The Role of Charge-Transfer Complexes in the Photooxidation of Ethers with Oxygen

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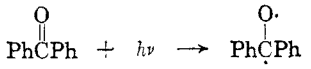
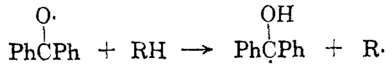
Schenck, *et al.*, have previously investigated the products of the photochemical oxidation of ethers.[1] In these studies, seven different ethers were reacted with oxygen in the presence of a photosensitizer, benzophenone; hydroperoxy ethers and -aldehydes were isolated from the reaction mixtures. It was proposed that the fundamental steps in the reactions were those given by eq 1–3.



$$\mathrm{Ph\overset{\overset{O}{\|}}{C}Ph} + h\nu \longrightarrow \mathrm{Ph\overset{\overset{O\cdot}{|}}{\underset{\cdot}{C}}Ph} \qquad (1)$$



$$\mathrm{Ph\overset{\overset{O\cdot}{|}}{C}Ph} + \mathrm{RH} \longrightarrow \mathrm{Ph\overset{\overset{OH}{|}}{\underset{\cdot}{C}}Ph} + \mathrm{R}\cdot \qquad (2)$$

$$\mathrm{R}\cdot + \mathrm{O_2} \longrightarrow \mathrm{RO_2}\cdot,\ \text{etc.} \qquad (3)$$

In this paper, we wish to report our work on the same reaction in the absence of photosensitizers. In a preliminary communication,[2] we have reported that ethers are converted primarily to esters when irradiated in the presence of oxygen. The interesting aspects of this reaction of ethers with oxygen was that neither oxygen nor the ethers have appreciable light absorption in the ultraviolet region and there is no third compound present to influence the reaction. A number of ethers have been photochemically oxidized with oxygen in our initial studies. All of the aliphatic ethers tested reacted; however, the acyclic ones gave only one major product whereas the cyclic gave more complex reaction mixtures. As a consequence, an acyclic ether, ethyl ether, was selected for a more detailed study.

The spectrum of an oxygen-saturated ethyl ether solution, with a nitrogen–ether solution as a reference, is illustrated in curve a of Figure 1. The solution begins to absorb at 280 mμ and increases toward a broad maximum around 210 mμ. This absorbance is considerable reduced when nitrogen is bubbled through the oxygen–ether solution (Figure 1, curve b) and could be reformed by again passing oxygen into the ether. Thus the absorbing species in solution is formed by a reversible reaction between ether and oxygen. The reversible appearance of high absorbance in the ultraviolet region for the ether–oxygen solution is in accord with the reported work by Munck and Scott.[3] Numerous other oxygen–organic solutions have also been reported to have more intense ultraviolet absorption than either component by itself.[4] This enhanced ultraviolet absorbance, we believe, can be attributed to the formation of a weak complex of oxygen with ether. Because this complex has the general properties of a charge-transfer complex, that is, reversible formation and enhanced ultraviolet absorbance, it most probably is of this type with oxygen acting as the electron acceptor and the ether as the electron donor.

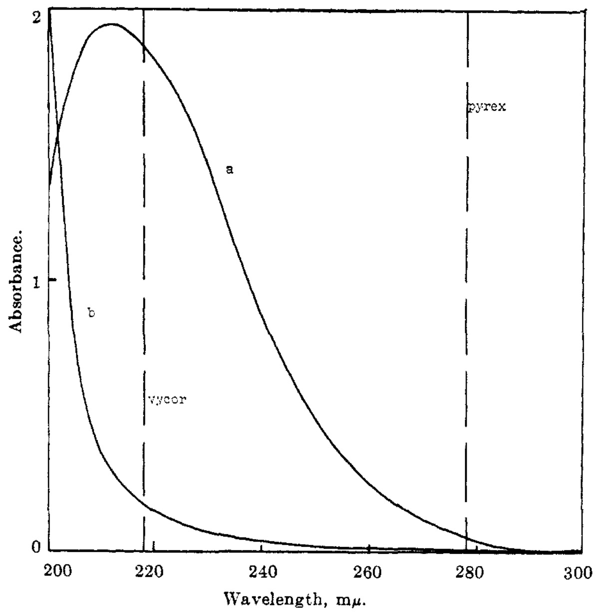


Figure 1.—Ultraviolet spectra of oxygen–diethyl ether with a nitrogen–ether solution as a reference (curve a) and nitrogen–diethyl ether (curve b) solutions with an empty cell as a reference with approximate cutoff regions for vycor and Pyrex filters. The spectra were determined with cells of 1-cm path length.

The ether had to be extremely pure for this work. In the method of purification devised, ozone was used to oxidize the unsaturated compounds, which might have been present, to ozonides. Ozonides, carbonyl compounds, alcohols, and most nitrogen-containing compounds present were converted to ionic species by $LiAlH_4$ and separated from the ether by double distillation.[5] Nitrogen was bubbled through the ether immediately after distillation and prior to recording the ultraviolet spectrum. In this way the optimum transparency could be obtained. The ether was used immediately after preparation because the optical transparency deteriorates with time. The tail-end absorption of ether prepared by the above scheme begins at about 215 mμ (Figure 1, curve b).

The high-purity ether does indeed react with oxygen when irradiated and ethyl acetate appears to be virtually the sole major product, 3% conversion, as detected and isolated by vapor phase chromatography. Upon evaporation of the irradiation solution, a nonvolatile, transparent oil was obtained which amounted to 0.4% conversion.

It was possible that oxygen passing through the ether solution could have been partially converted to ozone and the observed reaction caused by the ozone.[6] This was tested by passing a stream of oxygen–ozone through ether without ultraviolet light at the same rate and for the same length of time as the oxygen was employed for the irradiations. It was assumed that the 5% ozone in the oxygen gas from the ozone generator exceeds the actual concentration of ozone produced in

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[1] G. O. Schenck, H. Becker, K. Schulte-Elte, and C. H. Krauch, *Chem. Ber.*, **96**, 509 (1963).

[2] R. D. Olson and V. I. Stenberg, *Proc. N. Dakota Acad. Sci.*, **17**, 50 (1963).

[3] A. U. Munck and J. F. Scott, *Nature*, **177**, 587 (1956).

[4] H. Tsubomura and R. S. Mulliken, *J. Am. Chem. Soc.*, **82**, 5966 (1960).

[5] For a further discussion of the purification of ethers, see A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, Jr., "Technique of Organic Chemistry," Vol. VII, 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1955, p 366.

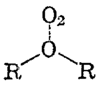
[6] P. S. Bailey, *Chem. Rev.*, 58, 925 (1958).

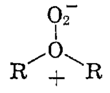
the oxygen stream of the irradiation experiments. Since there was no detectable ethyl acetate formed under these conditions with the ozone–oxygen mixture, ground-state ozone cannot be the agent responsible for ester formation and the reaction does not proceed in the absence of light.

The tail-end absorption of the ether (Figure 1, curve b) could conceivably have absorbed enough light energy and given rise to the reaction product observed. In exploring this possibility, the oxygen–ether solution was irradiated with light which had been passed through a vycor filter, a filter which excluded light of all wavelengths shorter than 218 mμ (Figure 1). There was no detectable diminishing of the yield of ethyl acetate under these conditions, hence the tail-end light absorption of the ether was not essential to the reaction. The ether–oxygen solution was also irradiated using a Pyrex filter which eliminates all wavelengths shorter than 278 mμ (Figure 1). This had the effect of completely stopping the formation of ethyl acetate under the conditions of the experiment. Therefore, the light responsible for the photochemical reaction has wavelengths between 218 and 278 mμ. This is the region where the charge-transfer band is prominent, *therefore the photochemical oxidation of diethyl ether with oxygen reported here provides a reasonable clear-cut example of a process where a charge-transfer complex is the absorbing species for ultraviolet light and the excited species produced therefrom leads to a photochemical reaction.* There are precedents for charge-transfer species being responsible for photochemical reactions.[7]

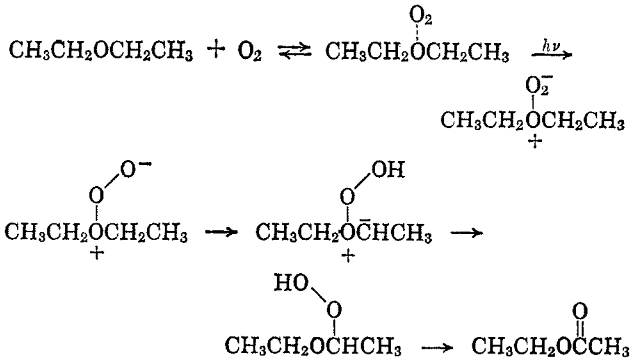
On the basis of the photosensitized reaction studies by Schenck, *et al.*, the primary product in our irradiation mixture might well have been α-hydroperoxy diethyl ether, which could have pyrolyzed to the corresponding ester on the vpc injector. To test this possibility, the infrared spectra of 1 aliquot of a freshly irradiated solution was recorded. The width and height of the carbonyl band indicated 2–3% conversion to ethyl acetate at the termination of the reaction and *prior* to injection in the vpc. However, freshly irradiated solutions gave a positive chromate test for peroxides.[8] Thus small quantities of peroxides are present at the end of the reaction and it may well proceed *via* an α-hydroperoxide intermediate. If this is true, the decomposition of the peroxides must proceed readily under the reaction conditions, perhaps by a photochemical process.

According to Mulliken's theory, the charge-transfer complex is a hybrid of a nonbonded (A) and charge-separated or "dative" bond (B) structure. The ground state of the weak complex has the major contribution from A and the excited state from B. We propose that the excited state of the complex undergoes a chemical reaction according to Scheme I. This is in agreement with the light-absorption dependence of the reaction and the trace amounts of hydroperoxides formed in the reaction solutions.


A


B

SCHEME I



The mechanism suggested by Schenck, *et al.*, for the photosensitized ether oxidation reaction has another plausible alternative; that is, the excited-state energy of the photosensitizer can be transferred to the charge-transfer complex of ether and oxygen to promote the reaction.

Experimental Section

Apparatus.—Infrared spectra were determined on a Perkin-Elmer Infracord. The ultraviolet spectra were prepared with a Cary recording spectrophotometer, Model 14. The nmr spectrum was done on a Varian A-60 spectrometer. The gas chromatograph used was an Aerograph Autoprep Model A-700, Wilkens Instrument and Research, Inc., fitted with a 0.25 in. × 6 ft column packed with firebrick impregnated with di-*n*-decylphthalate. The irradiations were performed with a quartz immersion-type 550-w Hanovia high pressure mercury arc lamp.

Purification.—Ozone, which was generated from Welsbach T-23 laboratory ozonator, was bubbled through anhydrous ethyl ether, Fisher reagent grade, for 12 hr. The ether was then refluxed with lithium aluminum hydride for 2 hr. The mixture was twice fractionally distilled.

Spectra.—The ultraviolet spectrum of an oxygen-saturated solution of ethyl ether was observed with nitrogen–ethyl ether solution as reference.

Irradiation of Oxygen-Saturated Ethyl Ether Solution.—Purified ethyl ether was put into two 3-ml ultraviolet quartz spectrophotometric cells which were placed into special cooling containers. The cooling containers were placed on each side of a quartz double-walled water-cooled jacket in which the mercury arc lamp was placed and the distance from the jacket to the two cells was kept at 3.5 cm. A Pyrex or vycor filter was placed between the cell and the lamp on one side while the other cell was irradiated without a filter. The oxygen (Linde, with purity of 99.69%, was further dried prior to use) was bubbled through the ether with a rate of about 2 ml/min by means of capillary tubes which were bent so that the bubbling caused the circulation of ether solutions. The oxygen flow rate was controlled by micro gas valves. Ethyl ether was added during the irradiation in compensation for small amounts of ether evaporated. The temperature was kept at 0° and the duration of irradiation was 4 hr. Duplicate irradiations were made in each case with only the filter interchanged. Irradiated mixtures (30 μl) were injected into a gas chromatography column which had a temperature of 60°. A flow rate of 85 ml/min of helium was used. The peak corresponding to ethyl acetate was found in all solutions except those where Pyrex filters were used. Quantitatively there was no detectable difference between those ether samples which had been irradiated through vycor and those through quartz. The latter ether samples contained about 3% ethyl acetate. The product was trapped from the eluant and identified by a comparison of its infrared and nmr spectra with an authentic sample of ethyl acetate.

Oxidation of Ethyl Ether with Ozone.—Ozone, which was generated from an ozonator, was passed through ethyl ether for 4 hr in the absence of ultraviolet light. The resulting mixture was analyzed by gas chromatography. Neither ether acetate nor other oxidation products was found in the mixture.

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[7] (a) J. A. Barltrop and R. Robson, *Tetrahedron Letters*, 597 (1963); (b) R. L. Ward, *J. Chem. Phys.*, **39**, 852 (1963); (c) J. A. Barltrop and B. Hesp, *Proc. Chem. Soc.*, 195 (1964); (d) G. Porter and P. Suppan, *ibid.*, 191 (1964).

[8] H. King, *J. Chem. Soc.*, 744 (1929).

Registry No.—Ethyl ether, 60-29-7.

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Ring–Chain Tautomers of 6-Substituted 2-Acetylbenzoic Acids

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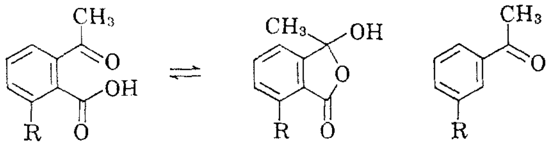
During an investigation in these laboratories, 2-acetyl-6-nitrobenzoic acid and the corresponding 6-amino and 6-hydroxy analogs were prepared according to published procedures.[1] These substances are of a class which could show ring–chain tautomerism, A $\rightleftharpoons$ B. The literature contains conflicting reports on the structure of 2-acetylbenzoic acid when the infrared spectrum was the criterion used. Grove and Willis[2] concluded that 2-acetylbenzoic acid in the solid state exists in the ring form B, whereas Jones and Congdon,[3] in a similar study, favored the chain form A. Wheeler[4] indicated that the ultraviolet spectrum supported the ring structure for the compound in solution. The subject of ring–chain tautomerism has been extensively studied, and was reviewed by Jones.[5] He suggested that nuclear magnetic resonance (nmr), which had not been used up to that time in such studies, should be very effective for ring–chain structural determinations. The advantage of nmr spectroscopy was demonstrated subsequently by Lansburg and Bieron[6] for normal and pseudo-ester tautomers. Similarly, Erley and coworkers[7] later reported that a single methyl peak at high field (δ 1.98 in deuteriochloroform) was evidence for the ring structure for 2-acetylbenzoic acid (Ic). This view was later modified[8] in favor of a ring–chain tautomeric mixture (predominantly ring tautomer) in fast equilibrium, A $\rightleftharpoons$ B, rather than the single tautomer B. A similar interpretation could account for the single methyl peak observed at δ 1.83 for 2-acetyl-6-methylbenzoic acid[8] in chloroform, although it is clear that the ring form predominates.



A B II

Ia, R = NH_2
b, R = OH
c, R = H
d, R = NO_2

We have found that the nmr spectrum of Ic in *dimethyl sulfoxide-d_6 solution* showed the presence of *both* forms A and B, with methyl bands located at δ 2.45 and 1.78, respectively. The former band is attributed to the chain form A, since acetophenone showed a methyl singlet at δ 2.58; the latter band is assigned to the ring form (B). Relative intensities of the bands indicated a ratio of 1:2 for A and B, and led to a weighted average chemical shift of δ 2.00. This value is in good agreement with δ 1.98 for the methyl peak observed in $CDCl_3$ solution by Erley and coworkers.[8] Furthermore, we found that the two bands coalesced to a single band at δ 2.02 when a trace of hydrochloric acid was added to promote fast interconversion of tautomers.

The infrared data (potassium bromide disks) for the four acetylbenzoic acids are listed in Table I. Ia showed zwitterion absorption and the spectrum was not obvious support for either tautomer. The strong intensity of a band at 3280 (bonded OH), a shoulder at 1742, and a strong band at 1704 cm^{-1} (chelated lactol carbonyl) indicated predominance of the ring form for Ib. A maximum at 1727 cm^{-1} indicated a ring tautomer for Ic, but the broadness (half-band width 90 cm^{-1}) indicated the presence of some chain form. The spectrum of Id showed bands at 1720 and 1695 cm^{-1} assigned to carboxylic acid and ketone groups.

The ultraviolet data (see Table I) indicated that Ia, Ib, and Ic[5] were predominantly in the ring form (entries 1, 2, and 3 resembled entries 9, 10, and 11, respectively, rather than entries 5, 6, and 7, respectively), and that Id was predominantly in the chain form (entry 4 resembled entry 8 rather than entry 12).

The nmr data for four 2-acetylbenzoic acids and the four corresponding acetophenones are summarized in Table I, and the following conclusions were made. (1) 2-Acetyl-6-nitrobenzoic acid (Id) exists predominantly as the chain structure A. (2) 2-Acetyl-6-hydroxybenzoic acid (Ib) and 2-acetyl-6-aminobenzoic acid (Ia) exist predominantly as the ring structure B. (3) 2-Acetylbenzoic acid (Ic) exists as a *mixture* of ring–chain tautomers A and B in a ratio of 2:1 (*vide supra*). The methyl group of the acetophenones and the chain tautomers (A) falls in the range of δ 2.53 ± 0.15 ppm, whereas that of the ring tautomers (B) falls in a different range, δ 1.73 ± 0.05 ppm. Also, the chemical shift of the methyl group of acetophenones was dependent upon the conjugative effect of the substituent *meta* to the ketonic substituent (with respect to δ values: $NO_2 > H > OH > NH_2$). The preference of 2-acetylbenzoic acids toward ring formation apparently follows the reverse trend: $NH_2 \cong OH > H > NO_2$.

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