Tetrahedron Vol. 28, pp. 4333 to 4339. Pergamon Press 1972. Printed in Great Britain

THE UV PHOTOLYSIS OF LIQUID DIETHYL ETHER[†]

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(*Received in the UK* 3 *February* 1972; *Accepted for publication* 22 *February* 1972)

Abstract—In the 185 nm photolysis of liquid (O_2-free) diethyl ether the following products (quantum yields) are formed: hydrogen ($0{\cdot}06_5$), methane (0·0008), ethylene ($0{\cdot}09_5$), ethane (0·12), propane ($0{\cdot}001_5$), butane (0·07), acetaldehyde (0·06), ethanol (0·46), ethyl vinyl ether (0·09), sec-butyl ethyl ether ($0{\cdot}19_5$), 1,1-diethoxyethane ($\leq 0{\cdot}0003$), and 2,3-diethoxybutane ($0{\cdot}06_5$). From material balance calculations it has been concluded that the most important primary process is the homolytic scission of the C—O bond into ethyl and ethoxy radicals (*ca.* 70%). Fragmentation into molecules and cage reactions yield ethane and acetaldehyde (*ca.* 10%), ethylene and ethanol (*ca.* 8·5%) and hydrogen and ethyl vinyl ether (*ca.* 11%). The scission of the C—C bond is of minor importance (< 0·5%).

INTRODUCTION

THE PHOTOLYSIS of diethyl ether has been studied by Harrison and Lake[1] in the gas phase. Absorption bands in the irradiated ether had been attributed to the products acetaldehyde, formaldehyde and ethylene. In the photolysis of ether in the liquid state[2, 3] no definite products could be isolated.

More detailed studies have been published on the gas phase Hg-sensitized photolysis of saturated aliphatic ethers, e.g. dimethyl ether,[4, 5] methyl ethyl ether,[6] and diethyl ether.[7] The Hg-sensitized photolysis leads to the formation of hydrogen and the dehydrodimers, and there is no indication that the scission of the C—O bond is of any importance. In the pyrolysis[8] of diethyl ether, together with chain reactions fragmentation processes into acetaldehyde and ethane as well as into ethanol and ethylene have been observed. Closest to the results of the present work are those from the γ-radiolysis.[9] However, it will be shown that excitation with light of wavelength $\lambda = 185$ nm opens up a smaller number of reaction channels than does γ-radiolysis.

Recently the 185 nm photolysis of aliphatic alcohols in the liquid phase has been studied, where it was found that in methanol,[10] ethanol,[11] n-propanol, n-butanol, n-pentanol,[12] and iso-propanol[13–15] the homolytic scission of the O—H bond is the most important primary process, other reactions playing a minor role. However, in the u.v. photolysis of tert-butanol[16–18] this reaction does not occur, the main process being the scission of a C—C bond. The scission of the O—H bond in the photolysis of the n-alcohols and iso-propanol has been explained by a localization of the absorbed energy near the oxygen,[12] because the transition which is excited by the 185 nm light has been attributed to a $n \rightarrow \sigma^*$ transition. In this transition a non-bonding electron of the oxygen is promoted to an antibonding σ^* level. However, the photolytic behaviour of t-butanol does not correspond with this picture.

[†] Part I of the series: Strahlenchemie von Aethern.

The lowest excited state of diethyl ether which is generated by the 185 nm radiation has been similarly attributed to a n → σ* state. It is of interest to compare the reaction paths of the ether from this excited state with those of the alcohols. In the ethers the O—H bond of the alcohols is substituted by an O—C bond. The scission of the C—O bond plays a minor role (3·5–10%) in the photolysis of alcohols.

RESULTS AND DISCUSSION

The products of the 185 nm photolysis of liquid diethyl ether together with their quantum yields are in Table 1. The conversion of the ether was between 0·007 and 0·1%. The yield of all products (except the methane yield) was linear with dose. About a hundred runs were made, giving individual quantum yields for each product within a spread of ca. 10% centered on the average value. $\phi(CH_4)$ increased linearly with dose. The value of 0·0008 (Table 1) is the initial quantum yield obtained by extrapolation to zero dose. At the highest dose used in this work $\phi(CH_4)$ was only 0·002. Therefore the increase in methane cannot be correlated experimentally with the decrease of another product (e.g. acetaldehyde). The quantum yield of 1,1-diethoxyethane formation was too low to be measured accurately, but is estimated at 0·0003. The quantum yield of ether disappearance through primary processes is estimated from the reaction scheme to be 0·6. The contribution of the 254 nm light to the photolysis of the ether is below 1%.

TABLE 1. QUANTUM YIELDS OF THE PRODUCTS IN THE 185 NM PHOTOLYSIS OF DIETHYL ETHER (LIQUID PHASE, O_2-FREE, AT ROOM TEMPERATURE)

Products	Quantum yields
H_2	$0{\cdot}06_5$
CH_4	0·0008
C_2H_4	$0{\cdot}09_5$
C_2H_6	0·12
C_3H_8	$0{\cdot}001_5$
$n\text{-}C_4H_{10}$	0·07
CH_3CHO	0·06
C_2H_5OH	0·46
$CH_2{=}CH{-}OC_2H_5$	0·09
$CH_3{-}CH(C_2H_5){-}OC_2H_5$	$0{\cdot}19_5$
$CH_3(CH(OC_2H_5)_2$	$\leq 0{\cdot}0003$
$(CH_3{-}CH{-}OC_2H_5)_2$	$0{\cdot}06_5$

Reactions and mechanism

In the u.v. photolysis of aliphatic systems the products are formed both by radicals as precursors and by direct fragmentation into molecules. Such elementary steps as could conceivably occur in the present system are discussed.

(a) *Scission of* C—H *bonds.* Homolytic scission of the C—H bond gives an H atom and a 1- or 2-ethoxyethyl radical (eq. 1).

$$C_2H_5OC_2H_5 \xrightarrow{h\nu} H^{\bullet} + CH_3{-}{}^{\bullet}CH{-}OC_2H_5 \quad (\text{or } {}^{\bullet}CH_2{-}CH_2{-}OC_2H_5) \qquad (1)$$

On the other hand, H_2 can be eliminated as a molecule (eq. 2).

$$C_2H_5OC_2H_5 \xrightarrow{h\nu} H_2 + CH_2{=}CH{-}OC_2H_5 \qquad (2)$$

The elimination of molecular hydrogen may have carbenes as intermediates (eq 2a) as has been shown in the u.v. photolysis of alkanes.[19]

$$\begin{array}{c} C_2H_5OC_2H_5 \xrightarrow{h\nu} H_2 + \bar{C}H{-}CH_2{-}OC_2H_5 \\ (\text{or}\quad CH_3{-}\bar{C}{-}OC_2H_5) \end{array} \qquad (2a)$$

(b) *Scission of the* C—O *bond.* If the C—O bond is broken, ethyl and ethoxy radicals are formed (eq. 3)

$$C_2H_5OC_2H_5 \xrightarrow{h\nu} C_2H_5O^{\bullet} + {}^{\bullet}C_2H_5 \qquad (3)$$

There are two further processes involving the scission of the C—O bond: the fragmentation into acetaldehyde and ethane (eq. 4), and into ethanol and ethylene (eq. 5).

$$C_2H_5OC_2H_5 \xrightarrow{h\nu} CH_3CHO + C_2H_6 \qquad (4)$$

$$C_2H_5OC_2H_5 \xrightarrow{h\nu} C_2H_5OH + C_2H_4 \qquad (5)$$

Cage reactions of the radicals formed by process (3) might also give rise to products such as acetaldehyde, ethane, ethanol, and ethylene. In this discussion the contribution of such cage reactions is not treated separately from the true molecular fragmentation processes.

(c) *Scission of the* C—C *bond.* The scission of a C—C bond yields a methyl and an ethoxymethyl radical (eq. 6). A non-radical process leading to methane will be accompanied by the formation of a cyclic ether (e.g. propenoxide).

$$C_2H_5OC_2H_5 \xrightarrow{h\nu} {}^{\bullet}CH_3 + {}^{\bullet}CH_2OC_2H_5 \qquad (6)$$

(d) *Radical reactions.* In reactions 1, 3 and 6, radicals are formed. These will yield products either by abstraction, combination, or disproportionation. The $H^{\bullet}$ and $C_2H_5O^{\bullet}$ radicals are rather reactive and readily abstract hydrogen (reactions 7 and 8).

The rate constant of the reaction of $H^{\bullet}$ with ether (eq. 7) is $4{\cdot}7 \times 10^7$ l/mole s in aqueous solution.[20] The rate constant of the ethoxy radical with the ether has not been determined, but the similarity in reactivities of different alkoxy radicals[21] allows some rough estimates. In methanol the methoxy radical reacts with $k = 10^4$ l/mole s.[22] Diethyl ether being an even better H donor (compare k(H + diethyl ether) = $4{\cdot}7 \times 10^7$ l/mole s; and k(H + methanol) = $2{\cdot}9 \times 10^6$ l/mole s[23]) will react with the ethoxy radical at a similar rate (i.e. $k_8 \approx 10^4$ l/mole s†).

To a smaller extent, methyl and ethyl radicals show the same abstraction reactions. However, combination reactions (12, 14, and 16) and disproportionation reactions (13, 15, 17, and 18) can compete with hydrogen abstraction.

Combination and disproportionation reactions are also given by the most stable radical of this sytem, the 1-ethoxyethyl radical (eq. 16–20, 22). Unimolecular

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† It is of interest that in the gas phase methoxy radicals show a higher reactivity than H atoms[24, 25] whereas in liquid methanol they react much more slowly than H atoms. This may be due to strong solvation of the methoxy radicals in liquid methanol.[26] If solvation of the ethoxy radicals is less in ether k_8 could even exceed the estimated value.

fragmentation of this radical (eq. 21) is not expected to occur here judging from its gas phase Arrhenius parameters[27] which are E = 23·5 kcal/mole, and log A = 10·9.

$$H^{\cdot} + C_2H_5OC_2H_5 \longrightarrow H_2 + CH_3{-}\dot{C}H{-}OC_2H_5 \qquad (7)$$

$$C_2H_5O^{\cdot} + C_2H_5OC_2H_5 \longrightarrow C_2H_5OH + CH_3{-}\dot{C}H{-}OC_2H_5 \qquad (8)$$

$$^{\cdot}CH_3 + C_2H_5OC_2H_5 \longrightarrow CH_4 + CH_3{-}\dot{C}H{-}OC_2H_5 \qquad (9)$$

$$C_2H_5^{\cdot} + C_2H_5OC_2H_5 \longrightarrow C_2H_6 + CH_3{-}\dot{C}H{-}OC_2H_5 \qquad (10)$$

$$2\,^{\cdot}CH_3 \longrightarrow C_2H_6 \qquad (11)$$

$$^{\cdot}CH_3 + C_2H_5^{\cdot} \longrightarrow C_3H_8 \qquad (12)$$

$$^{\cdot}CH_3 + C_2H_5^{\cdot} \longrightarrow CH_4 + C_2H_4 \qquad (13)$$

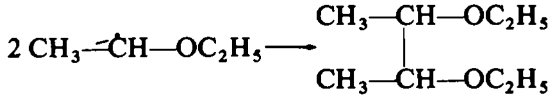
$$2\,C_2H_5^{\cdot} \longrightarrow C_4H_{10} \qquad (14)$$

$$2\,C_2H_5^{\cdot} \longrightarrow C_2H_6 + C_2H_4 \qquad (15)$$

$$C_2H_5^{\cdot} + CH_3{-}\dot{C}H{-}OC_2H_5 \longrightarrow CH_3{-}CH(C_2H_5){-}OC_2H_5 \qquad (16)$$

$$C_2H_5^{\cdot} + CH_3{-}\dot{C}H{-}OC_2H_5 \longrightarrow C_2H_6 + CH_2{=}CH{-}OC_2H_4 \qquad (17)$$

$$C_2H_5^{\cdot} + CH_3{-}\dot{C}H{-}OC_2H_5 \longrightarrow C_2H_4 + C_2H_5OC_2H_5 \qquad (18)$$



$$2\,CH_3{-}\dot{C}H{-}OC_2H_5 \longrightarrow \begin{array}{c} CH_3{-}CH{-}OC_2H_5 \\ | \\ CH_3{-}CH{-}OC_2H_5 \end{array} \qquad (19)$$

$$2\,CH_3{-}\dot{C}H{-}OC_2H_5 \longrightarrow CH_2{=}CH{-}OC_2H_5 + C_2H_5OC_2H_5 \qquad (20)$$

$$CH_3{-}\dot{C}H{-}OC_2H_5 \longrightarrow CH_3CHO + {}^{\cdot}C_2H_5 \qquad (21)$$

$$CH_3{-}\dot{C}H{-}OC_2H_5 + C_2H_5O^{\cdot} \longrightarrow CH_3{-}CH(OC_2H_5)_2 \qquad (22)$$

(e) *Material balance and reaction scheme.* Multiplication of the carbon, hydrogen, and oxygen contents of the products with their quantum yields gives the formula $C_4H_{10\cdot0}O_{0\cdot98}$.

This material balance justifies several conclusions as to the mechanism of the ether photolysis.

Dimerisation of methyl radicals to form ethane (eq. 11) is unlikely in this system since their concentration is very small compared to that of other radicals as evidenced by the low methane and propane yields. In general, combination of two radicals is favoured with respect to disproportionation unless the reacting radicals are tertiary, carrying hydrogen in the β-position. Thus the disproportionation/combination ratio of ethyl radicals (k_{15}/k_{14}) in the gas phase is about 0·1[21] while that of methyl and ethyl radicals (k_{13}/k_{12}) is about 0·05.[21] Values for k_{17}/k_{16} and k_{18}/k_{16} are not known. Therefore, in considering the material balance, the assumption has been made that the liquid phase value of k_{15}/k_{14} is the same as that in the gas phase; and further, that $k_{17} \approx k_{18}$, and that $(k_{17} + k_{18})/k_{16}$ is of similar magnitude to k_{15}/k_{14}, *viz.* about 0·1. This assumption, if not precisely true, will surely be correct to the right order of magnitude. The disproportionation/combination ratio of the ethoxyethyl radicals can be estimated in the following way: in the γ-radiolysis[9] of diethyl ether the yield of 2,3-diethoxybutane is greater than that of ethyl vinyl ether by a factor of 2·4.[9] Assuming that in the γ-radiolysis ethyl vinyl ether and 2,3-diethoxybutane are formed essentially only *via* reactions (19) and (20) one may equate k_{20}/k_{19} to 0·42, bearing in mind that this value will represent an upper limit since reactions such as (2) or (17) may contribute to the formation of ethyl vinyl ether as well.

Acetaldehyde quite predominantly arises from reaction (4) since, owing to the high abstractive reactivity of the ethoxy radical (eq. 8), disproportionation leading to acetaldehyde must be relatively unimportant. This view is supported by the fact that the only combination product of the ethoxy radical detected, 1,1-diethoxyethane, is formed with a quantum yield of not more than 0·0003.

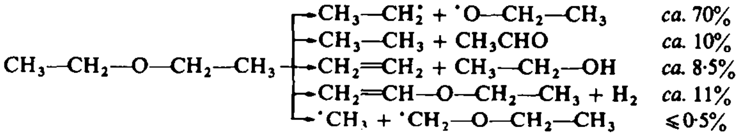
As noted above, cage reactions cannot be distinguished from genuine molecular fragmentation processes under the conditions of this work.

In order to establish the relative importance of the primary processes an estimate was made of the concentrations of various radicals. For example, reaction (14) is a "key" reaction to determine the steady-state ethyl radical concentration on the basis of the rate of formation of butane if the gas phase value of k_{14} is taken.[21] Similarly, with k_8 as given above, and taking $k_{19} \approx k_{14}$, the steady-state concentration of the ethoxy radical is found to be lower than that of the most stable radical in this system, ethoxyethyl, by more than two orders of magnitude. This is confirmed by the low yield ($\phi \leqslant 0{\cdot}0003$) of 1,1-diethoxyethane.

Radical concentrations so obtained are those in a layer *ca.* 0·1 mm thick since ε (λ = 185 nm) = 13·8 l/mole cm. Any radical reactions will mostly occur within this layer while stirring dilutes the products into the bulk of the liquid.

Based on the radical concentration estimates, on the rates of product formation, and on reasonable values of various rate constants, one then eliminates from a set of conceivable reactions those which will obviously be unimportant (e.g. $H + H \rightarrow H_2$, $CH_3 + CH_3 \rightarrow C_2H_6$). A subset remained (eq. 1–22), representing the mechanism, which is equivalent to a system of equations linear in the rates of the elementary steps, bearing in mind that the rate of formation of each product is a linear function of the elementary rates. Every such equation, in other words, is a material balance for a particular product. The steady-state hypothesis applied to each radical species furnished additional relationships, as did disproportionation/combination ratios, either known or estimated from analogy.

This system of equations, when solved, led to a scheme for the relative importance of the primary processes (Fig 1). It is of interest that the relative importance of these processes is not altered substantially when the quantum yields are varied over their range of uncertainty. Likewise, variation of disproportionation/combination ratios within reasonable limits does not decisively change the picture either.



$$CH_3{-}CH_2{-}O{-}CH_2{-}CH_3 \rightarrow \left\{\begin{array}{ll} CH_3{-}CH_2^{\bullet} + {}^{\bullet}O{-}CH_2{-}CH_3 & ca.\ 70\% \\ CH_3{-}CH_3 + CH_3CHO & ca.\ 10\% \\ CH_2{=}CH_2 + CH_3{-}CH_2{-}OH & ca.\ 8{\cdot}5\% \\ CH_2{=}CH{-}O{-}CH_2{-}CH_3 + H_2 & ca.\ 11\% \\ {}^{\bullet}CH_3 + {}^{\bullet}CH_2{-}O{-}CH_2{-}CH_3 & \leqslant 0{\cdot}5\% \end{array}\right.$$

FIG 1. Scheme of the primary processes in the 185 nm photolysis of liquid diethyl ether

The results demonstrate clearly the homolytic split of the C—O bond to be the most important process (*ca.* 70%). There is also a split of the C—O bond in the fragmentation reactions leading to acetaldehyde and ethane, and to ethanol and ethylene (adding up to another 18·5%). The elimination of molecular hydrogen (11%) finds its analogy in the u.v. photolysis of liquid n-hexane[28] where it could be shown that only 15% of the hydrogen is derived from H atoms as precursors. A similar fraction cannot be ruled out for the photolysis of diethyl ether since a quantum yield of 0·01 lies within the error margin of this material balance estimate.

The direct photolysis of diethyl ether differs, therefore, importantly from the Hg-sensitized photolysis of saturated aliphatic ethers[4–6] where a C—O split was not observed, contrary, however, to the behaviour of methyl vinyl ether where it has been found recently[29] that the CH_3—O bond is predominantly affected.

The greater variety of products in the γ-radiolysis[9] is not surprising as here the entire spectrum is excited and ionized molecules contribute to product formation to a high degree. In the case of the 185 nm u.v. photolysis the lowest electronically excited state (probably $n \rightarrow \sigma^*$) is occupied. With normal alcohols and iso-propanol the excitation of the $n \rightarrow \sigma^*$ transition leads to the rupture of the O—H bond. In analogy to this behaviour there is a C—O split of the diethyl ether molecule. However, the tert-butanol molecule fractures in an entirely different manner under the influence of u.v. light. Further work in this laboratory is being undertaken to establish whether tertiary ethers show a similar difference in their photolytic behaviour.

EXPERIMENTAL

Diethyl ether (Merck, analytical grade) was carefully fractionated and stored after repeated degassing in a Hg-free greaseless stopcock high vacuum line. No impurities could be detected by gas chromatography.

Chemicals used for comparison and calibration purposes were obtained commercially except for sec-butyl ethyl ether and 2,3-diethoxybutane, which were synthesized, the former in the conventional way from sec-butanol and ethanol in the presence of sulfuric acid,[30] the latter by the photolysis of di-tert-butyl peroxide in diethyl ether[31] and preparative gas chromatography of the product.

For the photolysis experiments 5 ml of the ether were distilled into the quartz cell (Hellma, 1 cm × 1 cm × 5 cm) fitted with a Westef stopcock and a small bulb for degassing the ether by the freeze-pump technique. The sample was photolysed in a thermostated block in front of a low pressure Hg arc (Gräntzel, Karlsruhe). Details have been given previously.[17] During photolysis the ether was magnetically stirred by means of a Teflon-coated iron bar. The flux of the 185 nm quanta was 2×10^{18} per cell volume (5 ml) per minute as determined by the ethanol actinometer (a 5 molar aqueous solution).[32] Its H_2 quantum yield of 0·4 can be derived[33] taking Dainton and Fowles'[34] values of 1·0 for the N_2 formation in the 185 nm photolysis of N_2O. Irradiation times ranged from 1 to 20 min.

The molar extinction coefficient of diethyl ether at $\lambda = 185$ nm has been measured with a variable quartz cell (Type BC-14, RIIC (München) to be 13·8 l mole^{-1} cm^{-1}. The O.D. at $\lambda = 254$ nm (the major line of the low pressure arc) is only small.[35] In the gas phase, however, $\varepsilon(\lambda = 185 \text{ nm}) = 1600$ l mole^{-1} cm^{-1}, in accordance with the literature.[36,37] Using a Vycor quartz filter which cuts off the 185 nm line, the photolytic behaviour of the ether at 254 nm could be investigated.

Product analysis was by gas chromatography on a Perkin–Elmer 900 device employing an F.I.D. The identity of the product compounds was established on the basis of their elution times and also by combined GC/MS. The cell was attached to a 2 l glass bulb into which the products were transferred and which was connected to the inlet system of the chromatograph. An aliquot of *ca.* 2 ml of the vapor was taken for analysis.

Three different gas chromatographic columns were used, made of 5 mm I.D. stainless steel tubing. n-Butane, ethyl vinyl ether, acetaldehdye, sec-butyl ethyl ether, ethanol, and 2,3-diethoxybutane were analysed on a 6 m P 4000 (15% on Celite/KOH treated: 60/100 mesh) column. Operation at a flow rate of 16 ml He/min was isothermal at 40° for 16 minutes, then temperature-programmed at a rate of 5°/min up to a final temperature of 150°. Under these conditoins the elution times (in minutes) of the products were as follows: n-butane, 9; (diethyl ether, 14) ethyl vinyl ether, 18; acetaldehyde, 20; sec-butyl ethyl ether, 23; ethanol, 38; 2,3-diethoxybutane, 42 and 43. The latter appeared as a double peak, representing both the meso and the d, l forms. Tailing of the diethyl ether peak caused a difficulty in the determination of the ethyl vinyl ether closely following it. To improve the separation of the two, and accurately to determine the ethyl vinyl ether the following technique was employed: when the n-butane had been measured and most of the diethyl ether eluted the carrier gas flow was reversed for 20 minutes, and all components still present in the column were collected at −196°. Placed between the inlet system and the column, the trap consisted of a stainless steel u-tube (overall length *ca.* 20 cm) filled with the same material as was in the column. The condensate was subsequently re-chromatographed. This procedure was repeated twice, after which a good separation of the ethyl vinyl ether was achieved. Further details on the analytical system are to be given in a later publication. Acetaldehyde even though it could be separated on this column was determined more accurately on a 2 m Porapak Q (100/200 mesh) column (where it precedes the diethyl ether), as also were ethylene, ethane, and propane. This column was operated at 125° and a carrier gas flow rate of 31 ml He/min. Hydrogen and methane were measured on a 4 m activated charcoal column as described elsewhere.[17]

In order to test the formation of acetal (1,1-diethoxyethane) a 100 m PPG capillary column of 0·5 mm I.D. was used.

Acknowledgement—We wish to thank Mr. F. Weeke for his contribution to the development of the inlet and trapping systems, and Mrs. B. Axer and Miss E. Bastian for their valuable assistance with the measurements.

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