perature and decomposing the product immediately, it is possible to secure the corresponding oxido carbinol; otherwise, the unstable magnesium derivatives decompose spontaneously into magnesium derivatives of aldehydes, and ketones which may subsequently be transformed into tertiary alcohols.

2.   Organic magnesium derivatives first transform α-oxido esters into α-oxido ketones; the final products are therefore the same as those obtained with these ketones.   Other results have been reported but the substance used in these cases was an α-ketonic ester and not the supposed isomeric α-oxido ester.

3.   Oxido carbinols are reactive substances which show unexpected properties.

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STUDIES IN AUTO-OXIDATION REACTIONS. II.
THE MECHANISM OF THE AUTO-OXIDATION OF CERTAIN ETHERS

BY NICHOLAS A. MILAS[1]

Introduction

In previous publications[2] from this Laboratory a general theory has been advocated, which, if properly applied, seems to account for the various phenomena and mechanism of auto-oxidation reactions.   Briefly stated, the theory assumes the addition of molecular oxygen to compounds containing molecular valence electrons comparable to valence electrons of atoms.   As a direct consequence of this theory, one would expect molecular oxygen to add directly onto the bivalent oxygen atom present in alcohols, ethers, ketones, aldehydes, etc., or onto the bivalent sulfur atom present in thio-alcohols, thio-ethers, thio-phenols, thio ketones, etc., or onto the trivalent nitrogen atom present in primary, secondary and tertiary amines, hydrazones and the like to form highly unstable dative peroxides which either rearrange or hydrolyze to yield other relatively more stable peroxides.   Certain ethers were chosen for the present investigation because of the existence of diversity of opinion regarding the fundamental mechanism of their auto-oxidation.

The auto-oxidation of ethyl ether has been the subject of several investigations of which only two will be mentioned here.   Clover[3] was the

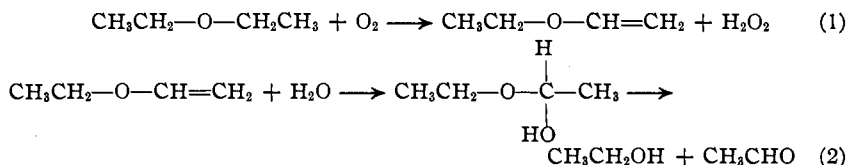[1] Research Associate, Massachusetts Institute of Technology.
[2] Milas, (a) J. Phys. Chem., 33, 1204 (1929); (b) THIS JOURNAL, 52, 739 (1930).
[3] Clover, ibid., 44, 1107 (1922).

first to make a serious attempt to elucidate the mechanism of the auto-oxidation of ethyl ether. He proposed the mechanism

$$CH_3CH_2-O-CH_2CH_3 + O_2 \longrightarrow CH_3CH_2-O-C\underset{\diagdown CH_3}{\overset{\diagup OOH}{-}}H$$
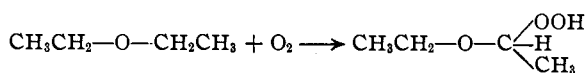
which was based on his claim to have isolated an ether peroxide having acidic properties. This claim, however, was later disputed by Wieland and Wingler,[4] who attributed the peroxidic properties of ethyl ether to "dioxy-ethylperoxide," which is assumed to be an addition product of one molecule of hydrogen peroxide to two molecules of acetaldehyde. To reconcile the oxidation of ethyl ether with Wieland's early views[5] on oxidation, Wieland and Wingler proposed a primary dehydrogenation of ethyl ether followed by the formation of hydrogen peroxide and vinyl ethyl ether with subsequent hydrolysis of the latter to form alcohol and acetaldehyde.

$$CH_3CH_2-O-CH_2CH_3 + O_2 \longrightarrow CH_3CH_2-O-CH=CH_2 + H_2O_2 \quad (1)$$

$$CH_3CH_2-O-CH=CH_2 + H_2O \longrightarrow CH_3CH_2-O-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle HO}{|}}{C}}-CH_3 \longrightarrow$$

$$CH_3CH_2OH + CH_3CHO \quad (2)$$

However, the dehydrogenation mechanism, as applied to the oxidation of ethers, seems to be in direct conflict with experimental evidence. It has already been shown elsewhere[2a] that the dehydrogenation theory is incapable of explaining true auto-oxidation reactions. The question, therefore, remains whether the oxidation of ethers fulfils the criteria of auto-oxidation reactions. This is answered in the affirmative in the experimental portion of this paper. The auto-oxidation of dibenzyl ether, for example, was found not only to be appreciably influenced by both negative and positive catalysts, but also to be capable of inducing the oxidation of substances otherwise inert to molecular oxygen.

Furthermore, the isolation of active organic peroxides from the oxidation of ethers makes the reaction of "active" hydrogen with molecular oxygen, rather than with these peroxides, very improbable. These peroxides, without doubt, ought to be far better hydrogen acceptors than molecular oxygen, since they liberate iodine instantly from a neutral solution of potassium iodide, which is relatively stable to molecular oxygen.

Besides, if vinyl ethers were to form during the oxidation of ethers, one would expect them to be oxidized by the active peroxides or peracids formed, leading to oxidation products different from those ordinarily found. Bergmann and Miekeley[6] have shown that vinyl ethyl ether is

[4] Wieland and Wingler, *Ann.*, **431**, 317 (1923).

[5] Wieland, *Ber.*, **45**, 484, 685, 679, 2603 (1912).

[6] Bergmann and Miekeley, *ibid.*, **54**, 2151 (1921).

easily oxidized by benzoperacid to a crystalline substance which hydrolyzes, in presence of mineral acids, to glycolic aldehyde and ethyl alcohol. No glycolic aldehyde has ever been isolated from the oxidation of ethyl ether.

Finally, we have found that tertiary butyl methyl, tertiary butyl benzyl, dibenzyl and methyl cresol ethers, 1,4-dioxane, anisole and even diphenyl ether form peroxides upon oxidation, yet it is quite difficult to conceive a dehydrogenation mechanism for these oxidations.

One may very reasonably conclude, therefore, that the oxidation of ethers with molecular oxygen is a true auto-oxidation phenomenon, which, according to our view, should proceed through the primary addition of molecular oxygen onto the bivalent oxygen atom of the ethers, and could be expressed in general

$$R{-}CH_2 : \ddot{O} : CH_2{-}R + \ddot{O} : \ddot{O} : \longrightarrow R{-}CH_2 : \ddot{O} : CH_2{-}R$$
$$: \ddot{O} :$$
$$: \ddot{O} :$$
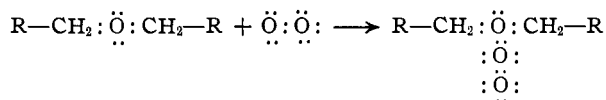
Such a dative or oxonium peroxide would be extremely unstable, but not improbable, since there exists considerable chemical evidence[7] to indicate that the oxygen atom in ethers is relatively unsaturated and can readily form oxonium compounds. The addition of molecular oxygen to ethers, as shown above, will induce a positive charge on the ether oxygen which will then have the tendency to attract toward it the electrons from the neighboring carbon atoms, leaving at least one of them positively charged. This displacement of electrons will cause a weakening of one of the linkages between the carbon atom and the ether oxygen, leading to the following possible changes
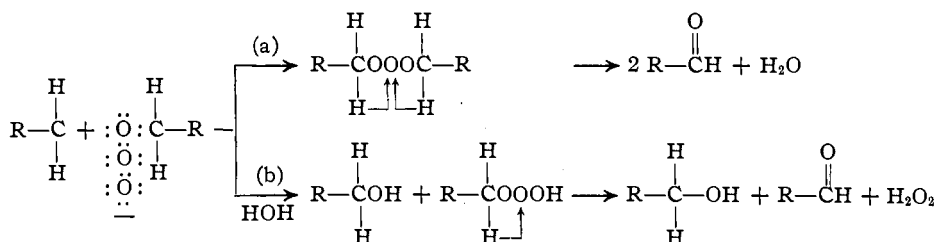
These reactions seem to account adequately for the initial products formed in the auto-oxidation of ethers. Reaction (b) seems to predominate although reaction (a) is indispensable to account for the products of reaction (b) appearing in the oxidation of very dry ethers.

The organic peroxide shown in reaction (b) seems to be identical with the primary peroxide formed in the auto-oxidation of alcohols.[8] More-

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[7] Ghosh, *J. Chem. Soc.*, **107**, 1789 (1915). For a somewhat complete bibliography on oxonium salt formation of ethers, see Rigby, Ph.D. Dissertation, M. I. T., June, 1930.

[8] Milas, unpublished results.

over, peroxides of this type exhibit properties similar to monoxyalkyl peroxides prepared by Woker[9] by mixing either formaldehyde or acetaldehyde with hydrogen peroxide preferably in the ratio of 1:1. This mixture yields with benzidine a blue color which is characteristic and is not produced by either the aldehyde or hydrogen peroxide separately. Quite recently King[10] has advanced the view that in deteriorated diethyl ether the main substance responsible for the peroxidic properties is monoxyethyl peroxide. Furthermore, our own experiments indicate that monoxyalkyl peroxides are formed as the primary decomposition products in the oxidation of ethers. These peroxides can further combine with free aldehydes to form dioxy-alkyl peroxides previously described by Nef[11] and by Wieland and Wingler.[4]

It may be mentioned here that during the oxidation of ethers side reactions seem to occur, which are responsible for the production of small quantities of esters and acids. These will not be considered in the present paper.

Experimental Part

The experimental part of this paper is divided into two sections: the first dealing with the oxidation of dibenzyl ether under the influence of various catalysts and the second with the oxidation of various ethers under the influence of ultraviolet radiation.

(1) **Oxidation of Dibenzyl Ether.**—This ether was chosen because preliminary experiments revealed that it has a higher rate of oxidation than any of the other ethers studied.[12] Moreover, the oxidation of this ether cannot be easily interpreted on the basis of the dehydrogenation theory.

The dibenzyl ether used was the c. p. quality furnished by the Eastman Kodak Company. This was further purified by shaking first with sodium carbonate solution to remove any benzoic acid present, then with sodium bisulfite containing potassium iodide to remove both the aldehyde and the peroxide present in the ether. The ether was finally washed with water, dried over anhydrous sodium sulfate and fractionated under reduced pressure in an atmosphere of pure nitrogen; the fraction boiling at 149.5 to 151.5° under 7 mm. pressure was collected and stored in a brown bottle under an atmosphere of nitrogen.

The experiments were performed in a shaking thermostat[13] at 40 ± 0.05°, and at a shaking speed of 248 complete strokes per minute. The thermostat consists of a Stanley insulated gallon jug fitted with a device in such a way as to permit thermoregulation while the thermostat is being shaken. This device (Fig. 1) consists of a coiled steel

[9] Woker, *Z. allgem. Physiol.*, **16**, 340 (1914); *Ber.*, **47**, 1024 (1914).

[10] King, *J. Chem. Soc.*, 738 (1929).

[11] Nef, *Ann.*, **298**, 292 (1897).

[12] Except tertiary butyl benzyl, which was prepared long after the experiments had been performed with dibenzyl ether.

[13] This was built for the author by Mr. C. L. Gallagher of the Research Laboratory of Physical Chemistry.

tube of 0.8 mm. internal diameter about 36 cm. long and contains sixteen loops. On one end it is welded directly onto a steel mercury well which is fastened inside the thermostat, and on the other end, it is cemented to a capillary glass tube thereby permitting the necessary connections with the relay, etc.

Before each experiment the apparatus was evacuated by closing stopcocks 2 and 3; oxygen, which had been previously dried by passing it through concd. sulfuric acid and phosphorus pentoxide, was allowed to fill the entire apparatus, then by means of a 10-cc. calibrated pipet the sample of the ether (10.36 g.) was dropped into the reaction chamber by removing the ground-glass stopper A. The apparatus was once again evacuated, refilled with oxygen and the reaction allowed to proceed. The total oxygen absorption at any given time was corrected to standard conditions, then changed to cc. per mole of the ether. Figure 2 shows the total oxygen absorption per mole as plotted against time, while Fig. 3 shows the average oxygen absorption rate against time. The results of the experiments with picric acid and p-benzoquinone as negative catalysts are not shown on the plots because the absorption was so small that it was impossible to read it without making a large percentage of error. For the sake of comparison the total volume of oxygen absorbed in each experiment at

Fig. 1.—Diagram of flexible connection to shaking apparatus for oxygen absorption measurements.

the end of a period of 120 hours, and the total peroxide found expressed both in cc. of 0.02 N thiosulfate and in peroxide oxygen per mole of the ether are given in Table I. It may be seen that the total peroxide oxygen is only a small part of the total oxygen absorbed. This is due to the fact that comparatively large amounts of benzaldehyde and benzoic acid are also formed, which account for the total oxygen absorbed.
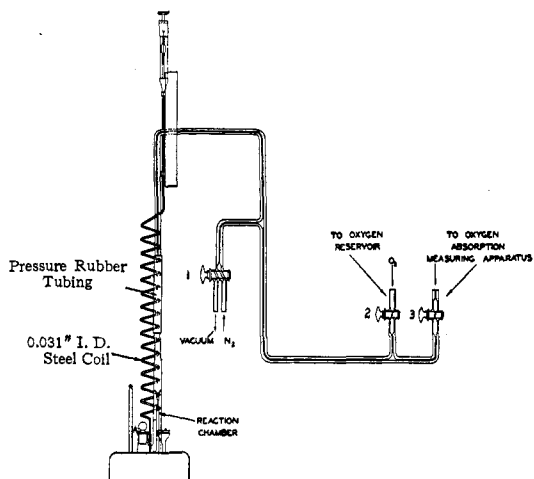
TABLE I

A COMPARISON OF THE TOTAL OXYGEN ABSORBED WITH THE TOTAL PEROXIDE FOUND IN DIBENZYL ETHER

Catalyst	Catalyst, moles/mole of ether	Total O₂ absorbed, cc./mole ether	Total peroxide oxygen, cc./mole ether	Total peroxide in cc. N/50 thiosulfate/mole ether
Iodine	0.002	109	...	..
Benzoquinone	.002	65	...	..
Picric acid	.002	30	3.2	29
Water	.010	1309	195.7	1747
Gold	.048	1172	134.7	1203
Silver	.088	1644	499.3	4458
Copper	.149	1745	212.0	1895
Mercury	.047	5233	498.0	4448
Iron	.172	1030	229.0	2044
Dibenzyl ether	...	650	109.0	977

For the titration of the peroxide the oxidized dibenzyl ether is removed from the catalyst, at the end of each experiment, by dissolving it in 30 cc. of pure benzene, the solution filtered and made up to a definite volume, an aliquot part of which is mixed in a special flask with 20 cc. of 5% solution of potassium iodide containing a few drops of freshly prepared starch emulsion and acidified with 5 cc. of glacial acetic acid. After fifteen minutes of standing the liberated iodine is titrated against $N/50$ thiosulfate solution, and the flask evacuated and allowed to stand in the dark, with occasional shaking, for ten hours when the final titration is made. Blanks are used at every stage. Later, under the section of oxidized ethers of lower boiling point than dibenzyl, the vacuum treatment is omitted.

When a sample of dibenzyl ether in a quartz flask is exposed to ultraviolet light[14] for ten hours at the same temperature but without shaking, the amount of peroxide found corresponds to 1592 cc. of $N/50$ thiosulfate per mole. This is almost twice the peroxide found when the ether is oxidized in the dark for 120 hours.

Among the oxidation products of dibenzyl ether, monoxybenzyl peroxide has been detected by the benzidine reaction, which yielded a deep green color changing quickly to brown. Benzaldehyde was isolated as the derivative of p-nitrophenylhydrazine, m. p. 191°. Benzoic acid was also isolated, m. p. 120.5–121°. An attempt to isolate benzoperacid from the oxidation products by distillation failed because of the high boiling point of the ether, and small amounts of a polymer which
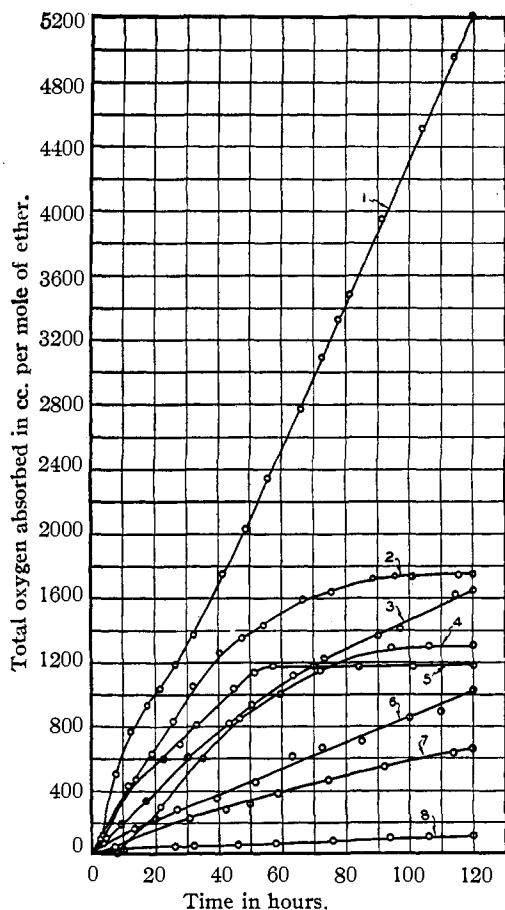

Fig. 2.—Effect of catalysts on the total oxygen absorption of dibenzyl ether. Curve 1, dibenzyl ether + Hg; Curve 2, dibenzyl ether + Cu; Curve 3, dibenzyl ether + Ag; Curve 4, dibenzyl ether + water; Curve 5, dibenzyl ether + Au; Curve 6, dibenzyl ether + Fe; Curve 7, dibenzyl ether alone; Curve 8, dibenzyl ether + I₂.

is also formed during the oxidation interfered when other methods such as precipitation by an inert solvent were attempted.

It may be remarked here that the catalysts used were of the purest quality obtainable: gold was "Corona" gold purchased from the White Mfg. Co.; silver had been prepared in this Laboratory by the electrolytic precipitation method; iron was in

[14] For description of the method used, see Section 2.

the powder form prepared by the reduction of iron oxide with hydrogen; mercury was purified in the usual manner; copper was used in the form of wire 3 to 4 mm. long previously polished and cleaned; iodine was of the pure "reagent" quality; picric acid of the c. p. quality, while p-benzoquinone was part of a pure sample previously used in other investigations.

Discussion of Results.—From the results shown in Table I and those represented by the curves of Figs. 2 and 3, certain significant conclusions may be drawn in regard to the auto-oxidation of dibenzyl ether.

Small quantities of inhibitors like iodine, picric acid and benzoquinone show a strong inhibitory action on the oxidation of dibenzyl ether. These substances have also been found to be excellent inhibitors in several auto-oxidation reactions.

Water in small quantities acts as a negative catalyst during the initial stages of the reaction, then as a positive catalyst as the reaction progressed.

Several metals which have been tried in small quantities show a definite acceleration effect. All metals studied were found to have undergone various degrees of oxidation, from a slight tarnish of gold to a complete oxidation of mercury. Silver, which is very resistant to atmospheric oxidation at 40°, was found oxidized to the extent of 2.35%. The results with copper seem to be at
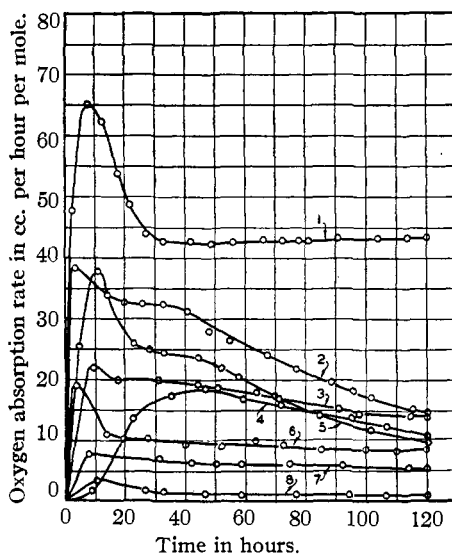

Fig. 3.—Effect of catalysts on oxygen absorption rate of dibenzyl ether. Curve 1, dibenzyl ether + Hg; Curve 2, dibenzyl ether + Cu; Curve 3, dibenzyl ether + Ag; Curve 4, dibenzyl ether + water; Curve 5, dibenzyl ether + Au; Curve 6, dibenzyl ether + Fe; Curve 7, dibenzyl ether alone; Curve 8, dibenzyl ether + I$_2$.

variance with those of Hewer,[15] who reports copper to have a retarding influence on the oxidation of ethyl ether.

(2) **Auto-Oxidation of Various Ethers under the Influence of Ultraviolet Radiation.**—In the foregoing section mention was made of the marked effect of ultraviolet radiation on the auto-oxidation of dibenzyl ether. Similar and more pronounced effects have been observed with several other ethers, the results of which will be presently reported. 1,4-Dioxane, for example, yielded, after eighty hours of continuous exposure to oxygen. an amount of peroxide equivalent only to 6.8 cc. of $N/50$

[15] Hewer, *Lancet*, **216**, 770 (1929); also quoted in *Am. J. Pharm.*, **101**, 840 (1929).

thiosulfate solution per mole, while on exposure to ultraviolet light the amount of peroxide formed for the same period of time was equivalent to 452 cc. of $N/50$ thiosulfate per mole of the ether.

The mechanism of the photochemical oxidation is not very well established at present, but our present results, which should be considered only preliminary, seem to indicate that it follows the same course as that of the oxidation in the dark. This view is particularly strengthened by the fact that the products formed in both reactions are not only identical but are those predicted by our theory. Furthermore, these facts stimulate the conclusion that the primary effect of ultraviolet radiation is to increase the energy content of the molecular valence electrons of the ether oxygen, thereby transforming the whole ether molecule from a relatively inert to a highly activated state. This view is in accordance with the general theory[2a] of auto-oxidation reactions recently proposed by the author. Thereby, the rate with which molecular oxygen combines with ethers to form oxonium peroxides will, presumably, depend not only on the nature of the original ether but also on the statistical average concentration of the activated ether and oxygen molecules present at any moment.

Experimental Procedure and Results

The reactions were carried out in a quartz vessel consisting of a bulb of 1000 cc. capacity and a neck 22 cm. long and 4 cm. in diameter. The neck was provided with an outer condenser jacket through which cold water was allowed to circulate during each reaction. A hollow ground-in pyrex stopper fitted onto the vessel served to connect the latter with a mercury manometer. Dry oxygen was introduced into the apparatus through a small side tube provided with a two-way stopcock and sealed onto one end of the manometer. The reaction vessel was suspended in an air-bath consisting of a rectangular well-insulated tinned iron box 23 × 23 × 36 cm., and ultraviolet light from a standard "Uviarc" lamp was allowed to fall horizontally only upon the bulb of the vessel through a side opening on the box of about the same size as the bulb. In all measurements the lamp was kept at a distance 35 cm. from the bulb. A very efficient fan driven by a high speed motor served to stir the air inside the box, thereby keeping the temperature at about 45 ± 1°.

There seem to be no data available in the literature to show the effect of ultraviolet radiation on the rate of peroxide formation during the oxidation of ethers. It was deemed advisable, therefore, in the present case, to follow the auto-oxidation of ethers by determining the peroxide formed with time of illumination. Although this method fails to account completely for the true rate of auto-oxidation, it affords an excellent semi-quantitative comparison of the tendency with which ethers oxidize.

One hundred cc. of freshly distilled ether, free from peroxide, was added to the quartz vessel after it had been evacuated and filled with pure oxygen. The reaction was then started and the time recorded when the "Uviarc" lamp was turned on. At the end of a definite period of illumination, usually ten hours, the lamp was turned off and the reaction mixture allowed to stand in the dark for one-half hour to acquire the temperature of the room (during this dark period the oxidation of ethers is extremely small, as compared with the photochemical oxidation, and could therefore be entirely neglected without introducing any serious error in the results), then pure oxygen was

admitted into the apparatus until the pressure became equal to the atmospheric pressure; the stopper was then removed and by means of a 5-cc. calibrated pipet, samples of 5 cc. were pipetted into an acidified solution of potassium iodide and the iodine liberated titrated against $N/50$ thiosulfate. Best results were obtained when the potassium iodide solution was acidified, just before use, with glacial acetic acid. Blanks were used in every titration. Figure 4 shows the total amount of peroxide found in each of the nine ethers tried expressed in cc. of $N/50$ thiosulfate consumed per mole of each ether plotted against time of irradiation. Duplicate runs made with some of these ethers were found to check within 4 to 6%. In addition to these ethers, phenetole, anisole, p- and o-methyl cresol and diphenyl ether developed after forty hours of irradiation the following amounts of peroxide expressed in cc. of thiosulfate per mole of each ether: 110.5, 59, 140.4, 115 and 15 cc., respectively. No attempt was made to isolate any of the oxidation products from the aromatic ethers.

Some interesting though only tentative conclusions, at present, seem to emerge from these results. With the majority of ethers studied the total peroxide formed increases, for long periods of time, proportionately with the time of irradiation. The groups to which the ether oxygen is attached exert a decided influence, just as it was anticipated, on the rate with which molecular oxygen adds on to this atom. In other words, the rate with which different ethers auto-oxidize, under the conditions of our experiments, bears a close relationship to their structure. It would be very interesting, however, to see if these relationships follow when the measurements are made using monochromatic radiation and the quantum yields determined. Such a method of approach is contemplated by the author.
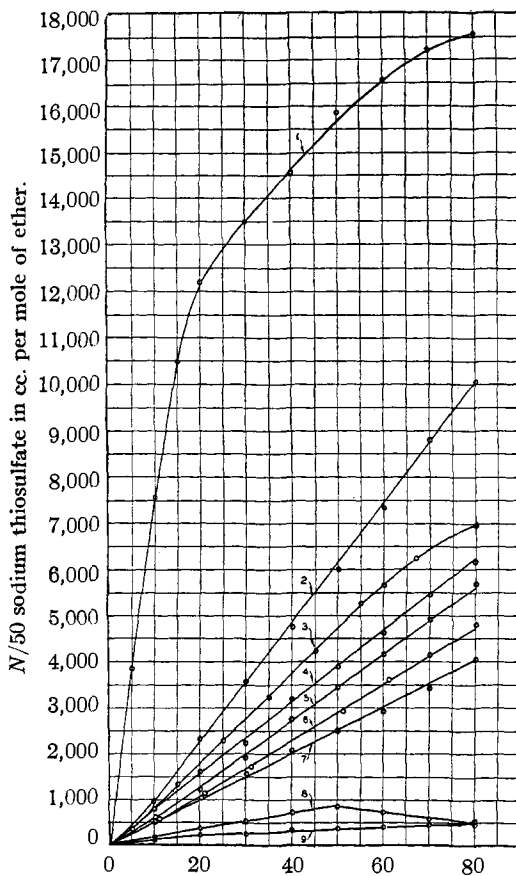

Fig. 4.—Effect of ultraviolet radiation on the oxidation of ethers: Curve 1, *tert.*-butyl benzyl; Curve 2, *sec.*-butyl ethyl; Curve 3, *tert.*-butyl ethyl; Curve 4, *n*-butyl ethyl; Curve 5, isobutyl ethyl; Curve 6, *tert.*-butyl *n*-propyl; Curve 7, *n*-dibutyl; Curve 8, 1,4-dioxane; Curve 9, *tert.*-butyl methyl.

Preparation and Purification of Materials

The following ethers have been prepared and purified in this Laboratory by Dr. George W. Rigby, and details will be found in his Dissertation:[7] *tert.*-butyl ethyl, *tert.*-butyl methyl, *tert.*-butyl *n*-propyl, *n*-butyl ethyl, isobutyl ethyl and *sec.*-butyl ethyl. All these ethers have been refractionated over metallic sodium just before use in order to destroy any peroxide that might have developed. The boiling points were found to agree very well with those determined by Dr. Rigby.

n-Dibutyl ether and 1,4-dioxane were the c. p. products purchased from the Eastman Kodak Company. Both of these ethers, but especially the latter, showed the presence of considerable amounts of peroxide and were further purified by fractionating over metallic sodium. It is quite interesting to note that 1,4-dioxane has been variously reported[16] to be indifferent to several oxidizing reagents, and consequently has been highly recommended as a solvent for molecular weight determinations.

Phenetole, anisole and diphenyl ether were also the c. p. products furnished by the Eastman Kodak Company, but were not further purified since they were found to contain only minute traces of peroxides and no aldehydes or phenols.

However, the methyl cresol ethers (Kahlbaum's c. p. quality) contained not only considerable amounts of peroxides, but also aldehydes and organic acids. These were removed and the ethers finally fractionated.

Tert.-butyl benzyl ether was synthesized, for the first time, by us and a brief description of its preparation here will not be irrelevant. Benzyl chloride was mixed with a large excess of sodium *tert.*-butylate and the mixture allowed to stand at room temperature for two months. At the end of this time the mixture was washed with water and the oil which had separated out was dried over anhydrous sodium sulfate and fractionated, the fraction boiling, with a slight decomposition, at 205.6–208° (corr.) collected and used immediately in our reaction. The density of this ether was found to be d_4^{25} 0.9439. Metallic sodium reacts with it vigorously and therefore cannot be used for its purification. Concentrated hydrochloric acid reacts with this ether, yielding *tert.*-butyl chloride and benzyl chloride. It oxidizes in the dark, yielding monoxy-benzyl peroxide and *tert.*-butyl alcohol. Attempts to separate the peroxide in the pure form were not successful. Both benzaldehyde and benzoic acid have been isolated from its oxidation products.

TABLE II
BOILING POINTS OF ETHERS

Ether	B. p., °C.	Literature
Tert.-butyl methyl	55.3	54–55
Tert.-butyl ethyl	73.1	70
Tert.-butyl *n*-propyl	97.4	..
Tert.-butyl benzyl	205.6–208	..
n-Butyl ethyl	92.3	91.4
n-Butyl *n*-butyl	142.2–143	140.9
Isobutyl ethyl	81.1	78–80
Sec.-butyl ethyl	81.2	..
1,4-Dioxane	100.9–101.1	101.2–101.4
Methyl *o*-cresol	170.1–171.6	171.3
Methyl *p*-cresol	175.5–176.0	176.5

No oxidation products of ethers other than the peroxides have been determined quantitatively. Attempts have been made, however, to iso-

[16] Anschütz and Broeker, *Ber.*, **59**, 2844 (1926); Reid and Hofmann, *Ind. Eng. Chem.*, **21**, 695 (1929).

late and identify all the important products.   Hydrogen peroxide was identified in the oxidation products of all ethers studied by the titanium sulfate test and by Jorissen's vanadic acid reagent.[17]   All aliphatic oxidized ethers studied yielded a strong benzidine reaction, which has been ascribed by Woker,[9] Wieland and Wingler[4] and others to the presence of monoxy-alkyl peroxides.   The aldehydes were identified by the preparation of their *p*-nitrophenylhydrazones, which were found to have melting points agreeing very well with those recorded in the literature.   *Sec.*-butyl ethyl ether yielded in addition to acetaldehyde methyl ethyl ketone.

The hydrazone of glycolic aldehyde isolated from the oxidation products of 1,4-dioxane is actually an osazone first described by Wohl and Neuberg,[18] m. p. 311°.   Dakin and Dudley[19] prepared it from glycolic acid, m. p. 302°, and Curtius[20] from glyoxal, m. p. 308°.   Our product was recrystallized several times from hot pyridine into fine red needles, m. p. 308.7°.   With this osazone alcoholic potash gives a greenish-blue color, changing to deep blue and slowly to violet and finally to reddish-brown.   That the aldehyde formed during the oxidation of 1,4-dioxane was not glyoxal was proved by its failure to reduce ammoniacal silver nitrate solution and its positive reaction with Fehling's reagent.

Tert.-butyl alcohol was isolated as the *tert.*-butyl choride, b. p. 50–51°, from the oxidation products of all *tert.*-butyl ethers.   Alcohols formed during the oxidation of the other ethers oxidized further and it was, therefore, impossible to isolate them as such.

Another oxidation product detected in small quantities by the mercuric chloride test in all ethers having either the methyl or ethyl groups is formic acid.   This acid was also isolated from the oxidation products of 1,4-dioxane.

Isolation of Some Organic Peroxides.—Four of the oxidized ethers were washed with sodium carbonate solution, dried and the unchanged ether removed by distillation in a vacuum at temperatures varying from 0 to 70°, the receiver being cooled in a mixture of solid carbon dioxide and ether.   Portions of the residue were then analyzed for active oxygen by the potassium iodide–thiosulfate method, and for the amount of aldehyde formed on hydrolysis in dilute sulfuric and subsequent distillation of the aldehyde by precipitation with *p*-nitrophenylhydrazine.   Three trial determinations by the latter method with known samples of propionaldehyde gave recoveries of the aldehyde of 95.6, 94.3 and 95.2%.

The analytic data obtained are given in Table III.   The calculated ratio of aldehyde to peroxide is based on the assumption that the first

[17] Jorissen, *Ann. chim. anal.*, **8**, 201 (1903).
[18] Wohl and Neuberg, *Ber.*, **33**, 3107 (1900).
[19] Dakin and Dudley, *J. Biol. Chem.*, **15**, 137 (1913).
[20] Curtius, *J. prakt. Chem.*, [2] **95,** 225 (1917).

formula of each possible pair is considered to be monoxy-alkyl perester $[RC(=O)-O-O-CH(OH)R]$, which on hydrolysis should yield aldehyde in the ratio of 1:1 of peracid, while the second formula representing dioxy-alkyl peroxide $[R-CH(OH)-O-O-(OH)CH-R]$ on hydrolysis should yield aldehyde in the ratio of 2:1 of peroxide.

<div align="center">

TABLE III

ANALYTICAL DATA

</div>

Ether formula	Possible formula of peroxide	Active oxygen Calcd.	Found	Ratio Aldehyde/Peroxide Calcd.	Found
$tert.\text{-}C_4H_9OC_2H_5$	$C_4H_8O_4$	13.33	13.14	1	0.71
	$C_4H_{10}O_4$	13.11	13.00	2	
$tert.\text{-}C_4H_9OC_3H_7\text{-}n$	$C_6H_{12}O_4$	10.81	11.12	1	0.70
	$C_6H_{14}O_4$	10.66	11.30	2	
$n\text{-}C_4H_9OC_4H_9\text{-}n$	$C_8H_{16}O_4$	9.09	8.88	1	0.72
	$C_8H_{18}O_4$	8.99	8.75	2	
$i\text{-}C_4H_9OC_2H_5$	$C_6H_{12}O_4$	10.81	10.58	1	0.68
	$C_6H_{14}O_4$	10.66	10.39	2	

These peroxides are all colorless oils which explode violently when heated directly in a flame and possess an odor resembling that of peracids. In ether solution they fail to give the benzidine or chromic acid reactions, but liberate iodine readily from a solution of potassium iodide and give a strong red color with p-amidodimethylaniline hydrochloride.

Inasmuch as the peroxide content differs only slightly in the two types of peroxides shown in the foregoing table, it was thought advisable to synthesize the dioxy-ethyl and dioxy-propyl peroxides and compare their behavior toward different reagents with that of the peroxides isolated from $tert.$-butyl ethyl and $tert.$-butyl n-propyl ethers.

The dioxy-propyl peroxide was prepared by allowing a 2:1 mixture of propionaldehyde and hydrogen peroxide in dry ether to stand at room temperature for twenty-four hours. Thereafter the mixture was treated and analyzed in the same manner employed above with the oxidized ethers. The percentage of active oxygen was found to be 10.10 as against 10.66 calculated for $C_6H_{14}O_4$, while the ratio of aldehyde to peroxide was 1.86:1 as against 2:1 calculated. This peroxide has a very disagreeable odor, fails to liberate iodine from neutral potassium iodide and gives only a very weak test with p-amidodimethylaniline hydrochloride. It clearly differs from the peroxide isolated from oxidized $tert.$-butyl n-propyl ether.

The dioxy-ethyl peroxide was also prepared in the same manner and was found to have in ether solution properties similar to dioxy-propyl but different from the peroxide isolated from $tert.$-butyl ethyl ether. An attempt to separate it in the pure form under the same experimental

conditions applied to *tert.*-butyl ethyl ether failed to leave any residue for analysis.

It is now quite obvious, from the evidence presented, that the peroxides isolated from the oxidation products of four ethers are different from the monoxy-alkyl and dioxy-alkyl peroxides, and therefore might be considered as peresters of the type described. However, neither the monoxy- nor the dioxy-alkyl peroxides are to be excluded from the oxidation products of ethers.

The author takes this opportunity to express profound appreciation to Professor James F. Norris for his coöperation.

Summary

1. Evidence has been brought forward to show that the dehydrogenation theory of Wieland, as applied by Wieland and Wingler to the auto-oxidation of ethers, is untenable.

2. The oxonium peroxide theory, based on previous views of the author, has been proposed to explain the auto-oxidation of ethers.

3. The rate of oxygen absorption by dibenzyl ether has been determined at 40°, and the effect on this rate of the metals gold, silver, copper, iron and mercury, of water, and of iodine, picric acid and benzoquinone has been studied.   .

4. Ultraviolet radiation has been shown markedly to accelerate the oxidation of various ethers. The rate of peroxide formation under these conditions has been found to depend largely on the type of groups attached to the oxygen atom of the ether.

5. *Tert.*-butyl benzyl ether has been prepared for the first time.

. 6. The oxidation products of several of the ethers have been identified, and four peroxides have been isolated and shown to differ in properties from monoxy- and dioxy-alkyl peroxides.

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