Studies in Vacuum Ultraviolet Photochemistry IV.[1] Diethyl Ether

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Diethyl ether has been photolysed at 147 and 123 nm in the gas phase at pressures of 2—200 Torr and conversions <0·5%. The most important primary process is that involving C–O fission [reaction (i)]. The majority of the

$$\text{Et–O–Et} + h\nu \longrightarrow \text{Et} + \text{EtO} \qquad \text{(i)}$$

ethoxyl radicals decompose in an early vibration by loss of a methyl radical [reaction (ii)]. There is a small contribution from a second primary process [reaction (iii)] involving elimination of hydrogen. The ratio process (i): process

$$\text{EtO} \longrightarrow \text{Me} + \text{HCHO} \qquad \text{(ii)}$$

$$\text{Et–O–Et} + h\nu \longrightarrow \text{EtOCH=CH}_2 + \text{H}_2 \text{ (or 2H)} \qquad \text{(iii)}$$

(iii) is *ca.* 60. The overall photochemistry is interpreted in terms of these primary processes, and subsequent reaction of the radical products.

THE first absorption band in simple ethers occurs at wavelengths below 200 nm; consequently little attention has been directed towards their photochemistry. Harrison and Lake [2] used a hydrogen discharge lamp ($\lambda < 192$ nm) to photolyse dimethyl and diethyl ether. No quantitative data were reported, but the products absorbing in the u.v. were formaldehyde from dimethyl ether, and ethylene, acetaldehyde, and formaldehyde from diethyl ether. A recent report [3] on the photolysis of dimethyl ether at 147 nm concludes that the major primary process is loss of a hydrogen atom, MeOMe + $h\nu \longrightarrow$ H + CH_2OMe, followed by decomposition of the methoxymethyl radical, $CH_2OMe \longrightarrow Me + HCHO$. A process leading to molecular hydrogen elimination also occurs to a small extent, MeOMe + $h\nu \longrightarrow H_2$ + HCOMe. In contrast with results from hydrocarbon photolysis, direct molecular elimination processes constitute a relatively small percentage of the overall decomposition.

Relative molar yields in photolysis [a] of diethyl ether at 123 and 147 nm

p_{Et_2O}/Torr	2	2	10	10	10	100 [b]	100 [c]	100	100	10	10	10	100
Additive	None	H_2S	None	H_2S	NO	None	None	H_2S	NO	None	NO	H_2S	None
λ/nm	123	123	123	123	123	123	123	123	123	147	147	147	147
Methane	18	93	19	87	*d*	23	20	79	*d*	20	*d*	85	20
Acetylene	1·9	1·1	0·8	0·3	1·6	0·5	0·4	0·4	1·0	0·7	4	0·6	0·3
Ethylene	54	16	48	14	100	47	45	10	100	47	100	13	42
Ethane	53	100	49	100	0·1	47	48	100	0·2	50	0·4	100	48
Propene	0·5	0	0·3	0	0	0·1	0·2	0	0	0·3	0	0	0·3
Propane	100	0·4	100	0·3	0·1	100	100	0·2	0·1	100	0·2	0·3	100
Isobutane	0·2	0	0·2	0	0	0·1	0·3	0	0	0·2	0	0	0·1
But-1-ene	1·1	0	1·5	0	0	1·2	2·2	0	0	1·1	0	0	0·8
n-Butane	51	0·1	58	0·3	0·1	69	69	0·2	0·1	56	0·2	0·3	61
Ethyl vinyl ether	4·3	1·8	3·9	1·8	13					4·0	15	1·9	
Ethyl isopropyl ether	11	0	13	0	0	14		0	0	12	0	0	
Ethyl s-butyl ether	14	0	16	0	0	18		0	0	15	0	0	
Acetaldehyde	4	1·4	4·5	1·6	1·4	5		1·9		5			
Ethanol	20	8·5	41	16		52				38			

[a] Conversions <0·1%. [b] Conversion *ca.* 0·025%. [c] Conversion *ca.* 0·13%. [d] Not measured.

We report here the photolysis of diethyl ether in the gas phase at wavelengths of 123 and 147 nm and pressures of 2—200 Torr (1 Torr = 133·32 N m^{-2}).

EXPERIMENTAL

The apparatus and experimental procedure have been described in previous publications.[1,4] Photolyses were carried out at ambient temperature (*ca.* 23°) at pressures of 2—200 Torr and conversions of 0·01—0·5%. In some photolyses either hydrogen sulphide or nitric oxide was added to intercept free radicals. Product analysis by g.l.c. was carried out on the following columns: 2 and 7 m squalane; 4 m 2,2′-oxydipropionitrile; 2 m silicone oil and 2 m Porapak P. The microwave powered resonance lamps were filled with BOC grade X krypton (123·6 nm) or xenon (147 nm) at *ca.* 0·5 Torr. Xenon lamps were fitted with lithium fluoride windows, while calcium fluoride windows were used on the krypton lamps to eliminate the line at 116·5 nm. MAR Grade diethyl ether was distilled *in vacuo* until the vapour was pure by g.l.c. analysis.

RESULTS

Photolysis at both wavelengths gave similar product yields. Important hydrocarbon products were methane, ethane, ethylene, propane, and n-butane. The relative molar yields of these products, together with those of minor hydrocarbon products, are shown in the Table. Also included are data obtained when H_2S or NO was added to

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[1] Part III, P. J. Carmichael, B. G. Gowenlock, and C. A. F. Johnson, *J.C.S. Perkin II*, 1973, 2019.

[2] A. J. Harrison and J. S. Lake *J. Phys. Chem.*, 1959, **63**, 1489.

[3] J. F. Meagher and R. B. Timmons, *J. Chem. Phys.*, 1972, **57**, 3175.

[4] B. G. Gowenlock and C. A. F. Johnson, *J.C.S. Perkin II*, 1972, 1150.

scavenge radicals. When H_2S was added methane, ethylene, and ethane were the important hydrocarbon products. When nitric oxide was added to the photolysis ethylene was the only important hydrocarbon product, with nitrosomethane and nitrosoethane being formed. Methane could not be detected when NO was added, as these two components were not resolved by the g.l.c. columns. However, if any methane was produced, the yield was very small (<5 relative to ethylene = 100).

Owing to the vast excess of unchanged diethyl ether overloading the g.l.c. columns, compounds with retention times longer than that of diethyl ether were just observable in the long tail of the ether peak. For this reason quantitative data could be obtained only in the low pressure photolyses. The following products (molar yields relative to propane = 100) were detected at 123 nm and 2 Torr: ethyl vinyl ether 4·3, ethyl isopropyl ether 10·8, ethyl n-propyl ether 0·2, ethyl s-butyl ether 13·5, tetrahydrofuran 0·5, and ethyl n-butyl ether 0·3. In the presence of H_2S, the yield of ethyl vinyl ether was unchanged, but the other ethers were absent. One further product, possibly an epoxybutane (*ca.* 0·4) was produced, its yield being unchanged when radical scavengers were present. Appreciable quantities of formaldehyde were produced, although quantitative data could not be obtained by g.l.c., and ethanol and small quantities of acetaldehyde were also formed.

Changes in product distribution due to an increase in pressure were small, the amount of ethylene produced in the presence of radical scavengers becoming smaller at high pressures, and the methane : ethane ratio in the presence of H_2S decreasing at higher pressures. This change in ratio is also reflected in a change in relative amounts of the combination products in the absence of radical scavengers. The yield of ethanol also increased to some extent at higher pressures.

DISCUSSION

In view of the product distribution, and the behaviour of the products when free radical scavengers are added, we are led to propose reaction (1) as the major primary process. The endothermicity of this bond fission is

$$\mathrm{EtOEt} + h\nu \longrightarrow \mathrm{Et} + \mathrm{EtO} \qquad (1)$$

330 kJ mol^{-1},[5,6] while the rare gas resonance lines at 147 and 123 nm correspond to energies of 815 and 970 kJ mol^{-1} respectively. Thus a considerable excess of energy will reside in the fragments produced.

The ethoxyl radical has two possible pathways for decomposition [reactions (2) and (3)]. The endothermicites of (2) and (3) are 50 and 92 kJ mol^{-1} respectively,[5,6]

$$\mathrm{EtO} \longrightarrow \mathrm{Me} + \mathrm{HCHO} \qquad (2)$$

$$\mathrm{EtO} \longrightarrow \mathrm{H} + \mathrm{MeCHO} \qquad (3)$$

hence it is to be expected that (2) is the preferred decomposition of the ethoxyl radical. Our data show that only small amounts of acetaldehyde are formed, while large quantities of methyl radical and formaldehyde are produced. Thus a large fraction of the ethoxyl radicals are decomposing in an early vibration, yielding methyl radicals and formaldehyde. The small pressure dependence of the methyl : ethyl ratio implies that some of the excited ethoxyl radicals can be deactivated by collision, but the majority decompose even at 200 Torr.

Small amounts of acetaldehyde are produced in the presence of radical scavengers. Thus reaction (3) makes a small contribution to decomposition of the ethoxyl radical. We estimate the ratio reaction (2) : reaction (3) as >30 under our conditions.

Ethylene is a primary product even in the presence of radical scavengers at high pressure. We assume this arises from the decomposition of ethyl radicals carrying an excess of energy from the primary photochemical process [reaction (4)]. The small pressure dependence

$$C_2H_5 \longrightarrow C_2H_4 + H \qquad (4)$$

of the yield of non-scavengable ethylene indicates some of these ' hot ' radicals are capable of collisional stabilisation, but at the pressures used here most decompose in an early vibration.

An alternative source of ethylene is reaction (5).

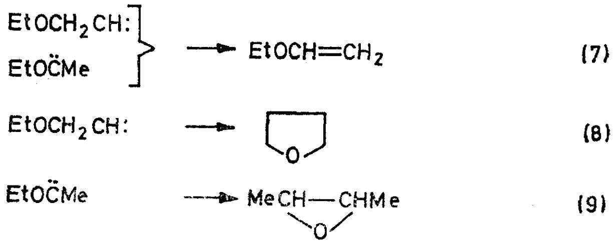
$$\mathrm{EtOEt} + h\nu \longrightarrow C_2H_4 + \mathrm{EtOH} \qquad (5)$$

As the endothermicity of this reaction[6] is only 84 kJ mol^{-1} the two fragments would contain a considerable excess of energy, and further decomposition is likely, especially at low pressures. This mechanism would predict an increase in non-scavengable ethylene at high pressures, rather than the decrease as observed. An increase in ethanol at high pressure is observed, but this, we assume, is due to increasing stability of the ethoxyl radical.

One further primary process remains to be considered. Small amounts of ethyl vinyl ether are produced under all conditions; thus primary process (6) occurs to some extent. Reaction (6) is 60 times less likely than the

$$\mathrm{EtOEt} + h\nu \longrightarrow \mathrm{CH_2{=}CHOEt} + H_2 \text{ (or 2H)} \qquad (6)$$

major primary process (1). Our data do not allow us to determine whether reaction (6) occurs by elimination of a molecule of hydrogen from the same carbon atom (as occurs in ethane photolysis[7]), or by elimination of two hydrogen atoms from adjacent carbon atoms. However, the appearance of tetrahydrofuran and



possibly an epoxybutane among the products could imply molecular elimination, followed by isomerisation or intramolecular insertion. Reactions of this type have

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[5] S. W. Benson, *J. Chem. Educ.*, 1965, **42**, 502.

[6] J. G. Calvert and J. N. Pitts, jun., ' Photochemistry,' Wiley, New York, 1966.

[7] R. F. Hampson, J. R. McNesby, H. Akimoto, and I. Tanaka, *J. Chem. Phys.*, 1964, **40**, 1099.

been observed in other vacuum u.v. photolyses, *e.g.* production of methylcyclopropane from isobutane.[8] Owing to the relative unimportance of reaction (6) as a primary process, further speculation is not warranted at this time.

The experimental data show clearly that the hydrocarbon products are almost entirely free radical in origin. The product distribution can be accounted for by mutual and cross combination and disproportionation of methyl and ethyl radicals. Our observed $C_2:C_4$ product ratios are consistent with the relative rates[9] of these reactions. *Ca.* 75% of the methane yield (no additives) must be produced by methyl radicals undergoing a hydrogen abstraction reaction, while only small amounts of ethane are produced in the analogous reaction of ethyl radicals. A relative rate of abstraction of *ca.* 10 in favour of the methyl radical is not unreasonable at room temperature.

There are two sites in diethyl ether at which hydrogen abstraction may occur [reactions (10) and (11)]. Combination of these radicals with methyl and ethyl radicals

$$R\cdot + CH_3CH_2OEt \longrightarrow CH_3\dot{C}HOEt + RH \qquad (10)$$

$$R\cdot + CH_3CH_2OEt \longrightarrow \cdot CH_2CH_2OEt + RH \qquad (11)$$

would yield propyl and butyl ethyl ethers. Our data imply that hydrogen abstraction occurs predominantly at the secondary hydrogen atoms, *i.e.* reaction (10), as the yields of the isopropyl and s-butyl products are much greater than the yields of the n-propyl and n-butyl products. This is entirely consistent with the known behaviour of radicals towards primary and secondary hydrogen atoms in abstraction reactions.[10]

The very small yields of other hydrocarbons can be satisfactorily accounted for by attack of radicals upon the major hydrocarbon products by addition or by hydrogen abstraction. The source of acetylene remains open to speculation. Decomposition of ethylene still carrying an excess of energy from the primary process, or direct photolysis of ethylene or ethane are possible routes (photolysis of ethylene[11] and ethane[7] are known to yield acetylene).

It should be noted that the ionisation potential[12] of diethyl ether is 9·6 ± 0·1 eV. The xenon resonance line at 147 nm corresponds to 8·4 eV, and the krypton line at 123 nm corresponds to 10·0 eV. It is therefore possible that photoionisation occurs at 123 nm. It has been shown in hydrocarbon photolyses[13] that the ionisation efficiency at wavelengths corresponding to a few tenths of an eV above the theoretical threshold is low, 'super-excited'[14] neutral species being produced. In view of the almost identical results obtained at wavelengths above and below the ionisation potential of diethyl ether, we conclude that ionised species play little part in the overall photochemical decomposition at 123 nm.

Conclusions.—The most important primary process in the photolysis of diethyl ether at 123 and 147 nm is that involving C–O bond fission [reaction (1)]. This is in marked contrast to the photolysis of dimethyl ether[2] at 147 nm which proceeds by C–H bond fission. Until further data are available for related compounds the reason for this change in mechanism cannot be determined. However, it is of interest to note that a ver similar change in fragmentation pattern is observed in the 70 eV mass spectra of these compounds.[15] Diethyl ether gives large peaks at *m/e* 29 and 45, corresponding to Et^+ and EtO^+, with little contribution from *m/e* 73, while dimethyl ether gives a base peak at *m/e* 45 ($M^+ - 1$), and much smaller contributions from Me^+ and MeO^+. In the case of ethyl methyl ether, EtO^+ is favoured over MeO^+ by a factor of five, and the contribution from *m/e* 59 ($M^+ - 1$) is much less important than in the case of dimethyl ether.

In the photolysis of diethyl ether the contribution from the primary process leading to ethyl vinyl ether is much less important than C–O bond fission. Molecular processes account for only a small proportion of the reactions occurring, as was observed for dimethyl ether,[3] and this contrasts with many hydrocarbon photolyses.

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