

purified by distillation. Low voltage mass spectral analysis showed the ester to be completely undeuterated.

A similar check on hydrogen-deuterium exchange between methyl dichloroacetate and methanol-*d* was made. Before work-up the reaction mixture was treated with acetyl chloride. The triethylamine hydrochloride was filtered, and the pentane and methyl acetate were removed on a rotary evaporator, leaving the methyl dichloroacetate which was shown to be undeuterated by nmr analysis.

Reaction of Phenylacetyl Chloride with Methanol in the Presence of Triethylamine and Triethylamine Deuteriochloride.—Phenylacetyl chloride (0.10 mol) dissolved in pentane (50 ml) was added dropwise to a stirred mixture of methanol (0.10 mol), triethylamine (0.10 mol), and triethylamine deuteriochloride (0.10 mol) in pentane (60 ml) at 0°. The reaction was worked up

according to the general procedure yielding methyl phenylacetate which was shown to be completely undeuterated by mass spectral analysis.

Registry No.—Triethylamine, 121-44-8; methyl 3-butenate, 3724-55-8; methyl 2-butenate, 18707-60-3.

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Photochemical Oxidations. II. Rate and Product Formation Studies on the Photochemical Oxidation of Ethers

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The rates of oxygen uptake during the photochemical oxidation of ethers have been determined. The rates correlate with the orders of basicity of acyclic and cyclic ethers to substantiate further the earlier postulated role of charge-transfer complexes in the photochemical oxidation of ethers. The products of the ether oxidations were determined for an acyclic ether, diethyl ether, and for a cyclic ether, tetrahydrofuran. Mechanisms are postulated for the products formed which involve hydroperoxide intermediates.

Work done by Chien has shown that the excitation of charge-transfer complexes is partially responsible for the photooxidation of hydrocarbons.² Also, in a previous publication we have presented evidence that the initial step in the photooxidation of diethyl ether is the absorption of light by a charge-transfer complex of molecular oxygen with ether.³ In this paper we shall discuss additional studies on this reaction in which a series of ethers, both cyclic and acyclic, were used. The discussion will center on the mechanistic implications of the results of an analysis of the products formed and the relative rates of reaction as indicated by both the rates of oxygen uptake and product formation during irradiation.

All of the ethers studied (Table I) reacted when they

TABLE I
O₂ UPTAKE AFTER 1 HR AND pK_a VALUES FOR ETHERS

	O ₂ uptake, mol	pK _a
Diethyl ether	2.0 × 10 ⁻³	-3.59
Di- <i>n</i> -propyl ether	1.3 × 10 ⁻³	-4.40
Diisopropyl ether	1.1 × 10 ⁻³	-4.30
Di- <i>n</i> -butyl ether	0.9 × 10 ⁻³	-5.40
Propylene oxide	0.1 × 10 ⁻³	
Trimethylene oxide	2.7 × 10 ⁻³	
Tetrahydrofuran	2.2 × 10 ⁻³	-2.08
Tetrahydropyran	1.2 × 10 ⁻³	-2.79

were saturated with oxygen and irradiated. The ethers had been previously subjected to a rigorous purification to eliminate the possibility of impurities participating in the reactions. On being irradiated for several hours, each of the ethers gave a mixture of

products, but a major product was always the ester or lactone. In addition, each irradiated reaction mixture contained peroxides. Since it has been previously shown that trimethylene oxide⁴ and propylene oxide⁵ may undergo photochemical decomposition, these compounds were first irradiated under a nitrogen atmosphere to see if they would decompose under the conditions used in these experiments. The results indicate that they do not decompose, and therefore we can be sure that the reaction observed with oxygen is not due to photodecomposition of ethers.

Diethyl ether and tetrahydrofuran, as representative cyclic and acyclic compounds, were chosen for a more detailed examination. As the irradiation time was decreased to a few minutes, it was found that tetrahydrofuran gave three products, butyrolactone, α -hydroxytetrahydrofuran, and water (see Figure 1). Thus the other unidentified compounds found for the longer irradiation times are formed as the result of secondary reactions. It is likely that some of these are the products of the photodecomposition of butyrolactone.⁶ On the other hand, the products found when diethyl ether is irradiated, *i.e.*, ethyl acetate, ethyl formate, ethyl alcohol, and acetaldehyde,⁷ appear even when the reaction is run for a very short time (Figure 2). Thus, it would seem that the cyclic and acyclic ethers may have slightly different reaction mechanisms.

That the mechanism involves the excitation of charge-transfer complexes for both cyclic and acyclic ethers with the difference in the reaction path for the two series occurring after this step can be inferred also from an examination of the relative rates of oxygen

(1) Taken in part from Ph.D. thesis, C. T. Wang, University of North Dakota, 1969.

(2) J. C. W. Chien, *J. Phys. Chem.*, **69**, 4317 (1965).

(3) V. I. Stenberg, R. D. Olson, C. T. Wang, and N. Kulevsky, *J. Org. Chem.*, **32**, 3227 (1967).

(4) J. D. Margerum, J. N. Pitts, Jr., J. G. Rutgers, and S. Searles, *J. Amer. Chem. Soc.*, **81**, 1549 (1959).

(5) R. Gomer and W. A. Noyes, Jr., *ibid.*, **72**, 101 (1950).

(6) R. Simonaites and J. N. Pitts, Jr., *ibid.*, **90**, 1389 (1968).

(7) The presence of acetaldehyde was verified by vpc. It could not be trapped owing to its low concentration. Its well-known photodecomposition most probably is the cause of its low concentration.

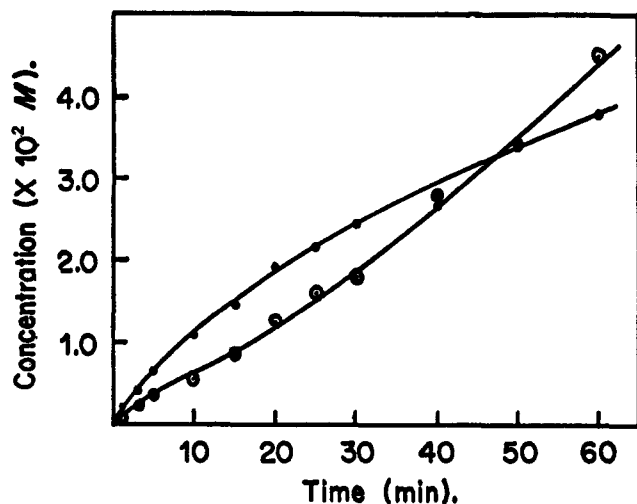


Figure 1.—Rates of product formation during the photooxidation of tetrahydrofuran. The products are butyrolactone, ○, and peroxide ●. These data were obtained using a flame ionization detector which is insensitive to water.

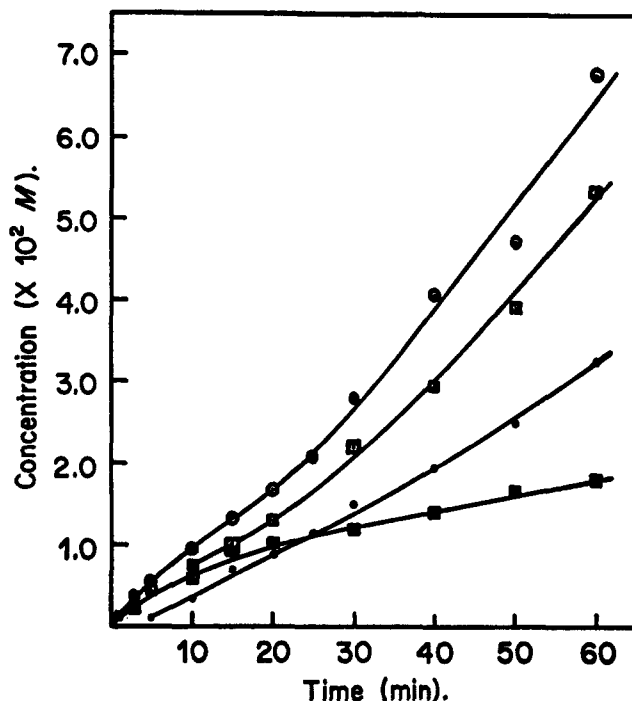


Figure 2.—Rates of product formation during the photooxidation of diethyl ether. The rates illustrated are for ethyl acetate, ○, ethyl alcohol, □, ethyl formate ●, and peroxide, ■.

uptake during irradiation. The results of these experiments are shown in Table I, where the amount of oxygen uptake after 1 hr for the several ethers is presented. During this time, only *ca.* 2% of the reaction has taken place and thus the effects of the secondary reactions mentioned above are minimal. Each of the values given have been corrected for the relative solubility of oxygen in the different ethers, using diethyl ether as the standard. Since the formation of the complex is the initial step in the reaction, it might be expected that there would be a correlation between ability to form a complex and the rate of reaction. As a measure of the complexing ability we have chosen the pK_a values of the ethers (Table I).⁸ If all of the compounds are examined, there is a poor correlation. However, if the cyclic and acyclic ethers are grouped separately, it can be seen that, in each group, there is a correlation in which the rate of reaction decreases with decreasing basicity. Although the results show an inversion in the order of *n*-propyl and isopropyl ethers, both the differences in basicity and oxygen uptake are small. If these differences are meaningful, the inversion can be attributed to steric factors. The O_2 molecule is larger than the hydrogen ion, and thus its ability to interact with isopropyl ether is less than that of the hydrogen ion.

For propylene oxide and trimethylene oxide, there are no values of pK_a reported; however, the basicity of these compounds toward $CHCl_3$ ⁹ and I_2 ¹⁰ indicate that the basic order is four- > five- > six- > three-membered cyclic ethers. Propylene oxide, the weakest base is also the least reactive of the ethers studied here. The weak basicity of propylene oxide is also indicated by the ultraviolet (uv) spectra of oxygen-saturated solutions. All of the ethers except propylene oxide, when saturated with oxygen, show a very great enhancement of absorption in the 280- to 210-m μ region, which is attributed to the charge-transfer complex. The propylene oxide-oxygen solution has only a very small absorption peak in this region even though

oxygen is more soluble in propylene oxide than in several of the other ethers, thus indicating its very weak basicity. This order of basicity of propylene oxide also correlates well with the spectroscopic work of Fleming, *et. al.*¹¹ The fact that there is a correlation of rate with basicity within each series indicates that a major feature of the reaction is the formation of the charge-transfer complex. Since the two series cannot be correlated with each other, we can again assume that there is a difference in the mechanism of the reaction as it involves cyclic and acyclic compounds.

To further explain the differences observed between cyclic and acyclic compounds, the detailed mechanism of the reaction must be examined. The initial step as postulated before² must be the excitation of the charge-transfer complex to form the intermediate peroxide. Three modes of decomposition of the peroxide (Scheme I) are suggested to explain the products found. Reaction pathways a and c have been proposed earlier¹² to explain the products derived from the ozonation of ethers, where a similar intermediate, the radical 2, has also been proposed. Reaction b is both new and unexpected; however, considering the bond energies involved when a C-C bond is broken and a C-O bond along with a π -C-O bond is formed, it is quite reasonable. It is noteworthy that the ozonation of diethyl ether also gives ethyl formate.¹³ On the basis of statistical considerations, RH in reaction c would be another molecule of ether. It is likely that the well-known nonphotochemical reactions d and e (Scheme II) assume importance once the peroxide concentration has reached a respectable level by means of the excitation of the complex. The reactions d and e are chain-

(8) (a) E. M. Arnett and C. Y. Wu, *J. Amer. Chem. Soc.*, **84**, 1680 (1962); (b) *ibid.*, **84**, 1684 (1962).

(9) S. Searles and M. Tamres, *ibid.*, **73**, 3704 (1951).

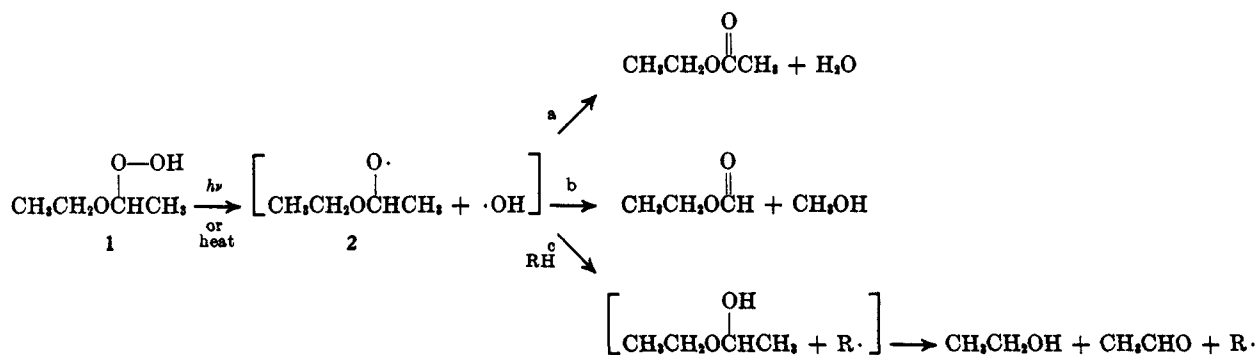
(10) M. Brandon, M. Tamres, and S. Searles, Jr., *ibid.*, **83**, 2129 (1960).

(11) G. Fleming, M. M. Anderson, A. J. Harrison, and L. W. Pickett, *J. Chem. Phys.*, **30**, 351 (1959).

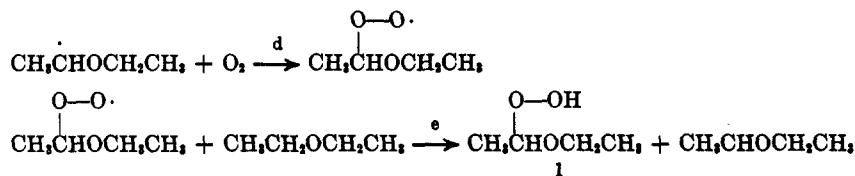
(12) For a review, see P. S. Bailey, *Chem. Rev.*, **53**, 925 (1958).

(13) (a) F. G. Fisher, *Ann.*, **476**, 233 (1929); (b) *ibid.*, **486**, 83 (1931).

SCHEME I
THE THREE MODES OF DECOMPOSITION OF THE PEROXIDE OF DIETHYL ETHER



SCHEME II
CHAIN PROPAGATION REACTIONS FOR THE GENERATION OF PEROXIDE



propagation reactions which continually add to the concentration of 1 in the reaction mixture.

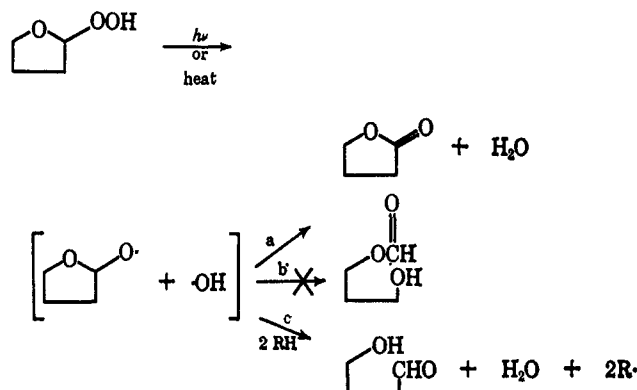
The lack of induction periods in the reactions of ethers is especially interesting, when compared with the induction periods observed during the photochemical oxidation of hydrocarbons.² There are two sources of the peroxide intermediates in the ether reaction solutions. The first is directly from the charge-transfer complex and the second is from the chain processes of reactions d and e. That no induction period is observed can be attributed to the rate of reaction of the charge-transfer complex exceeding the rate of formation of peroxide from reactions d and e, both initially and after the steady-state concentration of the peroxide has been obtained. In the case of hydrocarbons the analogous reaction rates might not be in the same ratio because the concentration of the complexes in the hydrocarbon solution is much lower owing to a lesser basicity than ethers; thus, an induction period is observed in these reactions.

Also noteworthy in the reaction of diethyl ether with oxygen is that after a period of time the rate decreases with time rather than increases. The uv absorption of ethyl acetate, one of the principal products, is such [λ_{max} 204 μ (ϵ 60)] that it acts as an internal filter for the absorption of the charge-transfer complex of ether and oxygen. Hence, after *ca.* 3% ethyl acetate has been formed in the reaction mixture, the oxygen uptake is greatly retarded.

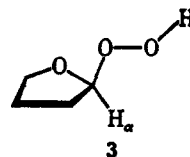
In direct contrast to the diethyl ether reaction is the tetrahydrofuran-oxygen reaction in which the principal isolable products are water, α -hydroxytetrahydrofuran, and butyrolactone. The water is formed much more rapidly in this reaction solution than for the reaction of diethyl ether. This clearly illustrates that, for tetrahydrofuran, paths analogous to reactions a and c for diethyl ether are the predominant reactions (Scheme III). However, it appears that path b is not operative for tetrahydrofuran.

Stereochemical effects must cause the nearly rigid ring system of the tetrahydrofuran to change the

SCHEME III
THE PHOTOOXIDATION OF TETRAHYDROFURAN



pattern of formation of products. The principal conformation of the hydroperoxide of tetrahydrofuran is shown in structure 3. This conformation minimizes the spacial interaction of the hydrogens and oxygen of the ring with the peroxide group. In this conformation the OH of the peroxide is *cis* in its orientation to the H_α . When the O-O bond is broken, the hydroxy radical is in the vicinity of H_α and removes it in preference to reacting with the carbon chain (path b).¹⁴



These radicals also abstract a hydrogen atom from solvent (path c). Thus, paths a and c are the predominant paths for the cyclic ether, whereas paths a, b, and c are all allowed in a freely rotating ether such as diethyl

(14) NOTE ADDED IN PROOF.—In more current work, there is evidence that butyrolactone is also formed directly from the excitation of tetrahydrofuran and oxygen.

ether. This concept of *cis* elimination in a free-radical reaction is a good illustration of stereochemical requirements for radical reactions.

Experimental Section

Reagents.—Diethyl ether and tetrahydrofuran (Fisher reagent grade), di-*n*-propyl ether and tetrahydropyran (from Matheson Coleman and Bell), diisopropyl ether (from Eastman Organic Chemicals), and di-*n*-butyl ether (spectroquality reagent, from Matheson Coleman and Bell) were purified as described previously³ except, instead of lithium aluminum hydride, sodium borohydride was used in the purification of tetrahydropyran. Purified diisopropyl ether and tetrahydropyran were further fractionally distilled in a Wheeler GE-125-2H "All Glass" fractionating column to remove traces of benzene. Trimethylene oxide (from Aldrich Chemical) and propylene oxide (from Eastman Organic Chemicals) were fractionally distilled over dry KOH, using the Wheeler column and the center cut of the distillations were collected. The purity of the ethers was checked by uv spectra and no detectable amount of impurities were shown. The ethers were then stored under nitrogen prior to use. The oxygen used in this work was brought from the Linde Co. and was specified as 99.69% pure.

Apparatus.—The photooxidations of ethers in the liquid phase were carried out in a cylindrical quartz reaction cell 30 cm long and 2.5-cm outside diameter. The top of the cell was connected, by means of a graded seal, to a three-way Teflon stopcock. The upper part of the cell was blanked out by aluminum paint so that the light irradiated only the liquid phase of the sample. The cell was then connected by glass tubing, with Tygon joints for flexibility, to a gas reservoir. The latter consisted of a mercury manometer and a Teflon stopcock for the admission of oxygen and for connection to the grease-free vacuum pumpout system. A 550-W Hanovia high pressure mercury arc lamp, mounted in a water-cooled immersion well, was used as a source of uv radiation. The reaction cell and the immersion well were immersed in a water bath through which distilled water, monitored for uv transparency, was circulated at $15 \pm 0.25^\circ$ from a constant-temperature bath. The arc was 3.0 cm from the front of the reaction cell. The reaction cell was very carefully cleaned before each run with ethanolic potassium hydroxide. It was then rinsed well with distilled water and dried under vacuum.

The operation of the complete apparatus, when making an oxygen uptake determination, is described as follows. The reaction cell was connected to the gas reservoir and the whole system was evacuated and then filled with 1 atm of oxygen. From the stopcock on the top of the cell 5 ml of ether was introduced into the reaction cell by means of a syringe with a long needle. The cell was then quickly closed, and the whole system was again filled with oxygen up to 1.5 atm. The ether was vigorously stirred by means of a small glass-covered magnetic stirring bar, and sufficient time was allowed for thermal equilibrium. Practically, there was no oxygen uptake before irradiation.

After irradiation, subsequent manometric readings were made at 1-hr intervals and were computed as number of moles of oxygen uptake. The irradiations of the different ethers were taken in random fashion to avoid systematic error. Each ether was irradiated several times and the values reported in Table I are averages.

Solubility of Oxygen in Ethers.—The solubilities were determined by making use of the Van Slyke-Neill manometric apparatus which is based upon the principle of extracting the gas from the solvent and measuring the pressure of the liberated gas.¹⁵ Solubilities of oxygen in eight different ethers at 15.0° , under oxygen pressures of 1 atm and 1.5 atm, were determined. The vapor pressure of ether needed for calculation of solubility was determined by the conventional isoteniscope method.

Product Determination.—The irradiation products of diethyl ether and tetrahydrofuran were preliminarily analyzed by preparative gas chromatography using an Aerograph Autoprop A-700 equipped with a Carbowax column (10 ft \times $\frac{3}{8}$ in.). The identification of the products was accomplished by the usual instrumental methods, *i.e.*, comparing their ir (using Beckman IR-12) and nmr (using Varian A-60) spectra with those of the authentic samples. The product yield as a function of irradiation time was determined by injecting each freshly irradiated sample into a Varian Aerograph 1200 gas chromatograph equipped with a flame ionization detector and a Carbowax column (10 ft \times $\frac{1}{4}$ in.). Quantitative measurements were made by comparing the irradiated samples with that of standard solutions. The analytical procedure used for all hydroperoxide estimations was the method described by Wagner, *et al.*¹⁶ This iodometric determination was made immediately after each irradiation and was reproducible. α -Hydroxytetrahydrofuran was quantitatively determined by ir spectroscopy and identified as the 2,4-dinitrophenylhydrazone.

Registry No.—Diethyl ether, 60-29-7; di-*n*-propyl ether, 111-43-3; diisopropyl ether, 108-20-3; di-*n*-butyl ether, 142-96-1; propylene oxide, 75-56-9; trimethylene oxide, 503-30-0; tetrahydrofuran, 109-99-9; tetrahydropyran, 142-68-7.

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(15) F. S. Orcutt and M. H. SeEVERS, *J. Biol. Chem.*, **117**, 501 (1936).

(16) C. D. Wagner, R. H. Smith, and E. D. Peters, *Anal. Chem.*, **19**, 976 (1947).