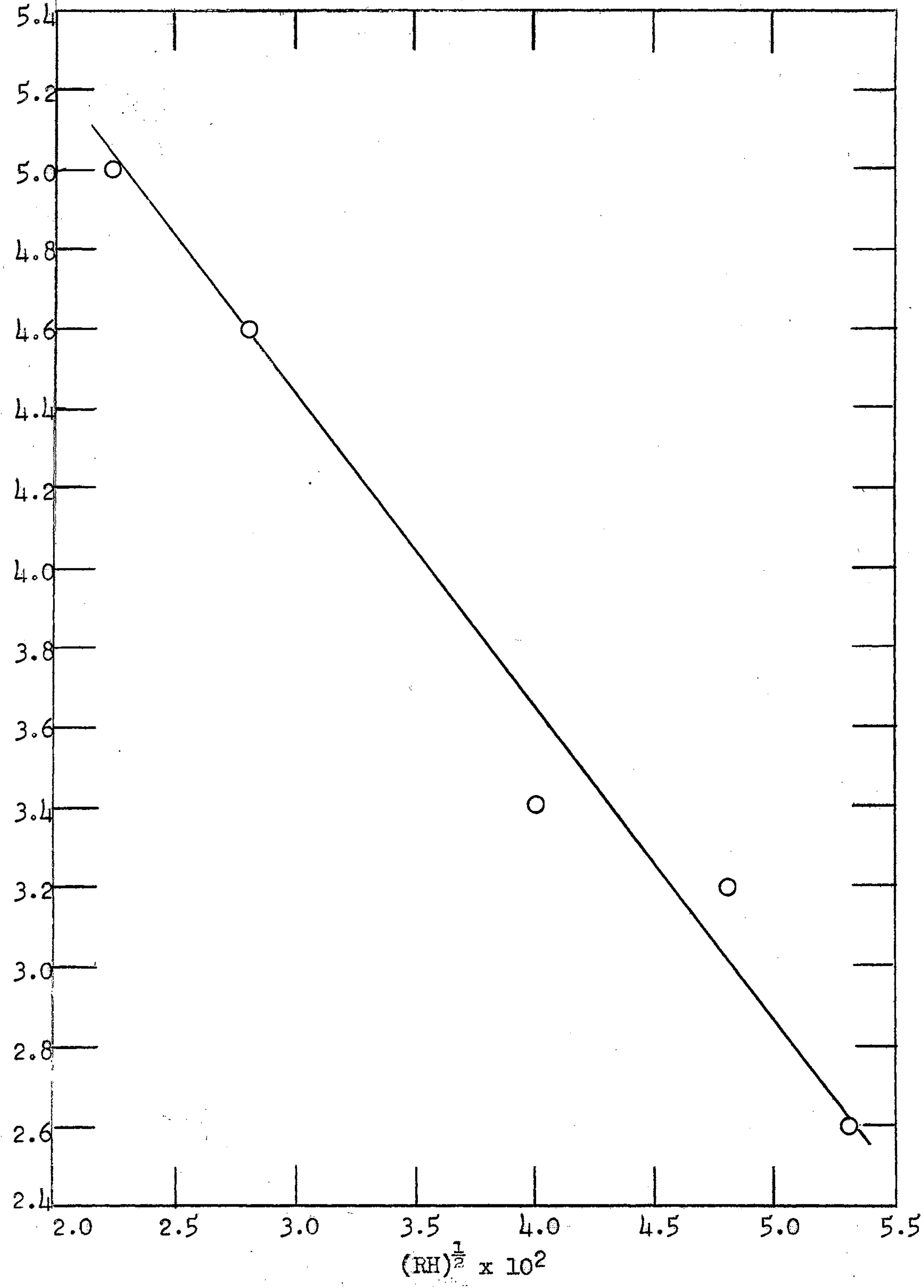


FIGURE 11

AUTOXIDATION OF DIBENZYL ETHER IN ANISOLE



## TABLE VII

## OXIDATION RATES OF CATALYZED AND INHIBITED DIBENZYL ETHER AT 50°

| Additive and Concentration (mole %) | Initial rate x $10^7$ (moles $O_2$/mole ether/sec.) | Steady rate x $10^7$ (moles $O_2$/mole ether/sec.) |
|---|---|---|
| Iron metal (powder), 2% | 1.5 | 4.1 |
| Mercury metal, 2% | 0.02 | |
| Manganese acetate, 0.02%* | 2.25 | 32.8 |
| Silica gel, 50 g./mole | 0.08 | |
| Pyrex glass wool, 15 g./mole | 0.03 | |
| Pyrex glass wool, 15 g./mole, + acetic acid, 5% | 0.372 | |

* No initiator

little acetic acid was added. Unexpectedly, the rate increased considerably, although it still remained low. An acidic surface was next tried using silica gel (Davison Chemical Corp., 200-mesh), treated in the same way as the Pyrex wool. In a concentration of 50 g./mole ether, the silica get produced a very low rate (see Table VII).

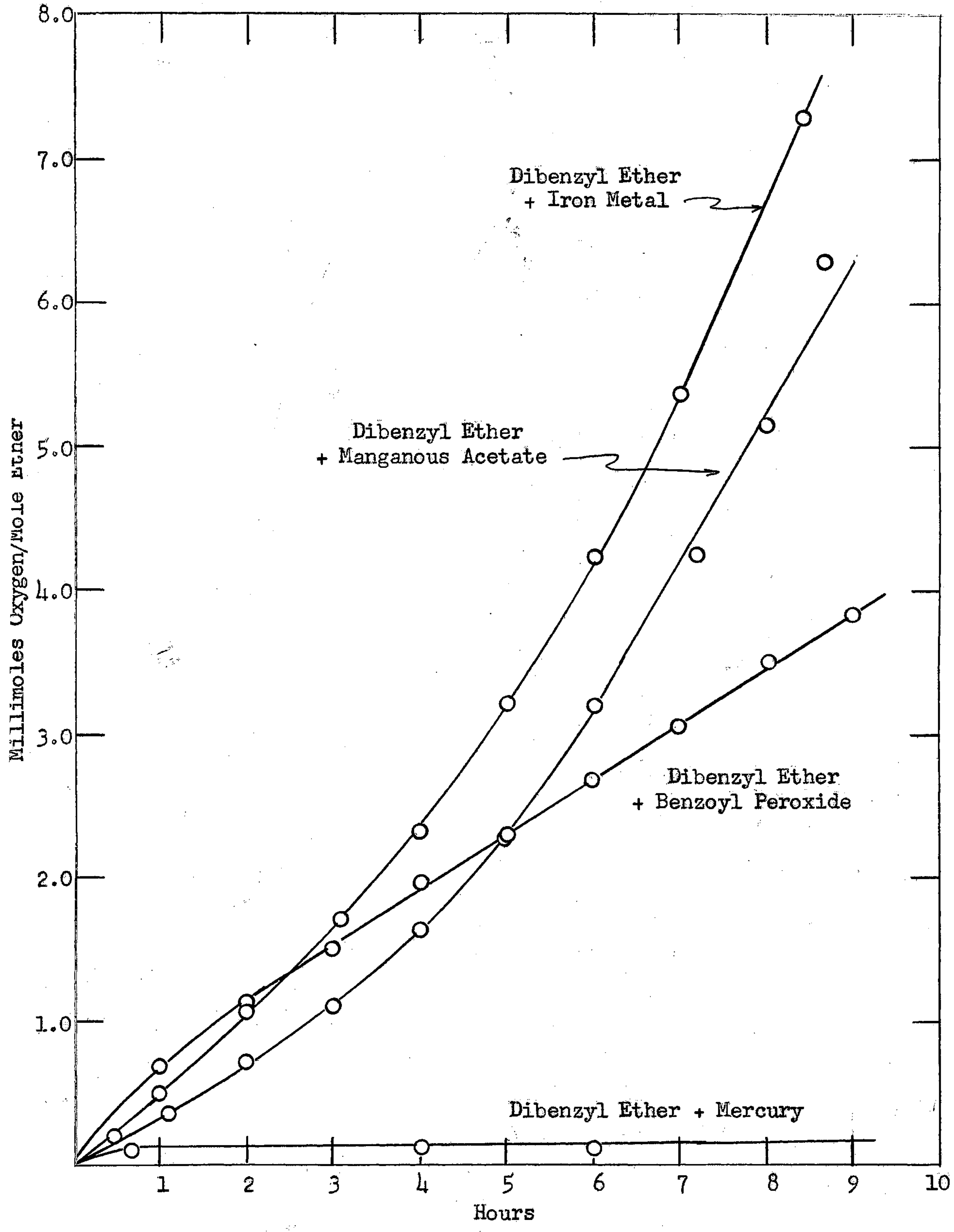
The rates of various other catalyzed and inhibited benzyl ether oxidations are also given in Table VII. Curves showing the effects of iron metal ("Iron by Hydrogen," Reagent grade, Merck & Co., Inc.), mercury, and manganous acetate tetrahydrate (C. P., J. T. Baker Chemical Co.) are given in Figure 12. Mercury completely inhibited the uninitiated oxidation and retarded the benzoyl peroxide-initiated reaction. In both reactions, the mercury recovered still possessed a bright metallic luster. A very rapid peroxidation did occur when the ether-mercury mixture was permitted to stand in bright sunlight at room temperature, 27°. The mercury was oxidized under these conditions.

The peroxide and carbonyl determinations made on most of the ethers were of little value because the rates of oxygen absorption as indicated by the sum of these determinations were invariably higher than those actually found. This phenomenon will be discussed in more detail later. The most important information obtained from these analyses was that the peroxide concentrations did not pass through maxima during the oxidations even though in some cases the reaction was extended beyond the "steady state."

Two runs were made with air instead of oxygen, but the rates remained essentially the same.

FIGURE 12

CATALYZED OXIDATION OF DIBENZYL ETHER



# DISCUSSION

## Radical Chains and the Activation Energy

There can be little doubt that ether autoxidation is a free-radical chain reaction. Certainly the effectiveness of benzoyl peroxide, a free-radical initiator, and manganous acetate, a known catalyst for free-radical oxidations, would have been much less if the reactions had followed a non-radical course. The low activation energy, 17.8 kcal., also supports belief in a chain reaction. It is unfortunate that the activation energies for oxidations of other benzyl ethers are not available; but, even in the case of the extensively studied aliphatic ethers, activation energies are available for only one, isopropyl ether. In the temperature range 10 to 50°, the activation energy was reported to be 12.5 kcal. (152); in the vapor phase at 360 to 400°, it was found to be 22 kcal. (40). The low activation energy for the liquid-phase oxidation is a definite indication of a long chain reaction, despite suggestions to the contrary by Neiman and co-investigators (159) in their interpretations of the weak inhibitory effects of common antioxidants in isopropyl ether. Ethyl ether oxidation is also believed to be a long chain reaction (182).

## Kinetics

The initiation step in ether autoxidation may be assumed to be the homolytic $\alpha$-hydroperoxide decomposition. Letting $R\cdot = R'\dot{C}HOR''$,

$$ROOH \xrightarrow{ka} RO\cdot + \cdot OH \qquad (a)$$

The hydroxyl and alkoxyl radicals then interact with the substrate to produce ether radicals as follows:

$$RH + \cdot OH \xrightarrow{k_1} R\cdot + HOH \qquad \text{(i)}$$

The propagation, or long chain reaction, involves both absorption of oxygen and regeneration of R·:

$$R\cdot + O_2 \xrightarrow{k_2} ROO\cdot \qquad \text{(ii)}$$

$$ROO\cdot + RH \xrightarrow{k_3} ROOH + R\cdot \qquad \text{(iii)}$$

The termination reactions may involve many different combinations. Considering that the ease of ether oxidation requires an ease of radical formation (or hydrogen atom abstraction) and that the reactivity of the radical produced is inverse to the ease of radical formation (17), the ether radicals must be present in concentrations larger than those ordinarily encountered in hydrocarbon oxidations. This was reported by Eastwood and Hinshelwood (61) for vapor-phase oxidation of ethers. Terminations involving these must then be possible and should not be overlooked.

Because even the highly stabilized triphenylmethyl radicals react readily with oxygen, the reactions of R· with oxygen should occur rapidly; consequently, the peroxyl radicals thus produced must represent most of the radical concentration.

From these considerations, the following termination reactions seem most probable:

$$ROO\cdot + \cdot OH \xrightarrow{k_4} ROH + O_2 \qquad \text{(iv)}$$

$$ROO\cdot + R\cdot \xrightarrow{k_5} ROOR \qquad \text{(v)}$$

$$2ROO\cdot \xrightarrow{k_6} ROOR + O_2 \qquad \text{(vi)}$$

To these must be added surface termination reactions, for it was shown that both Pyrex wool and silica gel retard the oxidation. Letting "$\underline{S}$" represent the surface,

$$ROO\cdot + \underline{S} \xrightarrow{k_7} \text{Products} \qquad \text{(vii)}$$

$$R\cdot + \underline{S} \xrightarrow{k_8} \text{Products} \qquad \text{(viii)}$$

Reactions (iv), (v), and (vi), if they were wall reactions, would be kinetically indistinguishable from the homogeneous reactions.

The other most probable wall reactions,

$$\cdot OH + \underline{S} \longrightarrow \text{Products}$$

and

$$2\cdot OH + \underline{S} \longrightarrow \text{Products}$$

may be the ones actually responsible for the observed low rate; but, since these are destructions of an initiator, the apparent order of the overall reaction would not change.

From the termination reactions, certain mathematical expressions may be derived in the following way. When oxygen is absorbed at a constant rate, that is,

$$-d(O_2)/dt = \text{a constant}$$

the long-chain cycle represented by equations (ii) and (iii) proceeds at a constant rate. Under these conditions, both $-d(R\cdot)/dt$ and $-d(ROO\cdot)/dt$ are assumed equal to zero; furthermore, the rate of initiation is equal to the rate of termination.

When equation (iv) is the termination step,

$$\text{initiation} = \text{termination}$$

$$k_1(RH)(\cdot OH) = k_4(ROO\cdot)(\cdot OH) \tag{ix}$$

$$(ROO\cdot) = \frac{k_1}{k_4}(RH) \tag{x}$$

$$\frac{d(ROO\cdot)}{dt} = 0 = k_2(R\cdot)(O_2) - k_3(ROO\cdot)(RH) - k_4(ROO\cdot)(\cdot OH)$$

$$k_2(R\cdot)(O_2) = k_3(ROO\cdot)(RH) + k_4(ROO\cdot)(\cdot OH) \tag{xi}$$

When the chain length is great, the termination rate occurring in equation (xi) may be neglected (17):

$$k_2(R\cdot)(O_2) \simeq k_3(ROO\cdot)(RH) \tag{xii}$$

thus

$$-\frac{d(O_2)}{dt} = k_2(R\cdot)(O_2) \approx k_3(ROO\cdot)(RH) \tag{xiii}$$

Substituting into this equation the value of (ROO•) from equation (x),

$$-\frac{d(O_2)}{dt} = \frac{k_1 k_3}{k_4}(RH)^2 \tag{xiv}$$

The other termination reactions were treated similarly, and the results are listed in Table VIII.

Plotting the data according to the rate equations in Table VIII gave most nearly a straight line for rate vs. $(RH)^{\frac{1}{2}}$ (see Figure 10). The results were a little better still when $(\text{rate})^{\frac{1}{2}}$ was plotted against $(RH)^{\frac{1}{2}}$ (see Figure 11). For Figure 10 it was assumed that the hydroperoxide

## TABLE VIII

## OXIDATION RATES ACCORDING TO TERMINATION MECHANISMS

| Equation | Termination Reaction | $\frac{-d(O_2)}{dt}$ |
|---|---|---|
| (iv) | $ROO\cdot + \cdot OH$ | $\frac{k_1 k_3}{k_4}(RH)^2$ |
| (v) | $ROO\cdot + R\cdot$ | $\left[\frac{k_a k_2 k_3}{k_5}(ROOH)(O_2)\right]^{\frac{1}{2}}(RH)^{\frac{1}{2}}$ |
| (vi) | $2ROO\cdot$ | $k_3\left[\frac{k_a}{k_6}(ROOH)\right]^{\frac{1}{2}}(RH)$ |
| (vii) | $ROO\cdot + \underline{S}$ | $k_a(ROOH) + \frac{k_a k_3}{k_7}(ROOH)(RH)$ |
| (viii) | $R\cdot + \underline{S}$ | $\frac{k_a k_2}{k_8}(ROOH)(O_2)$ |

concentration remained constant in the equation derived for reaction (v):

$$-\frac{d(O_2)}{dt} = \left[\frac{k_a k_2 k_3}{k_5}(ROOH)(O_2)\right]^{\frac{1}{2}}(RH)^{\frac{1}{2}}$$

This, of course, is not a valid assumption but was used because the actual concentration was not known. In fact, it is much more reasonable to assume that all of the absorbed oxygen appears as the hydroperoxide, for this is known to be true for a number of different types of compounds. Ritchie and co-workers (191) found that in the autoxidation of methyl dehydroabietate at 80° the hydroperoxide is the exclusive product until about 30% of the ester has reacted. Williamson (238) reported that 98% of the absorbed oxygen appeared as peroxides in the autoxidation of methyl linoleate. Sully (209) found that in the oxidation of tetralin and ethylbenzene even at 100° all of the absorbed oxygen forms hydroperoxides. Robertson and Waters (196) verified these results for tetralin, and George and Robertson (92) stated furthermore that 90% of the oxygen uptake in the steady state still produces hydroperoxides. If, then, it is assumed that all of the absorbed oxygen appears as the hydroperoxide, the hydroperoxide concentration is proportional to the oxidation rate,

$$(ROOH) \propto \frac{d(O_2)}{dt}$$

so

$$(ROOH)^{\frac{1}{2}} = k' \left[\frac{d(O_2)}{dt}\right]^{\frac{1}{2}}$$

where k' is the proportionality constant. Substituting this value of $(ROOH)^{\frac{1}{2}}$ into the equation gives

$$-\left[\frac{d(O_2)}{dt}\right]^{\frac{1}{2}} = k(O_2)^{\frac{1}{2}}(RH)^{\frac{1}{2}}$$

where $k = \left[\frac{k_a k_2 k_3 k'}{k_5}\right]$.

## The Effects of Structure on Reactivity

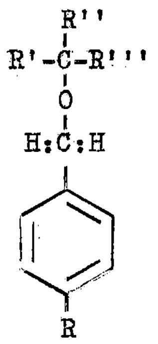
The rate-determining step in a series of reactions will be the slowest reaction. Starting with a radical-free ether, the rate of oxidation will depend upon the rate of initiation. As the reaction progresses, the relative amounts of initiator needed become less and less until, at the steady state, the initiator needs to furnish radicals only to replace those destroyed by terminations. During this steady state, the oxidation rate should depend upon one of the steps of the long-chain cycle, that is, either

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

or

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

Because reactions between radicals and oxygen occur readily, the first reaction usually is considered less important than the second as the rate-determining step. The ease of hydrogen-atom abstraction will depend upon the availability of electrons around the α-carbon. In the general benzyl ether structure



the α-carbon electron density may be varied in two ways: the R', R'', and R''' groups may be changed from R' = R'' = R''' = H to three alkyl groups; and the *para*-R groups may be changed from H to either an electron-donor or an electron-acceptor group.

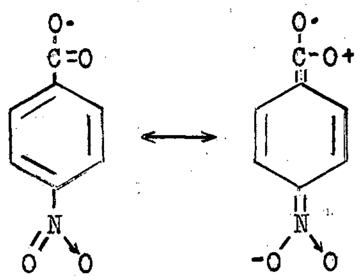
The first type of change showed in general that increasing the electron density around the α-carbon atom increases the oxidizability, thus supporting α-hydrogen abstraction as the rate-determining step. This finding is in agreement with that Chamberlain and Walsh (40) for the vapor-phase oxidation of isopropyl ether. The order of decreasing oxidizability is *tert*.-butyl $\gg$ ethyl $>$ methyl $>$ isopropyl $>$ *n*-propyl $>$ *n*-butyl. The reason for the relatively slow oxidation of benzyl isopropyl ether is not known. Oxidations of the alkyl groups are also possible and should occur to a limited extent. The two most susceptible to attack would be isopropyl and ethyl, and the two most resistant would be methyl and *tert*.-butyl.

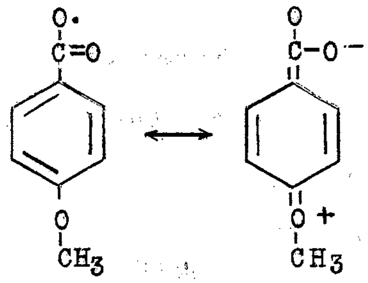
For the second method of varying electron densities, the basic structure chosen was again methyl benzyl ether. The decreasing order of reactivity found was *p*-H $>$ (*p*-Cl and *p*-CH$_3$) $>$ *p*-CH$_3$O $\gg$ *p*-NO$_2$; the *para*-substituted ether in every case reacted more slowly than the unsubstituted ether. The expected order of reactivity, according to Hammett's group constants, was *p*-CH$_3$O $>$ *p*-CH$_3$ $>$ *p*-H $>$ *p*-Cl $>$ *p*-NO$_2$.

Deviations from this order agree with the findings of Pausacker (172), who found that the phenylhydrazones of *meta*- and *para*-substituted benzaldehydes always oxidize more slowly than the unsubstituted compound, and Bogert and Davidson (26), who found that anisaldehyde and piperonal both oxidize much more slowly than unsubstituted benzaldehyde. Lucchi (137) reported similar results for anisaldehyde, but the *meta*- and *ortho*-methoxybenzaldehydes oxidized faster than benzaldehyde. More recently, Walling and McElhill (220) studied the autoxidation of benzaldehyde and substituted benzaldehydes by a series of competitive reactions using as a solvent acetic anhydride, which reacted with the perbenzoic acid formed. Under these conditions, the substituents gave a general agreement with Hammett's equation.

Jaffe (117) assumed that the frequent deviations of free-radical reactions from the Hammett equation were due to the greater difficulty in obtaining rate constants.

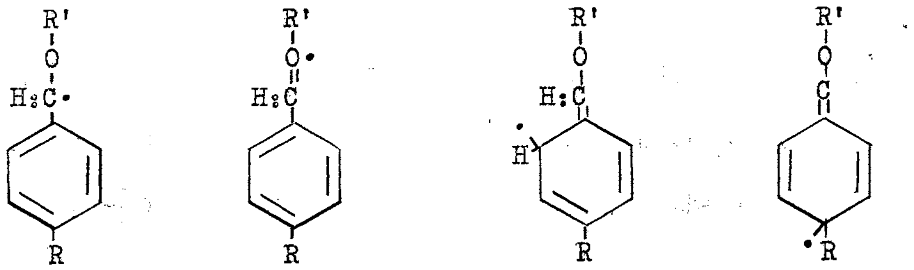
A different view has been expressed concerning the decomposition of benzoyl peroxide. Wieland and Rasuwajew (235) found that the decomposition of an unsymmetrical dibenzoyl peroxide (i.e., one containing an unsubstituted and a para-substituted benzoyl group) in benzene gives biphenyl and a para-substituted benzoic acid, showing that decarboxylation occurred preponderantly in the unsubstituted benzoate radical. Leffler (134) interpreted this as supporting the free-radical point of view in which the intermediate radicals may be resonance-stabilized. For the p-nitrobenzoate and p-methoxybenzoate radicals, the following forms were suggested:



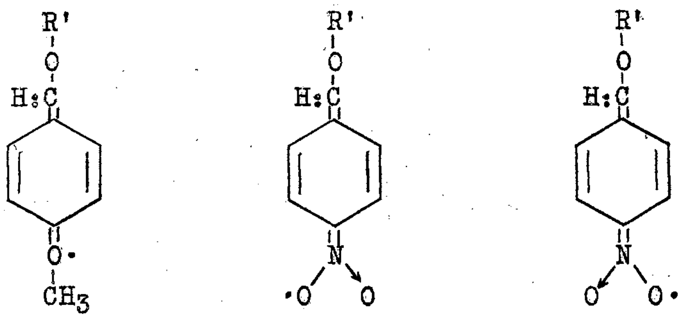


For some reason, Leffler failed to give resonance structures in which the free electron participated.

The same types of resonance structures may exist in the case of the ether radicals; but resonance structures involving the free electron are undoubtedly important also. In general, these are the following:



The para substituents may also participate:



The ease of hydrogen-atom abstraction should not be altered appreciably by the resonance of the molecule and should follow Hammett's equation. Since the rate of reaction is measured by the rate of oxygen absorption, it must be concluded that the rate-determining step can be dependent upon resonance stabilization of the ether radical. In other words, either

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

or

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

can determine the observed rate. This effect would not have been manifest in the study of alkyl benzyl ethers because practically the same resonance structures for radicals existed regardless of the nature of the alkyl group. Further support for the existence of resonance-stabilized radicals comes from the previous conclusion that the most probable termination reaction is $ROO\cdot + R\cdot$ In the usual autoxidation system, the concentration of $R\cdot$ is assumed too low for this reaction to be important.

The two principal methods of varying the electron density around the $\alpha$-carbon atom have now been discussed. A third method used only superficially in this work was by having substituents on the $\alpha$-carbon atom. The first compound of this type investigated was bis-($\alpha$-methylbenzyl) ether. As described in the "Experimental" section, not even a rigorous purification would yield an oxidizable compound. To a lesser degree, this sort of behavior has been noted before. Frank and Blackham (82) found that in the vapor-phase oxidation of some branched-chain aliphatic hydrocarbons the attack is preferentially at primary and secondary carbon-hydrogen bonds. This, they supposed, was due to a steric effect. Wibaut and Strang (234) similarly interpreted the slower autoxidation of liquid isooctane compared to n-octane at 110°. Both Murphy and Ravner (156) and Gisser (96) found a similar effect for liquid esters when the tertiary carbon-hydrogen bond is adjacent to the carboxyl group, but Gisser attributed the reduction in reaction rate to an inductive effect of the ester group. On the other hand, Sharp, Patton, and Whitcomb (202) found the hydroperoxide of diisopropyl ketone is easily formed and stable enough to isolate.

If oxidation had occurred to a slight extent, the oxidation of bis-($\alpha$-methylbenzyl) ether could have been conducted at several temperatures and the entropy of activation could have been calculated. A comparison of this with the activation entropy of dibenzyl ether should show a difference dependent upon the magnitude of the steric effect.

Benzaldehyde diethyl acetal (which could be called $\alpha$-ethoxybenzyl ethyl ether) is another compound which did not act as predicted. An increase in the resonance possibilities may account for part of the lower rate; however, it seems more reasonable to propose that this reaction is an exaggerated example of the retardation effected by the accumulation of oxidation products.

## The Effects of the Solvent

Anisole was chosen as a solvent because of its extreme inertness to oxidizing substances. As a solvent, it should participate only to a very limited extent in transferring radical chains; consequently, the effects produced were truly those of dilution. The relative increase in oxidation rate with dilution is indicative of increasing chain lengths. This, in turn, is indicative of a decreased chain-termination rate. The tendency for radical-radical interactions should be roughly proportional to the ether concentration and should not, therefore, be strongly decreased by dilution. The most likely cause for the decrease must then be the effective shielding of the wall from radical impact. This result is in agreement with the wall effects described previously and suggests furthermore that the reaction between ROO· and R· is a surface reaction.

The retardation effected by nitrobenzene is probably due to interaction of solvent molecules with free radicals (see p. 29). The slight acceleration brought about by acetic acid is less easily explained. It is possible that the effect is similar to that found for dilute acidified solutions of ethers in water for which very long chain reactions were operative (35). The net result would be a relative increase in radical concentration. It has been demonstrated that cobalt-catalyzed reactions in acetic acid and 90% formic acid proceed beyond the hydroperoxide or aldehyde stage to the acid (112, 144).

## Catalysis

The ability of manganous acetate to initiate the free-radical reaction in dibenzyl ether containing less than 2 milliequivalents of peroxide per mole is an indication that the catalyst strongly accelerates the hydroperoxide decomposition. In this type of catalysis, the reactions are probably either

$$M^{++} + ROOH \longrightarrow M^{+++} + RO^{-} + \cdot OH$$

or

$$M^{++} + ROOH \longrightarrow M^{+++} + RO\cdot + OH^{-}$$

The latter is more likely considering the stability of the ions and radicals produced.

Mercury was found to be an inhibitor in the dark and a catalyst in the light in the benzoyl peroxide-initiated oxidation of benzyl ether. This catalytic activity may be related to the ability of photosensitized mercury to dehydrogenate ethers (53) and to catalyze the vapor-phase oxidation of aldehydes (143) but differs from this in that the metal is strongly attacked in the oxidizing system.

The catalytic activity of powdered iron is not so easily explained. One explanation is that traces of an iron salt accelerate the hydroperoxide decomposition. Waters' mechanism, too, is a possibility:

$$M\cdot \text{ (electron source) } + O_2 \longrightarrow M{:}O\text{-}O\cdot$$

A clarification of this could be brought about by investigating the effects of oxygen pressure on the oxidation rate for the iron-catalyzed reaction.

Suggestions for Future Work

Some effort should be made to determine to what extent steric factors affect oxidation rates. For this purpose, both $\alpha$-substituted and ortho-substituted benzyl ethers could be studied. Examples of the former are benzhydryl methyl ether, $(C_6H_5)_2CHOCH_3$, and $\alpha$-methylbenzyl methyl ether. An example of the latter is 2,6-dimethylbenzyl methyl ether. Unfortunately, compounds of the latter type are not readily available and probably would not be easy to prepare. The methyl ethers are suggested because of their ease of preparation and purification and because of the resistance of the methyl group toward attack.

Solution studies should be continued using larger volumes of the solution to make the rates more easily measurable. Acetic acid could prove quite useful as solvent and should be further investigated.

Now that the general utility of the Dornte-type apparatus for studying ether autoxidation has been shown, improvements in the apparatus are advisable and should be directed toward the application of an automatic recording device which would permit operating the apparatus continuously over at least a twenty-four hour period.

The development of the apparatus to handle low-boiling compounds would be valuable not only to ether autoxidation studies but also to any other studies where low-boiling compounds interfere with the measurement of either the absorption or the evolution of a gas in this type of system. There are several possible methods by which this may be done. The use of a cold trap is one, but this has the disadvantage of removing from reaction a portion of the reactant liquid. A highly efficient condenser--perhaps one through which a very cold liquid is circulated--would return at least part of the liquid to the reactor. If the rate of return were sufficiently low so that the temperature of the reaction were not appreciably altered, this method would be better than the previous. Either of these two methods would be more successful if it was applied along with a lower rate of oxygen circulation. Probably a rate of flow of even one-tenth of that used in this work would be sufficient to maintain saturation. Owing to the mechanical difficulties of constructing such a system, the use of a pressure system would be less satisfactory than either of the previous two methods.

Improvements in analyses must be made. Until the rates of formation of at least some of the products, especially hydroperoxides, are known, the usefulness of any kinetic treatment of data will be impaired. That the oxygen uptake frequently is less than the apparent increase in the products of oxidation has been noted before. This was observed by Larsen, Thorpe, and Armfield (131) and especially by Mitchell and Shelton (151), who for example analytically found 2.57% of oxygen as oxygenated products of 5-phenyl-2-pentene after 5.5 hours autoxidation at 80°, whereas the oxygen uptake had amounted to only 0.93%!

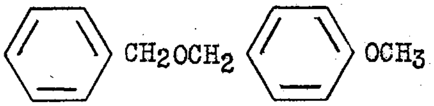
Egerton, Everett, and Minkoff (63) have recently shown that the amount of iodine liberated from an acidified iodide solution by an alkyl hydroperoxide is dependent not only on time and the type and amount of catalyst but also on the hydrogen peroxide concentration. Adding hydrogen peroxide greatly increases (in one case by 100%) the amount of iodine liberated over that liberated by the compounds individually.

The carbonyl method gives erroneous results probably because of the oxidation of hydroxylamine by the hydrogen peroxide.

So very little is known about the mechanism of decomposition of ether hydroperoxides that studies of this type would add immensely to the understanding of the autoxidation of ethers. Decompositions carried out in an oxygen-free inert solvent and atmosphere should show definitely if termination reactions producing oxygen (e.g., $2ROO\cdot \longrightarrow ROOR + O_2$) are important. Decompositions in the presence of molecules which would add free alkoxyl and hydroxyl radicals should prove whether the postulated fission actually occurs.

For these studies, pure ether hydroperoxides must be prepared. Two fairly stable compounds are tetrahydrofuran α-hydroperoxide (see p. 7) and 2-(5,6-dihydro-2<u>H</u> pyranyl) hydroperoxide (see p. 43), both of which should be simple to isolate and purify. Phthalan, which forms a peroxide readily, may also form a stable hydroperoxide. In preparing α,α-dimethylbenzyl hydroperoxide, the use of an alkaline (pH = 10.5) oil-in-water emulsion (5) and the use of an ammonia-oxygen mixture (46) have both been successful in increasing the yields of the hydroperoxides in isopropylbenzene oxidation. Similar procedures could possibly lead to a good preparative method for ether hydroperoxides.

The oxidation of unsymmetrical dibenzyl ethers, for example



under relatively harsh conditions, such as in the presence of cobalt acetate and acetic acid, should indicate the rate-determining step in substituted ethers. If the α-hydrogen atom of the substituted benzyl group is harder to remove because of the resonance within the molecule, the products would consist of benzaldehyde (or benzoic acid) and p-methoxybenzyl alcohol. If the α-hydrogen atom is easily removed but the radical-oxygen interaction occurs slowly, the products should be preponderantly anisaldehyde (or anisic acid) and benzyl alcohol.

# SUMMARY

Evidence obtained by studying the oxygen absorption of fifteen different benzyl ethers, especially dibenzyl ether, points toward the following mechanism of reaction.

Initiation: $$ROOH \xrightarrow{k_a} RO\cdot + \cdot OH$$

$$RH + \cdot OH \xrightarrow{k_1} R\cdot + HOH$$

Propagation: $$R\cdot + O_2 \xrightarrow{k_2} ROO\cdot$$

$$ROO\cdot + RH \xrightarrow{k_3} ROOH + R\cdot$$

Termination: $$ROO\cdot + R\cdot \xrightarrow{k_4} ROOR$$

The rate of oxygen absorption predicted from a mathematical treatment of this mechanism is

$$-\frac{d(O_2)}{dt} = k(ROOH)^{\frac{1}{2}}(O_2)^{\frac{1}{2}}(RH)^{\frac{1}{2}}$$

where $k = (k_a k_2 k_3/k_4)^{\frac{1}{2}}$. When the assumption is made that the absorbed oxygen appears as the hydroperoxide, then

$$-\left[\frac{d(O_2)}{dt}\right]^{\frac{1}{2}} = k'(O_2)^{\frac{1}{2}}(RH)^{\frac{1}{2}}$$

Excellent agreement of this equation with experimental results was obtained.

From the high oxidation rate and the low activation energy, the reactions are believed to be very long chain reactions in which the rates are dependent upon both hydrogen atom abstraction and radical-oxygen interaction.

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