

STUDIES ON THE AUTO-OXIDATION OF ETHERS

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INTRODUCTION

Auto-oxidation reactions (roughly speaking, spontaneous autocatalytic reactions with molecular oxygen) have received considerable study during the past twenty-five years. In the field of organic chemistry the auto-oxidations of hydrocarbons, drying oils, aldehydes, and ethers--all of great technical importance--have been investigated. Auto-oxidations in the field of biological chemistry have also been of much interest.

The simplest view of auto-oxidation regards it as addition of molecular oxygen to the substance being autooxidized with the formation of a highly reactive peroxide. This peroxide is subject to reversible dissociation, or to decomposition, with or without rearrangement, into new products. Milas (1) gives a detailed and still valid discussion of auto-oxidation reactions.

The auto-oxidation of diethyl ether has been investigated more than any other ether (2,3,4,5). This is because of the harmful effects the products of the auto-oxidation have upon use of the ether in anesthesia. Much of the study, therefore, has been devoted merely to the practical problem of discovering satisfactory inhibitors. Auto-oxidized ethers have been known to explode violently while undergoing distillation. Such explosions are attributed to the peroxides which accumulated as residues, became overheated, and decomposed violently.

The literature contains very few articles that give quantitative information on the ease of auto-oxidation of various ethers (6,7,8). Even these studies gave only semi-quantitative data. These investigations, however, especially that of Milas, along with that of Clover, Wieland, and Wingler, Landon, and Reimers on diethyl ether, have brought forth a great deal of information regarding the factors involved in auto-oxidation reactions. Mechanisms of reaction have been postulated to explain the

EXPERIMENTAL RESULTS AND THEIR INTERPRETATION

The ethers used in this research were purchased from Eastman Kodak Company. They were purified according to methods applicable to the particular ether. The aliphatic ethers were distilled over metallic sodium and fractions that came over at the accepted boiling points of the ethers were used as samples. The benzyl ethers were purified according to directions by Milas (6). In some cases the benzyl ethers were distilled over potassium iodide after preliminary cleaning, but the effect was not noticeable in the distillate. Paraldehyde, acetal, and 1,3-dioxolane were purified by repeated distillation over sodium. All samples gave negative tests for the presence of peroxides after the distillation and were immediately stored in dark bottles under an atmosphere of carbon dioxide. Each sample was used within twenty-four hours after purification and was again tested for the presence of peroxides just before use.

The distillations were carried out through a three-ball Snyder fractionating column. The apparatus was of all-glass construction. All distillations were accomplished in an atmosphere of carbon dioxide and when necessary under reduced pressure.

Several difficulties are encountered in making measurements of auto-oxidation of ethers: (a) the reactions are often very slow and thus liable to be greatly affected by trace amounts of promoters and inhibitors, the removal of which presents a problem in itself and (b) intermediate products in the reaction which can, in some cases, be isolated present other problems as will be shown in this work. For these reasons the greatest difficulty is encountered in reproducing results.

Several methods have been developed for measuring the auto-oxidation of ethers. These can be divided into two classes: (a) Measuring the dis-

appearance of reagent. This method consists of following the oxygen absorption by volume or pressure changes. The formation of gaseous by-products while the auto-oxidation reaction progresses is objectionable if this method is employed. Theoretically it would be ideal to measure the disappearance of the ether, but no quantitative method has been developed to accomplish this. (b) Measuring the appearance of a product of the reaction. The auto-oxidation of ethers has frequently been followed by direct titration of peroxides formed at different stages of the reaction. Milas (1) offers a good review on the various methods used to follow auto-oxidation reactions.

Preliminary experiments using the iodimetric method mentioned above gave such erratic results on peroxide determination that the method was discarded. Moreover the literature references disagree considerably as to the reliability of quantitative measurements obtained by this method. For these reasons this method was discarded.

The Barcroft-Warburg apparatus had been used successfully in various studies of auto-oxidation (9) including especially that of dioxolanes (8). It was decided, therefore, to follow the rate of auto-oxidation by measurement of oxygen uptake. This apparatus permits (a) running a number of samples at one time at constant temperature and at a constant rate of shaking, and (b) reading of oxygen absorption conveniently and accurately. One obvious limitation is the difficulty of studying ethers, such as ethyl ether, that have a high vapor pressure at the temperature convenient for operation of the apparatus.

The instrument used was of the oscillating rectangular type. The reaction flasks were of about twenty ml. capacity. These flasks were always cleaned by removing the grease from the flasks with an organic solvent

and then warming in a nitric acid-sulfuric acid bath for at least twenty-four hours. The flasks were then washed at least five times with tap water and then at least five times with distilled water to remove traces of catalysts. They were then heated at 110° for a minimum of twelve hours before use. The lubricating grease was that sold by A. H. Thomas and Co. of Philadelphia under the trade of Lubriseal. The work of Legault and Lewis (8) demonstrated its suitability in studies of this kind. Flask constants were calculated from data of Rothschild (22).

The samples of ether were introduced into the reaction flasks, which were then attached to the manometers. Temperature equilibration within the bath was accomplished before initial readings were made. The flasks were shaken at a rate of 90 vibrations per minute. This rate of shaking was arbitrarily chosen. Successive readings of oxygen uptake were made at varying intervals up to a total time of 30 hours in some instances.

Legault and Lewis (8), in their experiments with dioxolanes, noted that the Brodie manometer fluid customarily used in the apparatus made complications due to the diffusion of water vapor from the fluid. The reliability of the Brodie fluid as compared to dibutyl phthalate was investigated in this work also, but no noticeable error was brought out that might be attributed to the fluid. This may be seen by observing the following table.

TABLE I

O₂ Absorbed in ml. by Replicate Samples of Ethers

Ether used	Via Brodie fluid	Via Dibutyl Phthalate
Hexyl	58, 44	70, 56
Benzyl butyl	1779, 1424	1591
Tetrahydrofuran	243, 350	332
Benzyl ethyl	1127, 1214	1139, 1136

These results show that in our work the manometer fluid had little, if any, effect. However in our experiments, as will be shown later, aqueous potassium hydroxide solution absorbed on filter paper was introduced into the cup in the center of the reaction flask. Since this would supply water vapor no matter what manometer fluid was used, this evidence does not refute the observations of Legault and Lewis.

At the outset of our study, runs were made using the pure ether samples without catalyst, but the reaction was too slow for convenient measurement and the results were highly erratic. The variability of results was likely due to trace catalysts or inhibitors that were not removed by the purification techniques used. In order to overcome these difficulties a search was made for a catalyst efficient enough to eliminate induction periods and any other effects due to trace catalysts. Legault and Lewis (8) mentioned that benzoyl peroxide so accelerated the oxidation of the dioxolanes that oxygen was absorbed faster in the first five hours than the dioxolane without catalyst absorbed over any five-hour period. The use of this catalyst was, therefore, investigated and found to remove some of the difficulties noted above.

In the first experiments using benzoyl peroxide as catalyst unreasonable positive values were noted. (Positive values indicate that gas is being evolved, not absorbed). The positive values are believed to be due to carbon dioxide coming from decomposition of the benzoyl peroxide (10). Calculations show that the amount of catalyst used (about 2.5 mg.) could give off about 200 μ l. of oxygen. This would easily account for the positive values observed.

This problem was remedied by utilizing the biochemist's technique of introducing into the center cup of the reaction flasks a strip of filter

paper saturated with aqueous potassium hydroxide to absorb the carbon dioxide given off. It is probable that the high catalytic activity of the benzoyl peroxide made the effect, if any, of traces of water in the apparatus negligible.

It was suggested that a peroxide which dissolved in the sample immediately might be an even better catalyst than the benzoyl peroxide. Therefore di-tert-butyl peroxide was prepared according to the directions of Milas and Surgenor (11) and tested. Its efficiency as a catalyst in these test runs was low so the use of benzoyl peroxide was continued throughout the experiments. In these cases catalytic activity is evidently correlated with stability of the peroxide.

Experiments were run to see if the amount of catalyst would have an effect on the reaction. During most of the experiments about 2.5 mg. of catalyst was added to each flask just before attachment to the manometer. To insure exactly the same catalyst concentration in several samples, the catalyst was added to a larger portion of ether first and then aliquot parts were taken. In another experiment ten times as much catalyst was added to some samples. The results of these experiments are shown in the following table.

TABLE II

Total Absorption of O ₂ in μ l. at the End of 20 Hours			
Ether used	About 2.5 mg. via aliquots	About 2.5 mg. via sep. addns.	About 22 mg. via sep. addns.
Benzyl butyl	1106, 1163, 1365	1374, 1252	- - - -
Dioxane	- - - -	128, 103, 109, 168, 97	226, 177

Thus it appears that the absorption of oxygen by the ether, while not independent of the amount of catalyst, is far from proportional to it.

The temperature of the bath in which runs were made was maintained at

37° ($\mp .05^\circ$) by the use of the standard thermostat on the Warburg apparatus. This temperature was chosen because: (a) the temperature of the room in which the work was done was seldom below 25° so that the thermostat would not function for a temperature in this range, (b) a temperature higher than 25° would serve to speed up the reaction and (c) a temperature higher than 40° would have required a different joint grease, and consequent tedious work measuring the various effects on gas uptake.

Tests were made to study the effect of concentration of oxygen on the reaction. Reimers (5) reported that in his work the rate of peroxide formation did not depend on the volume of air above the sample. Stephens (12) noted that the oxidation of cyclohexene was zero order with respect to oxygen. These observations were checked by the use of air. The results of these experiments are shown as follows.

TABLE III

Absorption of O₂ in μ l. at the End of 27 Hours

Ether used	In Air	In Oxygen
Benzyl methyl	1500, 2080, 1185	909, 1362
Hexyl	118, 139, 165	95, 120
Benzyl methyl (uncatalyzed)	238, 282, 174	243, 202

From this table it may be seen that within the experimental error (about $\mp 20\%$) there is no difference between pure oxygen and air (20% O₂) as to the amount of oxygen absorbed.

All the experiments were done at atmospheric pressure, which rarely varied over more than twenty millimeters of mercury. Hence any effect due to change in pressure is well within our experimental error.

Various possible surface effects on the auto-oxidation reaction were then surveyed. Williams (7) and Reimers (5) noted that apparently identical samples of ether stored in different bottles often were widely

different in the rate of peroxide formation. Stephens (12) observed that the oxidation rate of cyclohexene is "strongly influenced by the solid surface area". He notes that the rate would depend in part on the balance between initiation and interruption of chains at the surface of the vessel. By reviewing all our data it was found that in no instance did one flask give consistently high or low results. The wide variance in most cases could be explained by reasoning like that of Stephens; or if the reaction rate is directly proportional to active surface area it could be attributed to minute changes in the flask surface due to cleaning.

Another check was made on effect of surface by introducing pyrex glass wool (cleaned along with flasks and subjected to extra rinsing with distilled water) into the reaction flasks. Figure I shows that the glass wool had a positive catalytic effect in the uncatalyzed runs, but a negative catalytic effect in the catalyzed ones. Apparent paradoxes like this have been noted before. Stephens' (12) results were obtained by using flasks made of different kinds of glass. Reimers (5) also noticed that different glass types resulted in different rates of auto-oxidation. In this work, however, the same type of glass and pyrex wool were used in all cases. These results, along with those of Stephens and Reimers, point out definite surface effects in the reaction other than those due to differences in the type of glass.

Another related effect was studied. If the reaction is dependent on surface, the effect of volume of ether might be studied. Trials were made using various amounts of ether samples run concurrently. Figure II plainly shows that the amount of oxygen absorbed is not directly proportional to the amount of ether present. The relative decrease in amount of oxygen absorbed can be accredited to the lack of proportionately larger solid-liquid interface to make and break reaction chains. This interfacial area

GRAPHS

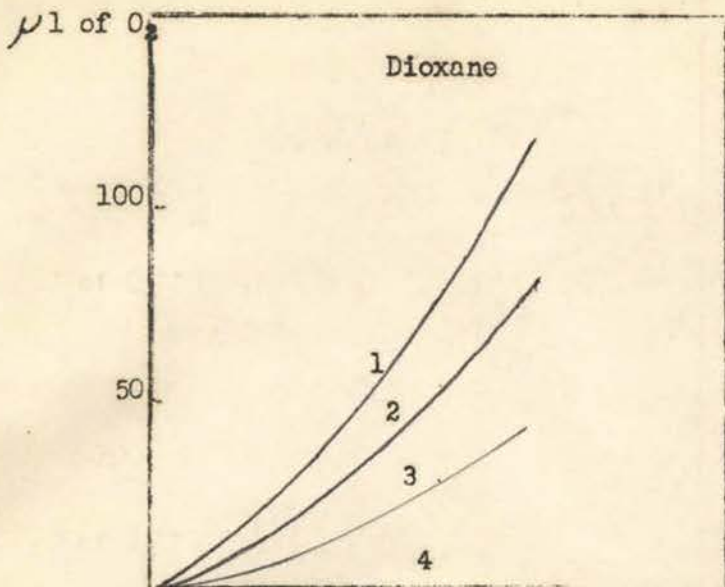


Figure I

1. No glass wool-cat.
2. Glass wool - cat.
3. Glass wool - cat.
4. No glass wool - no cat.

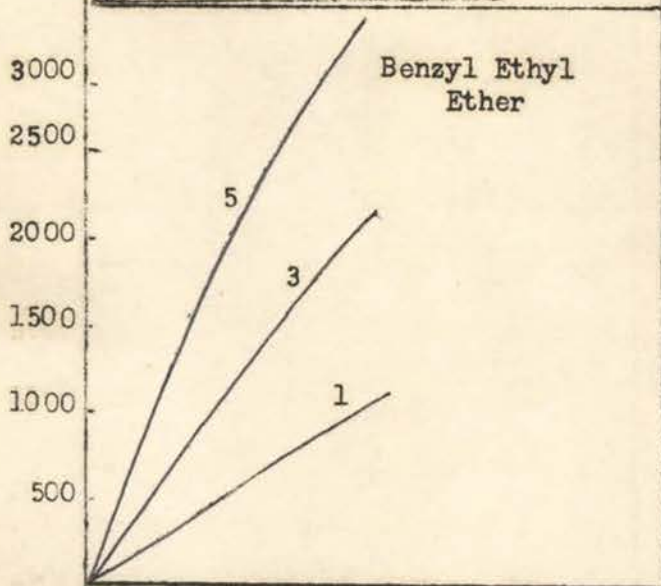


Figure II

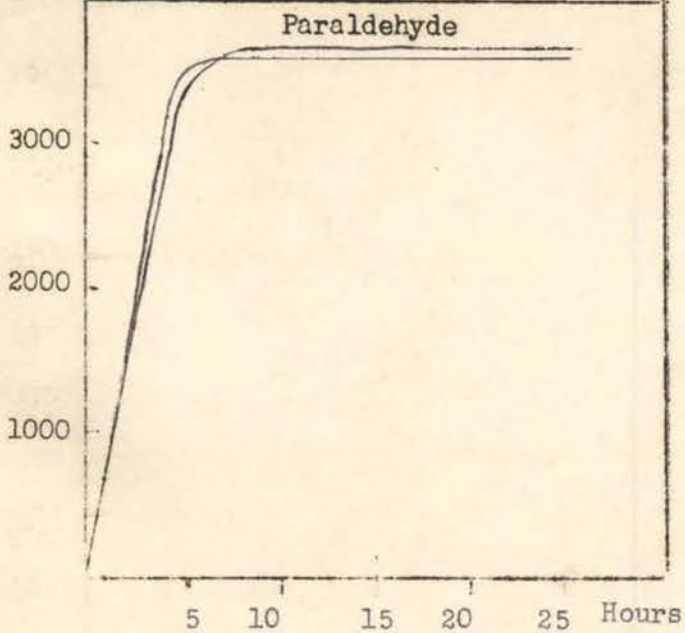


Figure III

is also reduced by reduced efficiency of shaking of the flasks as the sample increases in size. The necessity of thorough shaking was brought out by Milas (13). This effect of volume of ether was also noticed by comparison of runs made with benzyl ether at different times, but the effect is then less significant, because the ether samples were purified at different times. Three milliliters of benzyl ether absorbed about 3500 μ l. of O_2 while one milliliter absorbed about 2500 μ l. of O_2 over the same period of time.

Mercury has been reported to be a catalyst for the auto-oxidation of benzyl ether (6). Mercury was tried repeatedly as a catalyst in our work with benzyl ether, but gave no evidence of being one. It is noted that Milas (6) reports that copper, silver, and iron are also catalysts for this auto-oxidation, and iron has also been reported to catalyze other auto-oxidation reactions (15, 16) yet iron has been used as an inhibitor of auto-oxidation when storing diethyl ether (14). Milas notes also that Hewar (17) reported copper to have a retarding effect on the auto-oxidation of diethyl ether. These conflicting data seem to call for more study on the catalytic effects of the various metals on the auto-oxidation of ethers.

In order to obtain quantitative data with respect to structure several different types of ethers were studied. Benzyl, acyclic (including some chlorinated ones) and heterocyclic, aromatic, and acetal-type ethers were investigated.

Four ethers of the benzyl series were tested; dibenzyl, benzyl methyl, benzyl ethyl, and benzyl butyl. No direct relation was observed between oxygen absorption and structure within this series. The absorption of the four ethers is recorded in the following table.

TABLE IV

	Oxygen Absorption in μ l. after 14.5 Hours	Average
Benzyl ether	1805, 2538, 1485, 1613	1820, 2187, 2688 2019
Benzyl methyl ether	500, 620, 1000	740, 1020, 1190 845
Benzyl ethyl ether	1214, 1127	1170
Benzyl butyl ether	720, 820	713, 680, 780 743

Although there is quite a difference in the amount of oxygen taken up by supposedly identical samples identically treated it is of interest to note the similarity between the rate curves for the samples shown above. See Figure IV. The results are too few and too uncertain to make possible a definite conclusion as to the effect of structure on absorption. It is plain to see, however, that the benzyl group is the activating group.

A comparison of our results with those of Milas can be made in one instance. He found that one mole of uncatalyzed benzyl ether absorbed 150 cc of oxygen in 16 hours; our uncatalyzed benzyl ether took up 200 cc over the same period of time. His reactions were run at a temperature three degrees higher than ours.

A few of the simple aliphatic ethers were also studied. In these cases the absorption was very low when compared to that of the ethers of the benzyl group. As before no definite relation can be found between structure and oxygen uptake. The following total absorptions for various aliphatic ethers after twenty-one hours were obtained.

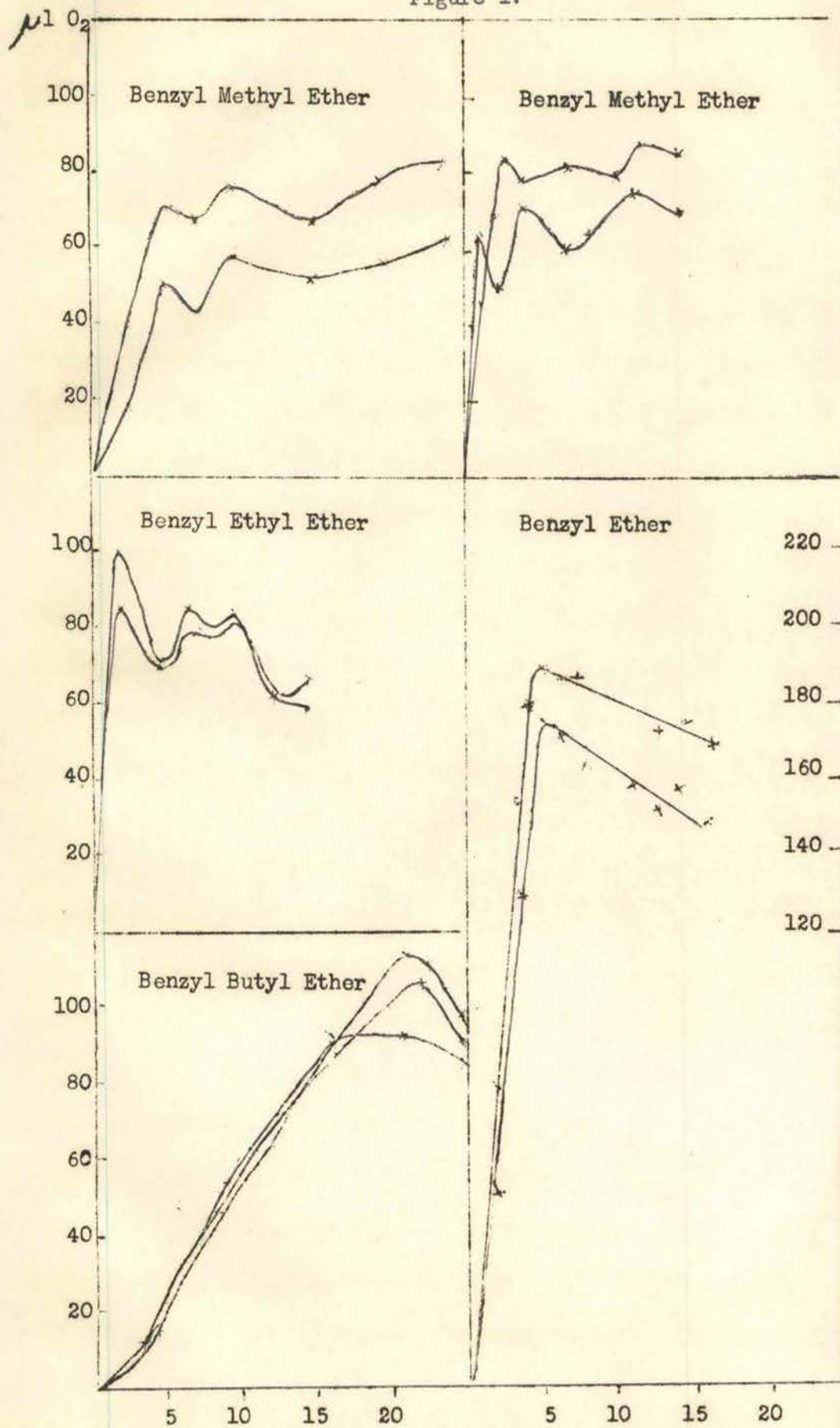
TABLE V

Hexyl ether	105, 72, 95
Isoamyl ether	160, 184, 90
Tetrahydrofuran	332, 250, 243
<i>B, B'</i> dichlorodiethyl ether	306, 119, 180
<i>B, B'</i> dichlorodiisopropyl ether	185, 199, 135
Butyl ether	120, 46, 68
p-Dioxane	128, 97, 103, 109, 168

Owing to the lower boiling points of ethyl and the two propyl ethers they were not run. The dichlorodiethyl ether, however, shows much greater absorp-

RATE CURVES FOR THE
BENZYL ETHERS

Figure IV



tion than would be expected for ethyl ether even though the values are scattered. It may be that the effect of the electron-attracting phenyl group of the benzyl ethers is duplicated, to a smaller extent, by the similarly electron-attracting chlorine atom here. Of the cyclic saturated ethers p-dioxane is surprisingly inactive considering its two available oxygen atoms. Tetrahydrofuran absorbed three times as much. This inactivity may be related to the low rate of peroxidation for n-alkyl ethers, because p-dioxane may be regarded as ethyl ether cyclized through another oxygen atom.

The typical aromatic ethers were also studied but they peroxidize much more slowly than any of the others studied. Anisole, m-cresyl methyl ether, and diphenyl ether were tested. All showed a negligible uptake of oxygen.

The acetals are in truth ethers of alkylidene glycols with the $>C(OR)_2$ linkage, and the cyclic aldehyde trimers are similar. Three different ethers of this type were run; 1,3-dioxolane, acetal, and paraldehyde. The unexpected results found in this group of ethers are of interest. All these ethers showed a very high initial rate of absorption. Acetal, dioxolane, and paraldehyde had initial rates respectively 2, 3, and 3.5 times as great as benzyl ether. This definitely appears to be a characteristic of the acetal-type linkage.

Several interesting observations were made during the study of the ethers in this group. First, of four presumably identical samples of paraldehyde three showed unexpected precision of results. Plots of the oxygen uptake are shown in Figure III. All four samples give similar curves. The sudden drop in absorption in these runs occurs long before a stoichiometric amount of oxygen has been taken up by the paraldehyde, and must rather be attributed to decomposition products of the peroxidized ether. Practically every author who has studied the auto-oxidation of ethers has observed

aldehydes among the decomposition products. As all three ethers that give these unusual results yield volatile aldehydes when their peroxides decompose it is believed that the sharp break is due to the evolution of these aldehydes. That this is the case was shown by the unusual color of the potassium hydroxide paper that was added to absorb carbon dioxide. In the case of paraldehyde the paper was brown and with acetal it was the red-brown color of aldol polymers. The dioxolane gave a paper with a yellowish color. As the dioxolane peroxide would decompose to give formaldehyde and possibly glyoxal, it would not be expected to show evidence of aldol condensation as paraldehyde and acetal did. Thus we may assume that at first the KOH paper absorbed all the gases evolved, but as soon as the aldol polymer coated over the KOH paper, the paper ceased to take up the aldehyde evolved and either this inhibited further oxygen uptake or the total gases evolved immediately amounted to more than the oxygen absorbed by the acetal. This would explain the sharp break in the absorption curves.

One odd observation made during the study of the acetals was that peroxidized paraldehyde did not give a positive test for peroxides in a solution of acetic anhydride, water, and potassium iodide but did so in the presence of acetic anhydride and potassium iodide in the absence of the water, while the dioxolane and acetal gave a positive peroxide test in both media.

IODIMETRIC METHOD

During the preliminary work on this problem an attempt was made to correlate the amount of oxygen absorbed by a given sample of ether with the peroxide value determined by the iodimetric method at the end of a run. A correlation was not obtained, the apparent peroxide always being less than the amount of oxygen absorbed. The result is in agreement with the findings of Milas (6) and Almquist (18). They attribute it to the decomposition of peroxide. Almquist shows that in the oxidation of benzaldehyde the oxygen added as peroxides and in benzoic acid formed is almost equal to the total oxygen absorbed.

Also at the outset reagent-grade samples of ethers were analyzed by measuring the amount of iodine liberated by the peroxides in the ether. These tests were made by adding the ether sample to a solution of water, potassium iodide, and 10 cc of acetic anhydride. The liberation of iodine was then traced by successive titrations of the same sample at intervals of a few hours. In these rough experiments it was observed that identical samples often gave variable results. The titration of impure isopropyl ether is an extreme example, but it shows the type result observed. Samples A and B were consecutively withdrawn from the same bottle.

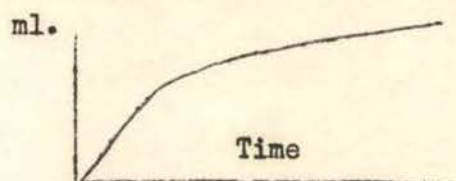
Iodimetric Determination of Peroxides in Isopropyl Ether

		Time in Hours							
		Sample	2.25	2.25	10.75	21.75	32	47.25	67.25
Titer in $\frac{cc}{cc}$:	A	1.2	2.8	4.1	5.7	8.5	10.6	13.7	
Titer in $\frac{cc}{cc}$:	B	4.3	7.9	11	16.9	21.4	23.8	32.1	

Throughout the work with the Warburg apparatus discordant results with identical samples identically treated often resulted. Although these variations were not as great as those in the rough iodimetric work mentioned above, they did point out the need for finding a better method for measuring the

rate of auto-oxidation of ethers that would give more reproducible results. One particular iodimetric method of analysis was finally investigated.

This method consisted of: (a) diluting 10 cc of acetic anhydride with 50 cc of water, (b) adding about a gram of potassium iodide, (c) adding exactly one milliliter of the ether sample, and (d) titrating with thiosulfate solution. It was observed that when step (d) immediately followed step (c) a very small titer was obtained, whereas when five to fifteen minutes intervened between these steps the same sample would give a titer two to three times as large. If such a titration is made on the same sample every five minutes over a period of one hour and the total titer is plotted against time, a curve of the following type is obtained.

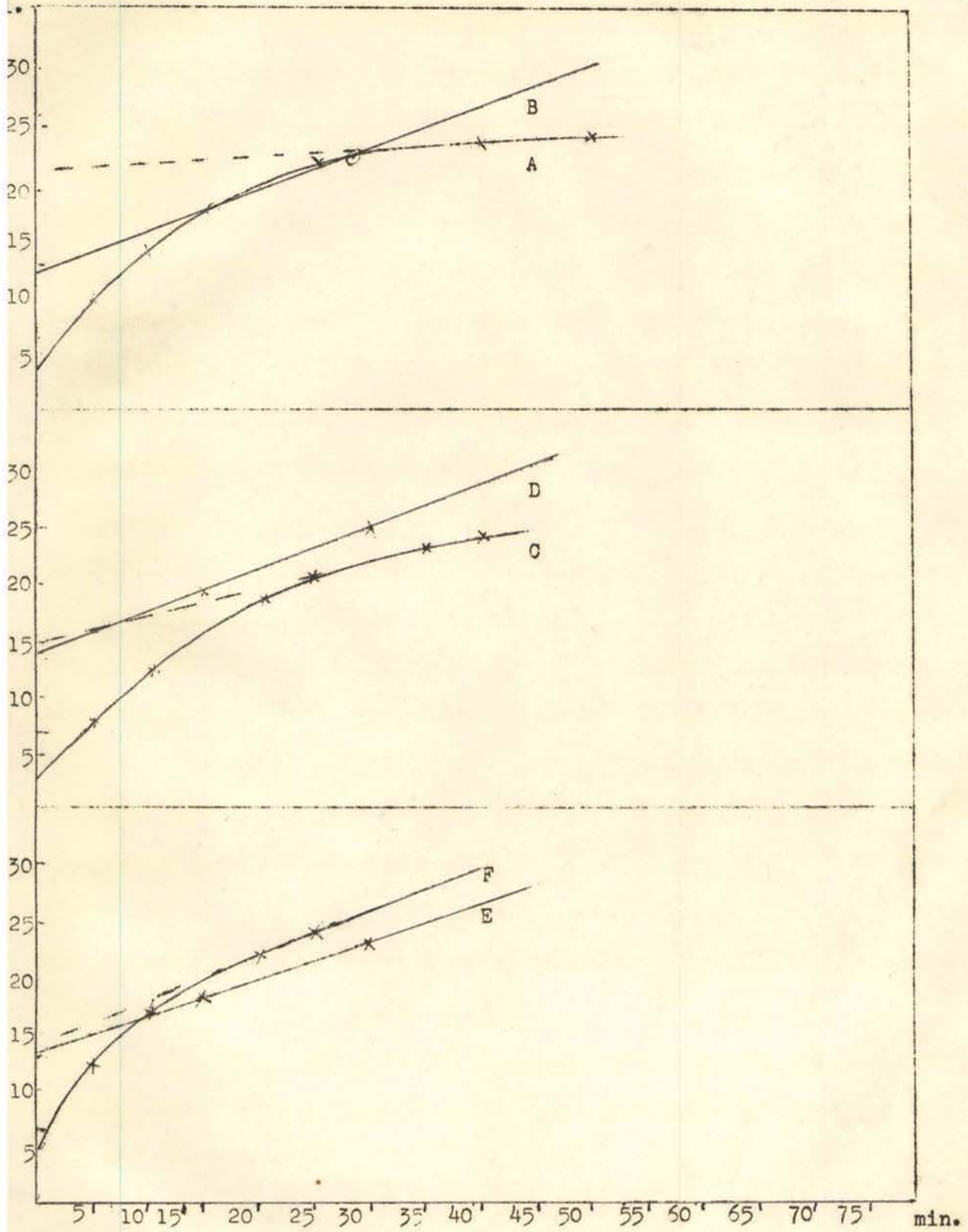


However, when identical samples were titrated by this method the initial slopes of the curve were often variable, as well as the location of the points of inflection. Thus the problem was to determine the point at which the total ether peroxides had been measured. The literature discussion of this subject is by no means conclusive (4, 5). Some articles state that titration after twenty minutes measures the peroxide value of the sample. Our values could not be duplicated at this or any other time interval, as can be seen by comparing curves A, C, F; K, G; and S, O.

Landon reports that one factor influencing the time required for a maximum of iodine liberation is the rate of hydrolysis of the ether peroxide to hydrogen peroxide, which in turn liberates the iodine. The question then is, when has all the ether peroxide been hydrolyzed?

It was observed that in all cases studied, the thiosulfate titer had

CURVES A THROUGH F



passed the point of inflection in the neighborhood of thirty minutes after the particular analysis was started, as would be expected from the results of Reimers and Landon. Beyond this point an approximately constant slope, corresponding to a small but steady increase in titer, was obtained. It was considered that this steady increase might be due to further auto-oxidation and subsequent hydrolysis of the ether peroxide so formed. If this were the case, then this oxidation must have occurred from the very beginning of the titration and its effect must be corrected for in order to obtain a true measure of peroxide in the original sample. Therefore, this part of the curve with small constant slope was extrapolated back to zero time. The titers so obtained for zero time were not the same for identical samples (again see curves A, C, F; K, G; and S, O); thus we cannot assume that this method gives a measure of the peroxide in the sample.

It was suggested that the tetrathionate produced from the thiosulfate might have an effect on the desired values; so instead of titrating the sample immediately in all cases, four aliquots were taken. Of these, one was titrated consecutively every five minutes, one was titrated every fifteen minutes, one every thirty minutes, and one every sixty minutes. The following data were obtained:

TABLE VI

Cumulative Titers (in ml.) of Benzyl Ether at Various Time Intervals

Curve	Time in Minutes											
	5	10	15	20	25	30	35	40	45	50	55	60
G	10.6	18.8	----	26.9	30.2	----	33.4	34.7	35.6	36.5	37.1	----
H			28.1			33.3			35.2			36.7
I						29.1						33.9
J												38.6
K	6.8	12.4	----	18.9	21.5	----	24.3	25.5	26.6	27.3	28.1	29.5*
L			25.7			35.4			37.9			39.5
M						26.7						32.3
N												36.4

*29.5 taken at 65 minutes

In this particular case the extrapolation back to zero of curves H and L also gives close results. The values obtained by extrapolating M and I curves vary widely. However, the plot of the first points on the H, I, J, and L, M, N, curves (note--these points represent values obtained for the first titer of each sample) when extrapolated back to zero give points that approach the value of each other.

This, along with previous results, led us to believe that if points assuredly on the flat portion of the curve could be obtained, extrapolation might give reproducible results. It is noted that data obtained by a different iodimetric method found, in the literature (19) gave reproducible results when plotted in this manner. Eight presumably identical samples of benzyl ethyl ether were titrated with results shown in Table VII, and later four more of benzyl ethyl and four of benzyl butyl ether. (See Table VIII).

TABLE VII

Cumulative Titers (in ml.) of Benzyl Ethyl Ether at Various Time Intervals

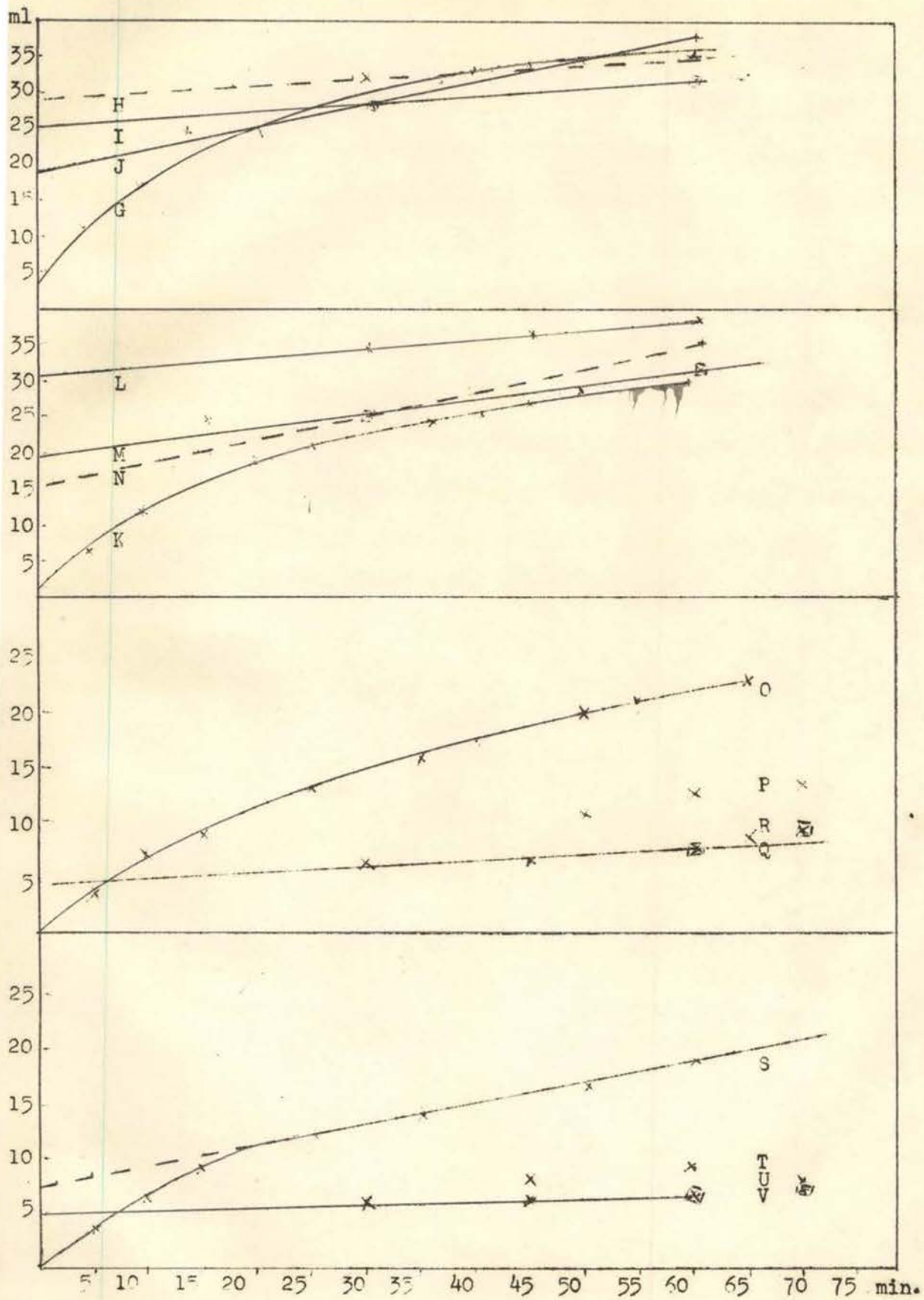
Curve	Time in Minutes													
	5	10	15	20	25	30	35	40	45	50	55	60	65	70
O	----	7.2	9.3	----	13.5	----	15.9	17.6	----	20	21.2	----	----	
P	----					6.3						12.9	----	
Q									6.7				8.9	
R												8.2		
S	----	6.7	9.3	11.2	12.5	----	14.2	15.7	----	17.9	----	----	----	21.7
T						6.2			8.4			9.9		
U									6.6					8.5
V												6.9		

TABLE VIII

Cumulative Titers (in ml.) of Benzyl Butyl Ether at Various Time Intervals

		<u>55</u>		<u>65</u>		<u>67</u> min.
A		27.3		28.1		
B		24.05		25.7		
C		24.9				26.2
D		27.0				27.7

CURVES G THROUGH V



Cumulative Titers (in ml.) of Benzyl Ethyl Ether at Various Time Intervals

	<u>40</u>	<u>45</u>	<u>55</u>	<u>60</u>	<u>65</u>	<u>67</u>
A	82.3				87.6	
B		91.1			94.1	
C			78.4		80.4	
D				104.5		107.8

Plots of the data from Table III could be made to bear out previous deduction, but the data of Table IV show that check results in the previous experiments were nothing but chance occurrences.

It is to be hoped that someone will make a thorough study of all iodimetric methods which have been utilized to measure peroxide in ether. Other methods in the literature should be tested, particularly those employing isopropyl alcohol (20) and acetic anhydride (21) as solvents.

CONCLUSION

Various factors affecting auto-oxidations reactions have been studied. Mercury, contrary to work by Milas, did not show any catalytic action. Varying results with presumably identical samples identically treated emphasize the sensitivity of auto-oxidation reactions to unknown influences. The rate of the reaction was the same no matter whether air or pure oxygen was used. The importance of surface effects is brought out in this study.

Although no direct relation between the structure of ethers in a homologous series and their reaction rates could be obtained, it was found that the ethers could be classed as to their relative rates of peroxidation into four groups: acetal-type ether > benzyl > (acyclic and heterocyclic) > aromatic.

Preliminary investigations on the iodimetric method of measuring peroxide in ethers showed that more work must be done on this method before it can be trusted to give quantitative data.

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BIOGRAPHY

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