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PHOTOLYSIS OF DIETHYL ETHER IN THE VAPOUR PHASE BY 184.9 nm RADIATION

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Summary

The products in the photolysis of diethyl ether (DEE) were methane, ethane, ethylene, propane, *n*-butane, ethanol, acetaldehyde, 2-ethoxybutane and 2,3-diethoxybutane (and formaldehyde), and their quantum yields were determined. An appreciable effect of DEE pressure on the quantum yields was not observed within the range 10 - 45 Torr. The effect of addition of nitric oxide, hydrogen iodide and hydrogen sulphide was studied. The dominant primary process is the fission of the C_2H_5—OC_2H_5 bond and its primary quantum yield is 0.61 ± 0.05. In addition, methyl radicals (and formaldehyde) are formed through the secondary decomposition of hot ethoxy radicals and/or the direct decomposition of excited DEE. The primary quantum yield of the methyl radicals is 0.20 ± 0.03. Whilst the sum of the quantum yields of the methyl and ethoxy radicals is 0.81 ± 0.07, that of the ethyl radicals is estimated to be 0.87 ± 0.08.

1. Introduction

In a previous paper the photolysis of dimethyl ether with 184.9 nm radiation has been reported [1]. Here we report the photolysis of diethyl ether (DEE) with 184.9 nm radiation for comparison with the photochemical behaviour of dimethyl ether. Harrison and Lake [2] have studied the photolysis of diethyl ether (as well as dimethyl ether) in the vapour phase with a hydrogen discharge lamp. Since their product identification was carried out with UV spectroscopy only, the formation of formaldehyde, acetaldehyde and ethylene was observed, but nothing was mentioned about alkane products. Calvert and Pitts [3] have tentatively proposed the following primary processes on the basis of the results of Harrison and Lake:

$$C_2H_5OC_2H_5 \longrightarrow \begin{cases} C_2H_5 \text{ (or } C_2H_4 + H) + C_2H_5O \text{ (or } CH_3 + HCHO) \\ C_2H_5OH + C_2H_4 \\ CH_3CHO + C_2H_6 \end{cases}$$

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However, they have not made an assessment of the importance of these processes. Johnson and Lawson [4] have studied the photolysis of DEE with 147.0 and 123.6 nm radiations and have determined the rates of formation of the products. They concluded that the most important primary process is C_2H_5—OC_2H_5 bond fission, and that the majority of ethoxy radicals further decompose into methyl radicals and formaldehyde. Von Sonntag *et al.* [5] have photolysed liquid DEE with 184.9 nm radiation and have determined the quantum yields of the products.

The electronic transitions of ethers in the 180 nm region has been assigned to an $n \rightarrow \sigma^*$ transition and the absorption spectrum of DEE appears to be similar to that of dimethyl ether in this wavelength region [6]. Doucet *et al.* [7] have pointed out the participation of a Rydberg transition ($n \rightarrow 3s$) in the first absorption band of alkyl ethers, but nothing is known about the photochemical behaviour of ethers characteristic of the participation of the Rydberg transition.

2. Experimental procedure

2.1. Apparatus

The apparatus was the same as described in a previous paper [1].

2.2. Materials

DEE was obtained from Merck Co. and used without further purification. Its stated purity was 99.5%, and no organic impurity was found by gas chromatography (with a flame ionization detector) methods. The radical scavenger materials (nitric oxide and hydrogen sulphide) were obtained from Takachiho Co., and hydrogen iodide was obtained from Matheson Co.; these materials were used without further purification. For the determination of the retention times for gas chromatography (GC), 2-ethoxybutane was synthesized [8] and 2,3-diethoxybutane was obtained from the product mixtures in the mercury-sensitized photolysis of DEE [9]. Other authentic samples for the determination of the retention times were all commercial products.

2.3. Procedures and analysis

The procedures were essentially the same as those described in a previous paper [1]. The total input of photons at 184.9 nm from the low pressure mercury lamp into the reaction cell was determined by actinometry of nitrous oxide. In a series of experiments of pure DEE photolysis the total input of photons was $(2.7 \pm 0.2) \times 10^{14}$ photons s^{-1} ($(8.6 \pm 0.06) \times 10^{13}$ photons cm^{-2} s^{-1}) and the irradiation time was 30 min. Since the cell window was coloured yellow during the trial experiments of photolysis of mixtures of DEE and hydrogen iodide, the cell was cleaned by treatment with dilute hydrofluoric acid. After cleaning the cell, the total input of photons at 184.9 nm was improved to 3.2×10^{15} photon s^{-1} probably because of the improved transparency of the cell window and the adjustment

of the lamp position. The photolysis of DEE and hydrogen sulphide mixtures was performed with the improved photon flux and the irradiation time was reduced to 5 min.

For the analysis of the organic products we used two GC columns. The conditions of GC analysis were as follows. Column I was a Porapak-Q(50/80) column 2 m long with helium carrier gas (50 ml min^{-1}); the column oven temperature was kept constant at 65 °C for 30 min and then raised at a rate of 1 °C min^{-1} for 30 min and afterwards at a rate of 3 °C min^{-1}. The retention times under these conditions were as follows: methane, 1.5 min; ethylene, 2.5 min; ethane, 3.0 min; propane, 13.5 min; acetaldehyde, 29 min; *n*-butane, 55 min; ethanol, 63 min; ethyl methyl ether, 69 min; ethyl vinyl ether, 78 min; DEE, 82 min; 2-ethoxybutane, 93 min; 2,3-diethoxybutane, 102 min. Column II was a PEG-4000 (60/80) column 4 m long with helium carrier gas (40 ml min^{-1}); the column oven temperature was kept constant at 25 °C for 10 min and then raised at a rate of 3 °C min^{-1}. The retention times were as follows: DEE, 6.5 min; diethoxymethane, 13 min; 2-ethoxybutane, 16 min; 1,1-diethoxyethane, 21.5 min; 1,2-diethoxyethane, 32 min; 2,3-diethoxybutane, 35 min. The retention time for ethyl *n*-propyl ether was separately determined to be 8 min with a PEG-4000 column 4 m long with helium carrier gas (40 ml min^{-1}) at 35 °C.

After we had confirmed that ethyl *n*-propyl ether, diethoxymethane and 1,2-diethoxyethane were not found in the products, only column I was used for the quantitative analysis of the products. In the present photolysis we could perform GC analysis of all the products except formaldehyde with this single column. The detection of hydrogen in the products was performed with argon carrier gas in gas chromatography with a thermal conductivity cell (GC–TCD) with a molecular sieve column 2 m long.

3. Results and discussion

3.1. Product identification, quantum yields and pressure effect

Irradiation of DEE in the vapour phase with 184.9 nm light at ambient temperature produced methane, ethane, propane, *n*-butane, ethanol, acetaldehyde, 2-ethoxybutane and 2,3-diethoxybutane. Hydrogen was not found in the products after irradiation for 30 min within the sensitivity limit of the argon carrier gas GC–TCD; this means that the quantum yield of hydrogen is less than 0.01. A rapid increase of hydrogen concentration was observed in the prolonged irradiation but this is due to the secondary photolysis of the product(s) (probably formaldehyde). Ethyl methyl ether, ethyl *n*-propyl ether, ethyl vinyl ether, diethoxymethane, 1,1-diethoxyethane and 1,2-diethoxyethane were possible organic products and were carefully looked for, but not found, in the products. Ethyl isopropyl ether is also a possible product. As an authentic sample of this compound was not available, we could not determine its retention time in the gas chromatograph under the present experimental conditions. However, all GC peaks in our gas chromato-

gram of the photolysis products were identified and no unidentified GC peaks remained. Although we could not completely exclude the possible overlapping of the ethyl isopropyl ether peak with other identified peaks, we assumed that ethyl isopropyl ether was not formed in the photolysis. Formaldehyde was produced but its quantitative determination was not performed since a separate colorimetric analysis was required.

The amounts of all the products increased linearly with irradiation time up to 30 min. The quantum yields of the products were determined in the pressure range from 13.8 to 44.7 Torr (1 Torr = 133.3 Pa) of DEE (Table 1), and we may conclude that the quantum yields are independent of the DEE pressure within this pressure range.

3.2. *Effect of radical scavengers*

The formation of methane, ethane, propane and *n*-butane was completely inhibited by adding 2 Torr NO to 30 Torr DEE, indicating that methyl and ethyl radicals were effectively scavenged by nitric oxide. The inhibition of ethane formation by nitric oxide addition shows that the molecular primary process to give ethane and acetaldehyde (see Table 3, reaction (VIII)) does not take place appreciably. The quantum yield of ethylene is decreased by the addition of nitric oxide but about a one-half of its original value (0.03) persists. As will be stated later, the ethylene formation is also reduced by the addition of hydrogen sulphide but is not completely suppressed. In ref. 1 it was reported that there was an unusual behaviour towards nitric oxide of the methoxy radicals formed in the photolysis of dimethyl ether, and again ethoxy radicals in the DEE photolysis are not effectively scavenged by nitric oxide. Probably the secondary photolysis of product alkyl nitrites may be involved, but we have to leave this point for future investigation.

Hydrogen iodide and hydrogen sulphide are known to be good radical scavengers especially towards alkyl radicals, resulting in alkane formation of the same carbon numbers as the original alkyl radicals. However, in the present reaction system we found that hydrogen iodide was not suitable, since the yield of ethanol was affected by the presence of hydrogen iodide and the product iodine. Hydrogen sulphide also seems to be a better radical scavenger in determining the yields of alkyl and ethoxy radicals. In Table 2 the product yields in the photolysis of mixtures of DEE and hydrogen sulphide are shown in units of the rates of product formation instead of the quantum yields, since we could not determine the number of photons absorbed by DEE owing to the simultaneous absorption of light at 184.9 nm by hydrogen sulphide. Unfortunately the molar extinction coefficient of DEE at 184.9 nm seems not to be well established, *e.g.* the values 1500 [10], 1800 [6] and 2600 [11] $l\ mol^{-1}\ cm^{-1}$ have been quoted, and the molar extinction coefficient of hydrogen sulphide at 184.9 nm is estimated to be 600 [12] and 700 [13] $l\ mol^{-1}\ cm^{-1}$ from the reported absorption spectra of hydrogen sulphide. Using the smallest value reported for the molar extinction coefficient of DEE, the tentatively estimated ratio of the absorbance at 184.9 nm by hydrogen sulphide to the absorbance by DEE is 0.24.

TABLE 1

Quantum yields of products in the photolysis of diethyl ether

DEE pressure (Torr)	*Quantum yields* $\times 10^2$								
	C_2H_4	$n\text{-}C_4H_{10}$	$CH_3CH(OC_2H_5)C_2H_5$	C_2H_6	C_3H_8	CH_4	CH_3CHO	C_2H_5OH	$CH_3(CH(OC_2H_5))_2CH_3$
13.8	5.7	27.6	7.7	8.4	15.9	0.84	3.3	55.7	21.4
21.3	6.6	30.9	9.2	9.0	18.9	1.05	3.6	57.9	23.6
28.3	5.7	27.6	8.1	9.9	14.4	—	3.0	60.0	23.6
29.5	6.9	30.0	—	10.5	16.2	0.95	4.5	—	—
35.3	6.0	25.2	—	9.3	14.4	0.81	3.3	—	—
37.3	6.0	27.0	9.4	8.7	15.3	0.96	3.3	62.0	27.9
44.7	6.0	24.0	7.5	9.3	13.2	0.90	3.0	53.6	23.6
Average	6.2	27.3	8.4	9.3	15.3	0.9	3.3	57.3	24.0
Standard deviation	0.4	2.0	0.9	0.6	2.0	0.1	0.6	4.2	2.4

The order of products is arranged according to the origin of the primary radicals ethyl, methyl and ethoxy. Ethane and propane are produced from both methyl and ethyl radicals.

TABLE 2

The rates of formation of products in the photolysis of DEE in the presence and absence of radical origin ethyl, methyl and ethoxy

Pressure (Torr)		*Rates of formation*[a] ($\times 10^{-11}$ mol s^{-1}) *assigned to primary radicals*							
H_2S	*DEE*	$R(C_2H_4)$	$R(n\text{-}C_4H_{10})$	$R(C_2H_6,d)$	$R(2\text{-}EB)$[b]	$R(C_3H_8)$	$R(C_2H_5)$	$R(CH_4)$	$R(C_3H_6$
5	32	10.3	3	405	0	5.2	427	103	5.2
		2.4	0.7	94.8	0	1.2	(100)	31	1.6
9	31	9.3	1	549	0	4.4	565	132	4.4
		1.6	0.2	97.2	0	0.8	(100)	29	1.0
18	30	2.2	0	263	0	6.6	272	62	6.6
		0.8	0	96.7	0	2.4	(100)	26	2.8
Average[c]		2.8	12.3	0.5	3.8	6.9	38.5	0.4	6.9
		7.3	63.9	1.3	9.9	17.7	(100)	1.0	19.8
		Quantum yield[d] *(liquid)*							
		$\phi(C_2H_4)$	$\phi(n\text{-}C_4H_{10})$	$\phi(C_2H_6,d)$	$\phi(2\text{-}EB)$[b]	$\phi(C_3H_8)$	$\phi(C_2H_5)$	$\phi(CH_4)$	$\phi(C_3H_8$
		0.09	0.07	0.12	0.19	0.001	0.54	0.0008	0.001
		16	26	22	35	0.2	(100)	0	0.2

[a] Rates in units of concentration may be obtained by dividing R by 113 ml, if a uniform
[b] 2-EB, 2-ethoxybutane.
[c] Average values from six different DEE pressure experiments (Table 1). The rates are
[d] Data from von Sonntag *et al.* [5]. The relative ratios are calculated, for the convenience
their proposed mechanism does not involve radical processes.

In Table 2 the average rates of formation of products in the photolysis of pure DEE and liquid DEE by von Sonntag *et al.* [5] are also shown for comparison. The approximately 11 times larger rate of formation (exemplified as $R(C_2H_5)$) in the photolysis of DEE and 5 Torr H_2S than that in the photolysis of pure DEE may be interpreted as being caused by the increase of input photon flux (about 12 times greater, see Section 2.3).

By adding hydrogen sulphide the product distribution is somewhat simplified, although some small amounts of minor products (ethylene, propane and acetaldehyde) persist. Assuming that methane, ethane and ethanol are all formed through the hydrogen abstraction from hydrogen sulphide by methyl, ethyl and ethoxy radicals respectively, we calculated the relative percentage ratios of the product distribution normalized to the rate of formation of ethyl radicals and to the sum of the rates of formation of methyl and ethoxy radicals (Table 2). The ratio $(R(CH_3) + R(C_2H_5O))/R(C_2H_5)$ indicates the material balance of the products on the basis of the assumed reaction mechanism. This ratio ranges from 0.78 to 0.87 and is not so well defined as that in the photolysis of pure DEE, indicating the absence of some of the products originating from the methyl and ethoxy radicals. It is not known whether this deficit is due to the incomplete recovery of the

hydrogen sulphide and the relative distributions of the product assigned to the primary

$R(C_2H_6,b)$	$R(CH_3)$	$R(CH_3CHO)$	$R(C_2H_5OH)$	$R(C_2H_5O)$	$R(CH_3)+R(C_2H_5O)$	$\frac{R(CH_3)+R(C_2H_5O)}{R(C_2H_5)}$
	108	28	195	223	331	
	32.6	8.5	58.9	67.4	(100)	0.78
	146	25	293	318	454	
	30	5.5	64.5	70.0	(100)	0.80
	62	12.6	156	169	237	
	28.8	5.3	65.8	71.1	(100)	0.87
0.9	9.1	1.5	25.8	27.3	36.4	
5.0	25.0	4.1	70.9	75.0	(100)	0.95
$\phi(C_2H_6,b)$	$\phi(CH_3)$	$\phi(CH_3CHO)$	$\phi(C_2H_5OH)$	$\phi(C_2H_5O)$		
	≈ 0	0.06	0.46	0.52		
	0.5	11.5	88	99.5	(100)	0.96

generation of products is assumed.

obtained by multiplying the quantum yields shown in Table 1 by 4.5×10^{-10} mol s^{-1}.
of comparison, assuming that all products are formed through radical processes, although

products or to some other reason. Some further discussions on the results of the photolysis of mixtures of DEE and hydrogen sulphide will be given later.

3.3. *Reaction mechanism and quantum yields of primary processes*

In the photolysis of DEE with 184.9 nm radiation (694 kJ mol^{-1}), the processes in Table 3 may be considered to be possible from the thermochemical data.

The quantum yields of the primary processes and their branching ratio depend largely on the electronic state of excited DEE as well as on the exothermicity of the primary reactions, and a reliable experimental determination of the values is required in order to discuss the photochemistry in terms of the exciting light wavelength.

Since the quantum yield of hydrogen was less than 0.01, reactions (V), (VI) and (VII) can be disregarded. Since the ethane formation was completely suppressed by the addition of nitric oxide, reaction (VIII) (molecular formation of ethane and acetaldehyde) is also less probable. For the formation of methyl radicals, reactions (II), (III) and (IV) may be considered as possible but reaction (IV) can be disregarded since ethyl *n*-propyl ether and diethoxymethane were not found at all in the products, indicating that the ethoxy-

TABLE 3

Possible processes in the photolysis of diethyl ether

Process		ΔH (kJ mol^{-1})	*Exothermicity for 184.9 nm radiation*	*Reaction*
$C_2H_5OC_2H_5 \rightarrow$	$C_2H_5 + C_2H_5O$	323	371	I
	$C_2H_5 + C_2H_5O^* \rightarrow C_2H_5 + CH_3 + HCHO$	381	313	II
	$C_2H_5 + CH_3 + HCHO$	381	313	III
	$C_2H_5OCH_2 + CH_3$	356	338	IV
	$C_2H_5OCHCH_3 + H$	394	300	V
	$C_2H_5OCH_2CH_2 + H$	415	279	VI
	$CH_2{=}CHOC_2H_5 + H_2$	113	581	VII
	$C_2H_6 + CH_3CHO$	1	693	VIII
	$C_2H_4 + C_2H_5OH$	84	610	IX

methyl radical as the counterpart of the methyl radical in reaction (IV) does not exist as an intermediate. The molecular formation of ethylene and ethanol through reaction (IX) cannot be completely excluded since a small amount of ethylene still persists, as seen in Table 2, although most of the ethylene formation is suppressed by the addition of nitric oxide or hydrogen sulphide. Johnson and Lawson [4] observed similar behaviour for ethylene in the photolysis of DEE with 147.0 nm radiation. They ascribed this behaviour to the too rapid decomposition of energy-rich ethyl radicals into ethylene and hydrogen regardless of the presence of radical scavengers or high pressure DEE. They consider that the molecular formation of ethylene is less probable because the secondary decomposition of energy-rich ethylene should take place (the excess energy for reaction (IX) is 734 kJ mol^{-1}), even if reaction (IX) does take place. Although it is not certain whether a similar situation may be considered in the photolysis with 184.9 nm radiation (the excess energy is 610 kJ mol^{-1}), the contribution of reaction (IX) to the total quantum yield of the primary processes is certainly quite small, considering the small value of the rate of formation of ethylene in the photolysis in the presence of scavengers.

Eventually, reactions (I), (II) and (III) are left as possibilities and obviously reaction (I) is the most important. The primary quantum yield of the ethoxy radical (reaction (I)) is estimated to be 0.61 ± 0.05, as the sum of $\phi(C_2H_5OH)$ and $\phi(CH_3CHO)$, assuming that acetaldehyde is formed only through the disproportionation reactions (XVIa) and (XVIIIa) (see later). Since no appreciable amounts of diethyl peroxide were confirmed, we disregard the combination of two ethoxy radicals.

Now only reactions (II) and (III) are considered for the mechanism of methyl radical formation. Since both reactions give the same final products, it is difficult to differentiate between these two reactions by the product analysis experiments, and hereafter we describe the quantum yield (or the

rate of formation) of methyl radicals without discriminating between reaction (II) and reaction (III). If reaction (II) is a unimolecular decomposition of a vibrationally excited ethoxy radical, we may expect a sensitive pressure effect on the ratio of the quantum yield of methyl radicals to that of ethoxy radicals. As far as the results in Table 1 are concerned, an appreciable pressure effect is not observed.

In determining the primary quantum yields of methyl and ethyl radicals in the photolysis of pure DEE, it is necessary to partition the yields of ethylene and ethane according to the modes of the participating processes of formation of the products, but we leave this estimation for later.

In the photolysis of mixtures of DEE and hydrogen sulphide, we have seen that the hydrogen abstractions from hydrogen sulphide by the primary radicals (methyl, ethyl and ethoxy) become dominant. Although the three experiments of photolysis of mixtures of DEE and hydrogen sulphide may not be enough to proceed with quantitative discussions, we should like to note the following points.

If we assume that the branching ratio of reaction (II) plus reaction (III) to reaction (I) plus reaction (II) plus reaction (III) is given by the ratio $R(CH_3)/(R(CH_3) + R(C_2H_5O))$, it will be seen that this ratio decreases slightly with an increase in hydrogen sulphide pressure (0.33 at 5 Torr H_2S, 0.30 at 9 Torr H_2S and 0.29 at 18 Torr H_2S), apparently suggesting a quenching effect of hydrogen sulphide towards excited ethoxy radicals. However, this ratio in the photolysis of pure DEE, calculated through the procedures described later, is 0.26, which is smaller than those in the presence of hydrogen sulphide. Further, the following points are not well understood at present. First, $R(C_3H_8)$ has some value even in the photolysis at 18 Torr H_2S, whereas the value for $R(n\text{-}C_4H_{10})$ is remarkably reduced. Secondly, the ratio $R(CH_3CHO)/R(C_2H_5OH)$ in the photolysis of mixtures of DEE and hydrogen sulphide is rather larger than that in the photolysis of pure DEE. This is against our expectation that the disproportionation reaction between two ethoxy radicals is suppressed by the addition of hydrogen sulphide. Thirdly, the rates at 9 Torr H_2S (exemplified as $R(C_2H_5)$) are larger than those at 5 Torr H_2S. The experiments of photolysis of mixtures of DEE and hydrogen sulphide were originally attempted to discriminate the molecular process from the radical process and further investigations are required to make these points clear. Under some circumstances it may be possible that hydrogen sulphide plays some other role than as a simple radical scavenger, causing a change in the primary photochemical process of DEE.

The secondary processes in the photolysis of pure DEE are more complicated. The possible secondary processes in the present system may be as shown in Tables 4, 5 and 6.

It is certain that the processes to give methane, propane and *n*-butane can be assigned uniquely to reaction (X), reaction (XVb) and reaction (XIVb) respectively.

Among the four processes of combination considered, reactions (XIX) and (XX) have been confirmed, since 2-ethoxybutane and 2,3-diethoxy-

TABLE 4

Hydrogen atom abstraction from diethyl ether by methyl, ethyl and ethoxy radicals

Process			ΔH (kJ mol^{-1})	*Reaction*
CH_3 + DEE	→	$CH_4 + C_2H_5OCHCH_3$	−33	X
C_2H_5 + DEE	→	$C_2H_6 + C_2H_5OCHCH_3$	−12	XI
C_2H_5O + DEE	→	$C_2H_5OH + C_2H_5OCHCH_3$	−25	XII

TABLE 5

Disproportionation and combination between two primary radicals in the photolysis of diethyl ether

Process			*Rate constant* (cm^3 mol^{-1} s^{-1})	k_a/k_b[a]	*Reaction*
$2CH_3$	→	C_2H_6	2.2×10^{13}		XIII
$2C_2H_5$	→	$C_2H_6 + C_2H_4$ n-C_4H_{10}	2.5×10^{13}	0.15 ± 0.01	XIVa XIVb
$CH_3 + C_2H_5$	→	$CH_4 + C_2H_4$ C_3H_8	5.0×10^{13}	0.04 ± 0.02	XVa XVb
$C_2H_5 + C_2H_5O$	→	$C_2H_6 + CH_3CHO$ DEE		1.3 ± 0.2	XVIa XVIb
$C_2H_5O + C_2H_5$	→	$C_2H_5OH + C_2H_4$ DEE		2.3 ± 0.3	XVIIa XVIIb
$2C_2H_5O$	→	$C_2H_5OH + CH_3CHO$ $C_2H_5OOC_2H_5$		12	XVIIIa XVIIIb

[a]Data taken from ref. 14; a and b denote the disproportionation and combination reactions respectively.

TABLE 6

Combination involving the secondary radical ethoxyethyl in the photolysis of diethyl ether

Process			*Reaction*
$C_2H_5 + C_2H_5OCHCH_3$	→	$C_2H_5OCH(CH_3)C_2H_5$ (2-ethoxybutane)	XIX
$2C_2H_5OCHCH_3$	→	$(C_2H_5OCHCH_3)_2$ (2,3-diethoxybutane)	XX
$CH_3 + C_2H_5OCHCH_3$	→	$C_2H_5OCH(CH_3)_2$	XXI
$C_2H_5O + C_2H_5OCHCH_3$	→	$(C_2H_5O)_2CHCH_3$	XXII

butane have been identified in the gas chromatogram of the photolysis products. Reactions (XXI) and (XXII) probably do not take place appreciably, since ethyl isopropyl ether and 1,1-diethoxyethane have not been identified

in the gas chromatogram of the products. When we consider that the steady state concentrations of methyl and ethoxy radicals must be very small compared with those of ethyl and ethoxyethyl radicals, it is understandable that these reactions were not observed.

We assumed that ethanol is formed mainly through the abstraction of hydrogen by an ethoxy radical from DEE and that the contribution from reaction (XVIIIa) to the ethanol yield is small. The low quantum yield of acetaldehyde supports this assumption as well as the small contribution of reaction (XVIa). The value of the rate constant k_{12} for reaction (XII) has not been reported but it may be of the order of 10^7 - 10^8 cm^3 mol^{-1} s^{-1} at room temperature. The rate constants k_{10} and k_{11} for reaction (X) and reaction (XI) respectively are also not known but they may be somewhat smaller than k_{12} since the reactions may have larger activation energies. The small quantum yield of methane supports this assumption and the quantum yield of ethane by reaction (XI) must also be small (see later). Among the secondary processes to give ethane, reaction (XIVa) must be the most important but reactions (XI), (XIII) and (XVIa) cannot be excluded. It is difficult to assess their contribution accurately but we attempt to evaluate them with some simplifications. Since each of the processes to give propane and *n*-butane is a single process, we may calculate the ratio $[CH_3]_s/[C_2H_5]_s$ of the steady state concentrations of methyl radicals to ethyl radicals from the following equation:

$$\frac{\phi(C_3H_8)}{\phi(n\text{-}C_4H_{10})} = \frac{[CH_3]_s[C_2H_5]_s k_{15b}}{[C_2H_5]_s^2 k_{14b}} \tag{1}$$

Combining our experimental quantum yields of propane and *n*-butane with the reported values of k_{15b} and k_{14b}, we obtain 0.25 for the ratio of methyl to ethyl steady state concentrations. When we put this value and the reported values of k_{13} and k_{14b} into the equation

$$\frac{\phi(C_2H_6,b)}{\phi(n\text{-}C_4H_{10})} = \frac{[CH_3]_s^2 k_{13}}{[C_2H_5]_s^2 k_{14b}} \tag{2}$$

we obtain 0.02 for the quantum yield of ethane formed through methyl–methyl radical combination ($\phi(C_2H_6,b)$).

On the basis of these estimates of the quantum yields, the quantum yield for methyl radicals is given by the equation

$$\phi(CH_3) = \phi(CH_4) + \phi(C_3H_8) + 2\phi(C_2H_6,b)$$
$$= 0.20 \pm 0.03$$

The process to give ethylene is also not a single process. Reaction (XIVa) may be the dominant process but the molecular formation of ethylene (reactions (IX) and (XVIIa)) may make small contributions to the quantum yield of ethylene. The contribution of reaction (XVa) may be very small, since the reported value of the ratio k_{15a}/k_{15b} is 0.04 and the ratio $[CH_3]_s/[C_2H_5]_s$ is 0.25. We cannot assess the contribution of reactions (IX) and (XVIIa) on the formation of ethylene. If we suppose that all the ethylene

is formed through reaction (XIVa), we obtain 0.23 for the ratio k_{14a}/k_{14b} = $\phi(C_2H_4,a)/\phi(n\text{-}C_4H_{10})$, whereas the reported value of the ratio at 25 °C is 0.15, indicating some overestimation of $\phi(C_2H_4,a)$. Conversely, if we adopt the reported value of the ratio of the rate constants, we obtain 0.04 instead of the observed value of 0.06 for the quantum yield of ethylene by reaction (XIVa) ($\phi(C_2H_4,a)$) from the observed quantum yield of *n*-butane. Now, we obtain 0.03 for the quantum yield of ethane by reaction (XI) according to the following equation:

$$\begin{aligned}\phi(C_2H_6,d) &= \phi(C_2H_6,\text{observed}) - \phi(C_2H_6,b) - \phi(C_2H_6,a)\\ &= \phi(C_2H_6,\text{observed}) - \phi(C_2H_6,b) - \phi(C_2H_4,a)\\ &= 0.03\end{aligned}$$

However, we must admit that this calculated value of $\phi(C_2H_6,d)$ may contain large errors, since it is obtained by indirect calculation with the reported rate constants.

Now we calculate the primary quantum yields for ethyl radicals on the basis of the estimated product quantum yields, bearing in mind that the calculation of the primary quantum yield of the ethyl radicals is interrelated with that of the methyl radicals. We obtain 0.87 ± 0.08 for $\phi(C_2H_5)$ from the following equation:

$$\phi(C_2H_5) = \phi(C_3H_8) + 2\phi(n\text{-}C_4H_{10}) + \phi(\text{2-ethoxybutane}) + 2\phi(C_2H_4,a)$$

Propane, *n*-butane and 2-ethoxybutane definitely have their origin in common as the ethyl radicals but $\phi(C_2H_4,a)$ is an indirect value, as noted above. Meanwhile, we obtained the value 0.81 ± 0.07 for the sum of $\phi(CH_3)$ and $\phi(C_2H_5O)$, and the agreement between these two values is satisfactory, although it may be somewhat fortuitous. In a previous paper [1] it was reported that the photolysis of dimethyl ether with 184.9 nm radiation proceeds through C—O bond fission and its primary quantum yield is nearly unity. It is interesting to study the mode of ethyl methyl ether photolysis and to determine its quantum yield.

Additionally we compare the quantum yields of the primary radicals which participate in the abstraction from DEE with that of the secondary ethoxyethyl radical ($C_2H_5OCHCH_3$) which is formed by the abstraction. According to the above estimates, we obtain the total quantum yield of the radicals which abstract hydrogen from DEE as follows:

$$\begin{aligned}&\phi(CH_3) + \phi(C_2H_5) + \phi(C_2H_5O, \text{abstract})\\ &\quad = \phi(CH_4) + \phi(C_2H_6,d) + \phi(C_2H_5OH,d)\\ &\quad = 0.58 \pm 0.04\end{aligned}$$

where $\phi(C_2H_5OH,d)$ is the quantum yield of ethanol by reaction (XII), given by subtracting $\phi(C_2H_5OH,a) = \phi(CH_3CHO)$ from reaction (XVIIIa) from the total quantum yield for ethanol; some contributions from other radical–radical reactions (reactions (XVa), (XVIa) and (XVIIa)) are neglected.

Meanwhile, we obtain the quantum yield of the secondary radical simply, as follows:

$$\phi(C_2H_5OCHCH_3) = \phi(\text{2-ethoxybutane}) + 2\phi(\text{2,3-diethoxybutane})$$
$$= 0.56 \pm 0.03$$

The agreement between the two values is satisfactory.

Finally we briefly compare our result with that for photolysis of liquid DEE reported by von Sonntag *et al.* [5]. Their procedure to determine the branching ratio is sophisticated, solving the rate equations of the composite primary and secondary processes. Originally they considered six primary and 16 secondary processes but the relatively important primary processes are reactions (I), (VII), (VIII) and (IX) and the branching ratios of these reactions are estimated to be 0.70, 0.11, 0.085 and 0.10 respectively. Although the molecular processes (reactions (VII), (VIII) and (IX)) appear to have some importance, these researchers admitted that the cage reactions of radical–radical reactions ($C_2H_5 + C_2H_5O \rightarrow C_2H_6 + CH_3CHO$ and/or $C_2H_4 + C_2H_5OH$ in a solvent cage) cannot be distinguished from the genuine molecular processes (reactions (VIII) and (IX)). The reason that reaction (VII) was observed in the liquid phase but not in the vapour phase is not known. Although these researchers did not give the quantum yields of the primary processes, we tentatively calculate the values by combining the quantum yields of the final products and the branching ratio. The calculation gives a value $0.41 = \phi(C_2H_5) \times 0.70/(0.70 + 0.085)$ as the primary quantum yield for ethoxy radicals in the liquid phase and 0.58 as the sum of the quantum yields of four primary processes. Considering the solvent quenching, it is understandable that the quantum yield in the liquid phase is less than that in the vapour phase. Further, it is interesting that the quantum yield for methyl radicals (as the sum of those for methane and propane) is very small, and this may be interpreted as being caused by the quenching of hot ethoxy radicals or excited DEE by the frequent collisions in the liquid phase, which prevents the primary or secondary decomposition of the energy-rich species (reaction (II) and/or reaction (III)).

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