Radiation Chemistry of Ethers. Part VI.† Photolysis at 254 nm of the Diethyl Ether–Oxygen Charge Transfer Complex

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Oxygen-saturated diethyl ether exhibits a charge transfer absorption band ($\lambda_{max.}$ 215 nm) with considerable absorption at 254 nm. Photolysis was carried out with a low pressure mercury arc. Photolysis of products was avoided by keeping conversion low, and chain reactions were minimized by working at −30°. The major products (quantum yields) were: H_2O_2 (0·24), 1-ethoxyethyl hydroperoxide (0·04), ethyl acetate (0·26), acetaldehyde (0·18), ethanol (0·18), ethyl formate (0·04), methanol (0·035), formaldehyde (0·005), and ethyl vinyl ether (0·013). A satisfactory material balance was obtained. The products formed are consistent with a primary photoprocess involving transfer of an electron to the O_2 to give O_2^-. Further, deprotonation of the ether radical cation in the presence of O_2 leads to the 1-ethoxyethylperoxyl radical. With the exception of 1-ethoxyethyl hydroperoxide all major products are believed to arise from disproportionation reactions of these two radicals.

It is known that ethers containing dissolved oxygen readily form peroxides when exposed to light. These peroxides are believed to be formed largely by the action of light on impurities such as carbonyl compounds which can initiate a chain reaction as has been studied using benzophenone as carbonyl compound.[1] It has been noted that O_2 forms charge transfer complexes with a series of compounds, among them ethers.[2,3] The charge transfer (CT) complex of diethyl ether with O_2 begins to absorb at *ca.* 290 nm, its maximum absorption being at 215 nm (Figure 1). These CT complexes have been shown to be photochemically active.[3,4]

In earlier work on this subject [3,4] mechanisms were suggested involving thermal and photochemical decomposition of 1-ethoxyethyl hydroperoxide to account for the products observed. In the present paper the elucidation of the primary processes is attempted by excluding photolysis of products and thermal decomposition of the peroxide as well as possible chain reactions. For this reason the experimental work was carried out at −30° which has the advantage of increasing the O_2 solubility and hence the absorbance due to the CT band as well as reducing chain reactions. Further, by keeping the degree of conversion more than an order of magnitude smaller than in the previous work [3,4] we were able to determine all products in a dose range where their yield increased linearly with dose, and where they did not absorb an appreciable amount of the photolysing light. It will be shown that the 1-ethoxyethyl hydroperoxide is only a minor product amounting to *ca.* 8% of the ether converted and that all products can be explained on the basis of an electron transfer from the ether to oxygen as the primary process.

EXPERIMENTAL

Materials.—Diethyl ether (Merck, analytical grade) was further purified by distilling over sodium under argon on a column (2 m) filled with Wilson glass spirals (2 mm) and stored under argon at 0° in the dark. No impurities could

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

[4] N. Kulevsky, C. T. Wang, and V. I. Stenberg, *J. Org. Chem.*, 1969, **34**, 1345.

be detected by g.l.c. after this procedure. Other chemicals used were triphenylphosphine (BASF; pract; 99%), methanol, ethanol, acetaldehyde, ethyl acetate, formyl acetate, formaldehyde (35% in water), H_2O_2 (30%), *NN*-dimethyl-*p*-phenylenediammonium dichloride (Merck), H_2O_2 (50%) (Peroxid Chemie), and ethyl vinyl ether (Fluka). Gases were supplied by Messer–Griesheim. Acetaldehyde was redistilled prior to use. 2,3-Diethoxybutane was prepared by photolysing di-t-butyl peroxide in diethyl ether.[5] 1-Ethoxyethyl hydroperoxide was prepared by the method of Milas *et al.*[6]

Spectra and Irradiation.—The u.v. absorption spectra were measured on a SEM Brückl HRS 400/C recording photometer equipped with a low temperature set-up. The solubility of O_2 in diethyl ether was taken from the literature.[7] Irradiations were performed with a Gräntzel low pressure mercury arc as described previously [8] except that the 185 nm line was eliminated by a Vycor quartz plate. This ensures that direct photolysis of diethyl ether [5] does not take place. The whole irradiation system was installed in an air-tight compartment which permitted purging with dry N_2. Frosting of the cell was thus reduced to a minimum. The low temperature was maintained by circulating precooled methanol through the brass cell block. The methanol was thermostatted with a flow of cold N_2 from a liquid N_2 reservoir. Actinometry was done with $K_3Fe(C_2O_4)_3$.[9] Corrections were made for longer wavelengths, which photolyse the actinometer not the diethyl ether–oxygen charge transfer complex. This was done by comparison of the actinometry with and without a Pyrex filter. Oxygen was dried by a combination of silica gel, P_2O_5, and molecular sieve traps, the latter cooled with solid CO_2. Samples were prepared by bubbling dried oxygen through the ether for 10 min prior to irradiation.

Analysis.—(a) *G.l.c.* Since not all products could be successfully determined by g.l.c. under any single set of experimental conditions, these were optimized for separation and quantitative determination for each product. Flame ionization detection was used if not specified otherwise. Acetaldehyde, ethyl acetate, and ethyl formate were determined on a steel capillary column (100 m × 0·5 mm i.d.) coated with polypropylene glycol operated at 40°, in Perkin-Elmer F 20; ethanol on a Porapak N column (2 m × 3 mm i.d.) operated at 140°, in Perkin-Elmer 900; methanol on a steel column (3 m × 3 mm i.d.) packed with 15% P 4000 on Chromosorb G, operated at 60°, in Perkin-Elmer F 20; ethyl vinyl ether by a heart cutting technique; [10] diethoxybutane on a steel capillary column (100 m × 0·5 mm i.d.) coated with polypropylene glycol at 90° in Perkin-Elmer F 20; formaldehyde on Porapak N (2 m × 3 mm i.d.) at 140°, thermal conductivity detection, carrier gas He in Perkin-Elmer 900. 1-Ethoxyethyl hydroperoxide is labile under normal g.l.c. conditions but can be gas chromatographed without noticeable decomposition in a specially designed all-glass system,[11,12] Varian 1400, on a glass capillary column (24 m × 2 mm i.d.), coated with PPG, carrier gas H_2, operated at 60°. The determination of the gases has been described previously.[10] Within one set of experiments linear dose *versus* yield curves were obtained (Figures 2 and 4). The slope derived from repeated sets of experiments showed deviations of ±10%.

(b) *I.r. spectroscopy*. The total content of C=O containing compounds was measured by i.r. spectroscopy on a Perkin-Elmer 621 i.r. grating spectrophotometer.

(c) *Peroxide determination*. Total peroxide was titrated according to the method of Wagner *et al.*,[13] and by the $TiOSO_4$ method.[14,15] Separation of H_2O_2 and the 1-ethoxyethyl hydroperoxide was done by t.l.c. on silica gel plates (Merck), with diethyl ether as eluant, $R_F(H_2O_2)$ 0·24, R_F (1-ethoxyethyl hydroperoxide) 0·54. The spots were made visible by spraying with *NN*-dimethyl-*p*-phenylenediammonium dichloride.[16] Quantitative measurements were possible after extraction and titration of the corresponding zones. Polarography was done on a Princeton Applied Research model 170 instrument. Half-wave potentials in ethanol containing 0·1M-$LiClO_4$ *versus* s.c.e. were for H_2O_2 −1·11 V, and for 1-ethoxyethyl hydroperoxide, −0·82 V. For g.l.c. determination of 1-ethoxyethyl hydroperoxide see above. The peroxide content of a sample and the ratio of H_2O_2 to 1-ethoxyethyl hydroperoxide remained constant over several hours.

RESULTS

(a) *Absorption Spectrum*.—Diethyl ether like other saturated ethers begins to absorb significantly near 200 nm.[17,18] When saturated with O_2, however, a broad CT-absorption band ($\lambda_{max.}$ 215 nm) is observed [3] with an appreciable O.D. at 254 nm, the major emission line of the low pressure Hg arc used in our experiments. The solubility of O_2 in diethyl ether increases with decreasing temperature.[7] This causes an increase in O.D. (Figure 1) which is not linear with the O_2 concentration (Table 1) suggesting changes in the equilibrium constant.

(b) *Peroxide Products*.—In their study on the photolysis of the diethyl ether–O_2 charge transfer complex Stenberg *et al.*[3,4] have assumed that the peroxide formed is the 1-ethoxyethyl hydroperoxide (3). However, t.l.c. on silica gel plates (Merck) with diethyl ether as eluant reveals two peroxides A and B with R_F values of 0·24 and 0·54 respectively. The R_F value of A is identical with that of H_2O_2, both showing somewhat diffuse spots, whereas the R_F values of B and 1-ethoxyethyl hydroperoxide coincide. Quantitative t.l.c. and titration of the silica scraped from developed plates show that the ratio A : B is 6 : 1 over a wide range, even in the non-linear part of the yield *versus* dose curve (Figure 2). 1-Ethoxyethyl hydroperoxide is stable under these conditions and is not hydrolysed into H_2O_2. Polarographic studies further support the conclusion that there are two peroxides. 1-Ethoxyethyl

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hydroperoxide and H_2O_2 give two distinct polarograms (Figure 3, curves b and c). A test mixture of H_2O_2 and 1-ethoxyethyl hydroperoxide (6 : 1) in diethyl ether, as well as an irradiated sample, gave comparable polarograms (Figure 3, curves d and e). Under suitable conditions the yield of 1-ethoxyethyl hydroperoxide can be determined quantitatively by g.l.c. (Figure 2). These three independent results prove that the peroxide B is 1-ethoxyethyl hydroperoxide. The other A is believed to be H_2O_2. This view is supported by the fact that on treating irradiated O_2-saturated diethyl ether with triphenylphosphine [19] triphenylphosphine oxide equivalent to total peroxide is formed without significant change in the quantum yields of other products as determined by g.l.c., and since the contribution of 1-ethoxyethyl hydroperoxide has been shown to be only 14% of total peroxide a drastic change is ruled out. It is noted that under less gentle g.l.c. conditions 1-ethoxyethyl hydroperoxide is decomposed into ethyl acetate and water [*e.g. ca.* 85%, Varian 1400, Perkin-Elmer 7 G 3 (polypropylene glycol) steel capillary column (100 m × 0·5 mm i.d.) operated at 80°]. The decomposition may be recognized from the characteristic tailed shape of the ethyl acetate peak. An irradiated sample under these conditions also showed some tailing, though to a lesser extent, again indicating that 1-ethoxyethyl hydroperoxide contributes to the peroxide yield, and in this case to the ethyl acetate yield, only to a small extent. H_2O_2–diethyl ether mixtures did not form any products under the g.l.c. conditions of these experiments.

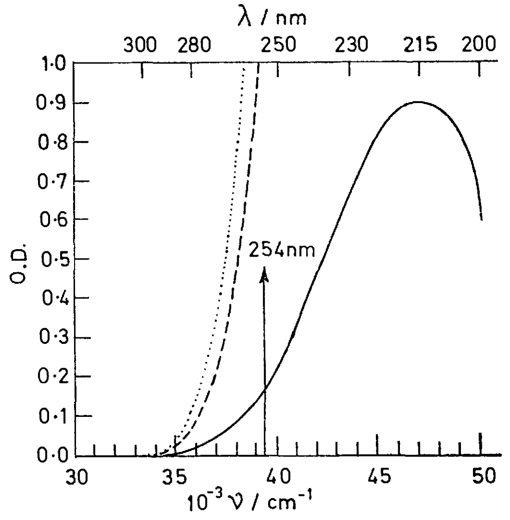

FIGURE 1 Wavelength dependence of the optical density (path length 1 cm) of O_2-saturated diethyl ether at +28° (——), at −30° (— — —), and at −60° (· · · ·)

TABLE 1

Solubility of O_2 in diethyl ether, and the optical density (1 cm path length) induced by the diethyl ether–O_2 charge transfer complex at 254 nm at various temperatures

Temperature (°C)	Solubility of O_2 (mol l^{-1})	O.D. (254 nm)
+28	$4{\cdot}25 \times 10^{-3}$	0·18
−30	$2{\cdot}03 \times 10^{-2}$	1·2
−60	$2{\cdot}46 \times 10^{-2}$	2·0

(c) *Non-peroxide Products.*—The major non-peroxide products are ethyl acetate, acetaldehyde, ethanol, ethyl formate, and methanol. These products were separated by g.l.c. using varying conditions in order to optimize their quantitative determination. Their yield is linear with dose at low conversions (Figure 4) and hence quantum yields (ϕ) can be calculated (Table 2). Ethyl vinyl ether, a further product, is formed in rather low yields but can nevertheless be determined easily in the presence of diethyl ether by means of a heart cutting technique.[10] Further small products are 2,3-diethoxybutane (ϕ $1{\cdot}5 \times 10^{-3}$) and formaldehyde. The latter had to be determined with a thermal conductivity detector, because formaldehyde has a very low response to flame ionization detection. Its sensitivity and thus the accuracy of the formaldehyde quantum yield is lower. In the chromatograms a signal is seen with lower retention than formaldehyde. It has been assigned to CO_2 but it is doubtful whether it is due to a

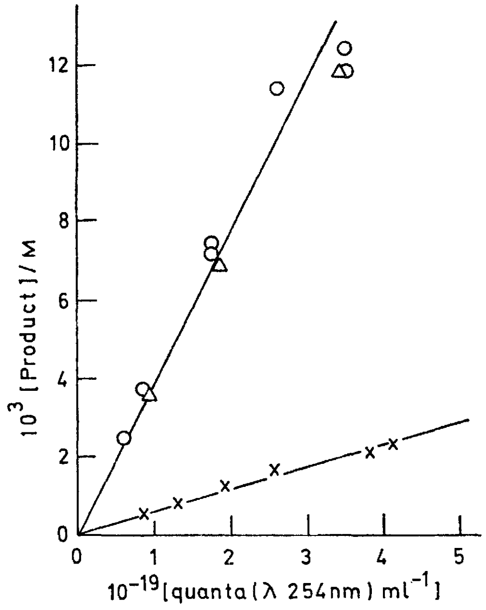

FIGURE 2 Photolysis (λ 254 nm) of O_2-saturated diethyl ether at −30°. Yields (mmol l^{-1}) of total peroxide (○, determined by titration; △, determined by photometry), and of 1-ethoxyethyl hydroperoxide (×, determined by g.l.c.) as a function of the absorbed dose [quanta (λ 254 nm) ml^{-1}]

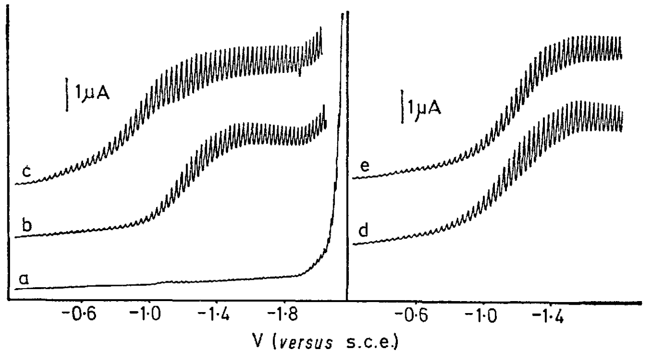

FIGURE 3 Polarograms in 0·1M-$LiClO_4$ in ethanol vs. s.c.e.: a, base line; b, 4×10^{-4}M-H_2O_2, half-wave potential −1·11 V; c, 4×10^{-4}M-1-ethoxyethyl hydroperoxide, half-wave potential −0·82 V; d, test mixture, 4×10^{-4}M-H_2O_2 and $0{\cdot}8 \times 10^{-4}$M-1-ethoxyethyl hydroperoxide; e, irradiated sample, peroxide content *ca.* 5×10^{-4}M

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[19] L. Horner and W. Jurgeleit, *Annalen*, 1955, **591**, 138.

primary product. Its quantum yield is *ca.* 10^{-2} at a dose of 3×10^{19} quanta ml^{-1}. Products easy to measure but of minor importance are H_2 (ϕ $1{\cdot}7 \times 10^{-3}$), methane (ϕ 8×10^{-5}), ethylene (ϕ 8×10^{-5}), and ethane (ϕ 1×10^{-5}). By means of the osazone reaction [20] which is undergone by glycolaldehyde as well as ethoxyacetaldehyde a quantum yield of 0·02 for the total of such products was found. Quantitative i.r. studies showed that the C=O double bond containing compounds mentioned above are not produced during the g.l.c. procedure. The O.D. in the C=O region of a reference mixture was identical with that of an irradiated sample which proves that there are no carbonyl compounds other than those identified as products. Initiation by carbonyl compounds does not occur in this work, as the ether employed was pure, and as the product carbonyl compounds' quantum yield is independent of dose within the range of doses applied.

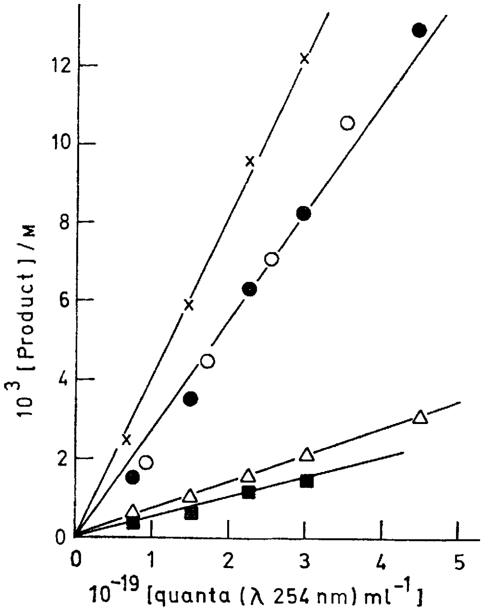


FIGURE 4 Photolysis (λ 254 nm) of O_2-saturated diethyl ether at −30°. Yields (mmol l^{-1}) of ethyl acetate (×), acetaldehyde (●), ethanol (○), ethyl formate (△), and methanol (■) as a function of the absorbed dose [quanta (λ 254 nm) ml^{-1}]

TABLE 2

Quantum yields of the major products in the photolysis (λ 254 nm) of O_2-saturated ether at −30°

Product	Quantum yield
Peroxide (total) [a,b]	0·28
H_2O_2 [c,d]	0·24
$CH_3CH(OOH)OC_2H_5$ [c–e]	0·04
$CH_3CO_2C_2H_5$ [e]	0·26
CH_3CHO [e]	0·18
C_2H_5OH [e]	0·18
$HCO_2C_2H_5$ [e]	0·04
CH_3OH [e]	0·035
CH_2O [e]	0·005
$CH_2{=}CHOC_2H_5$ [e]	0·013

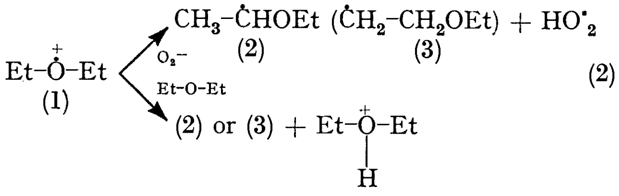
Method of determination: [a] titration; [b] photometry; [c] quantitative t.l.c.; [d] polarography; [e] g.l.c.

DISCUSSION

The absorption band which appears when O_2 is dissolved in diethyl ether has been attributed to a CT transition.[2,3] In this complex electron density is transferred from the ether to the oxygen molecule. Our results can be explained by assuming that on excitation an ion pair is formed [reaction (1)]. The ether radical

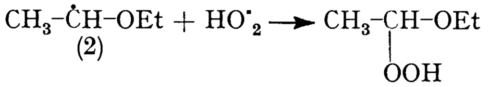
$$\text{Et–O–Et}\cdots O_2 \xrightarrow{h\nu} \underset{(1)}{\text{Et–}\overset{+}{\dot{\text{O}}}\text{–Et}} + O_2^- \qquad (1)$$

cation (1) is expected to eliminate a proton giving rise to either 1- (2) or 2-ethoxyethyl radical (3). The solvent ether and/or O_2^- are suitable proton acceptors [reaction (2)]. Cage combination of the ethoxyethyl radicals



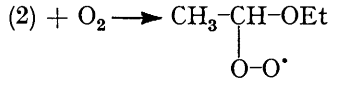
(2)

with the $HO^{\cdot}_2$ radicals will give rise to ether hydroperoxides, preferentially 1-ethoxyethyl hydroperoxide (4) [reaction (3)], since proton elimination from C-2 to



$$\underset{(2)}{CH_3\text{–}\dot{C}H\text{–}OEt} + HO^{\cdot}_2 \longrightarrow CH_3\text{–}\underset{\underset{(4)}{OOH}}{\underset{|}{C}}H\text{–}OEt \qquad (3)$$

give (2) is favoured over that from C-1 to give (3). If diffusion of the radicals (2) and $HO^{\cdot}_2$ from the cage takes place, then radicals (2) are scavenged by O_2 in a nearly diffusion controlled process [reaction (4)].[21] Only a



$$(2) + O_2 \longrightarrow CH_3\text{–}\underset{\underset{(5)}{O\text{–}O^{\cdot}}}{\underset{|}{C}}H\text{–}OEt \qquad (4)$$

few escape scavenging and dimerize to give 2,3-diethoxybutane ($\phi = 1{\cdot}5 \times 10^{-3}$).

Pulse radiolysis studies of diethyl ether (carried out, however, in aqueous solution) in the presence of O_2 have led other workers [21] to the conclusion that the primary step in the disappearance of the peroxyl radicals (5) is their dimerization followed by a fragmentation into ethyl vinyl ether, and a hydrotetraoxide which in turn splits off O_2 to the hydroperoxide. In our case this route can only be of very minor importance since the quantum yield of ethyl vinyl ether is very low (Table 2).

Disproportionation reactions of the peroxyl radicals can account for the products. Cyclic transition states as proposed previously [22] for autoxidation reactions can also be formulated here. Reaction (5) can account for ethyl acetate, acetaldehyde, and ethanol [the hemiacetal (6) being the intermediate]. An analogous reaction (8) for the 1-ethoxyethylperoxyl and hydroperoxyl radical pair will lead to ethyl acetate, water, and oxygen.

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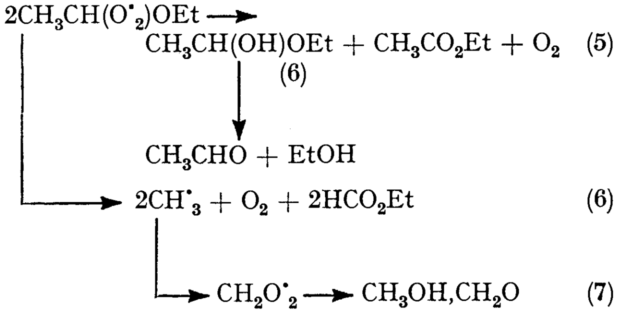
Therefore ϕ(ethyl acetate) must be larger than ϕ(acetaldehyde) and ϕ(ethanol) × ϕ(acetaldehyde) must



$$2CH_3CH(O^{\bullet}_2)OEt \longrightarrow CH_3CH(OH)OEt + CH_3CO_2Et + O_2 \quad (5)$$

$$CH_3CH(OH)OEt \xrightarrow{(6)} CH_3CHO + EtOH$$

$$2CH_3CH(O^{\bullet}_2)OEt \longrightarrow 2CH^{\bullet}_3 + O_2 + 2HCO_2Et \quad (6)$$

$$CH^{\bullet}_3 \longrightarrow CH_2O^{\bullet}_2 \longrightarrow CH_3OH, CH_2O \quad (7)$$

$$CH_3CH(O^{\bullet}_2)OEt + HO^{\bullet}_2 \longrightarrow CH_3CO_2Et + H_2O + O_2 \quad (8)$$

$$2HO^{\bullet}_2 \longrightarrow H_2O_2 + O_2 \quad (9)$$

equal ϕ(ethanol). This is in agreement with the experimental results (Table 1). H_2O_2 is largely formed *via* reaction (9). The C–C fragmentation products ethyl formate, methanol, and formaldehyde may also have a tetraoxide precursor but follow a different reaction path (6). This process may be a concerted one but could also be stepwise since after O_2 elimination from the unstable tetraoxide the resulting oxyl radicals are believed to fragment readily by splitting the C–C bond rather than the C–O bond.[23] The activation energy for this process is expected to be low (*cf.* other oxyl radicals [24]). A competing reaction of the oxyl radical is the hydrogen abstraction from the ether yielding (6) and (2). The Arrhenius parameters of such a process are expected to be similar to those of reaction (6), and some competition might occur under our experimental conditions. This and the other source of (6), reaction (5), cannot be resolved. Practically all methyl radicals formed *via* reaction (6) will be scavenged by O_2 [reaction (7)] to give methylperoxyl radicals. Very few will abstract hydrogen and give methane [$\phi(CH_4) = 10^{-5}$]. The $CH_3O^{\bullet}_2$ radicals are expected to give similar disproportionation reactions as does (5) resulting in the formation of methanol and formaldehyde.

Apparently there is only a small probability that the primary radical cation eliminates a proton to give the 2-ethoxyethyl radical (3). We were unable to detect ethoxyacetaldehyde by g.l.c. but the osazone test was positive. We therefore suggest that (3) also may play a role, but not a large one. Preliminary experiments with methyl t-butyl ether [25] show that proton elimination from the t-butyl group [ϕ(2-methoxy-2-methylpropanal) = 0·03] competes noticeably with that from the methyl group [ϕ(t-butyl formate) = 0·21].

Hydrogen, ethane, and ethylene have been observed as minor products. The formation of hydrogen has been observed in decomposition reactions of peroxide compounds.[26] Another explanation would be the occurrence of an O_2-sensitized photolysis of the ethyl ether. In the direct photolysis (λ 185 nm) hydrogen, ethane, and ethylene are formed as molecular products.[5]

It is emphasized that the CT band is highly photoactive, the quantum yield of product-yielding primary processes being *ca.* 0·5. The photolysis of an ether–O_2 CT complex may well be an important route in the initiation of ether autoxidations.

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