Tetrahedron. Vol. 29, pp. 1811 to 1818. Pergamon Press 1973. Printed in Great Britain

THE UV PHOTOLYSIS ($\lambda = 185$ nm) OF LIQUID t-BUTYL METHYL ETHER*

H.-P. SCHUCHMANN and C. v. SONNTAG
Max-Planck-Institut für Kohlenforschung, Abt. Strahlenchemie, 433 Mülheim (Ruhr), W.-Germany

(*Received in the UK* 16 *October* 1972; *Accepted for publication* 8 *January* 1973)

Abstract—t-Butyl methyl ether has been UV photolysed ($\lambda = 185$ nm) to a maximal conversion of less than 0·1%. A study of the products (quantum yields) has been made: methanol ($0{\cdot}40_5$), t-butanol (0·20), isobutene ($0{\cdot}17_8$), t-butyl neopentyl ether ($0{\cdot}14_2$), t-butyl ethyl ether ($0{\cdot}13_4$), 1,2-di-t-butoxyethane (0·097), methane (0·056), isobutane (0·046), isopropenyl methyl ether (0·030), hydrogen (0·020), neopentane (0·016), ethane (0·015), formaldehyde (0·012), 2-methoxy-2-methyl-4-t-butoxybutane (0·005), hexamethylethane (0·0048), 2-methoxy-2-methylbutane (0·0027), 2-methoxy-2-methyl-3-t-butoxypropane (0·002), isopropyl methyl ether (0·0015), formaldehyde t-butyl methyl acetal (0·001), formaldehyde di-t-butyl acetal (0·001), 2-methoxy-2-methyl-4,4-dimethylpentane (0·001), 2-methoxy-2-methyl-3,3-dimethylbutane (0·0003), 2,5-dimethoxy-2,5-dimethylhexane (0·0002), di-t-butyl ether ($5 \cdot 10^{-5}$), 2,2-dimethyloxirane (?, $\leqslant 0{\cdot}001$). There is no decomposition of the t-BuO radical into acetone ($< 5 \cdot 10^{-4}$) and CH_3. Cyclisation reactions leading to α,α-dimethyloxetane ($< 10^{-4}$) and 1-methoxy-1-methylcyclopropane ($< 10^{-4}$) do not occur. The material balance yields $C_5H_{11{\cdot}97}O_{1{\cdot}018}$.

The main modes of fragmentation (*ca* 82%) are represented by the homolytic C—O bond split, either into t-butyl and methoxy (*ca* 52%) or into t-butoxy and methyl (*ca* 30%). Fragmentation into methanol and isobutene (8·5%) as well as into formaldehyde and isobutane (2%) are further modes of decomposition. The break of a C—C linkage (4·5%) mainly occurs by elimination of molecular methane. A C—H bond split has a probability of *ca* 3% with the methoxy C—H bond the more likely one to break.

INTRODUCTION

Until recently, the photolysis of liquid aliphatic ethers has received little attention since these ethers begin to show pronounced absorption only in the vacuum UV, and quantum yields of product formation are very low above 200 nm. Following the investigation of the 185 nm photolysis of some aliphatic alcohols[1–5] it appeared desirable to compare the photochemical behavior of ethers with that of the alcohols. There, t-butanol[5] exhibits a remarkable anomaly. While MeOH,[1] EtOH,[2] i-PrOH,[3] and ethylene glycol,[4] undergo an O—H split as the most important primary process, in t-BuOH the C—C bond is preferably cleaved.[5] Similarly, the C—C bond split is a very minor process (< 0·5%) with diethyl ether.[6] By analogy, one would expect that in the case of t-butyl methyl ether (t-BuOMe) studied in the present work the C—C split would become important.

In the thermal decomposition of t-BuOMe the route to isobutene and methanol is strongly favoured. Pyrolysis already occurs at the comparatively low temperature of 433° and leads exclusively to these products ($E = 61{\cdot}5$ kcal/mol; $\log A = 14{\cdot}38$).[7] It is conceivable that photochemically too this route could be the preferred one. With diethyl ether the analogous reaction leading to ethylene and ethanol occurs to an extent of 8·5% at the most.

In the photolysis of diethyl ether[6] the most important process, the homolytic scission of a C—O linkage, can only lead to OEt and Et radicals. In the t-BuOMe molecule the two C—O bonds are not equivalent. The fact that the t-Bu radical is stabilised compared to the Me may influence the probabilities with which the different C—O bonds are broken.

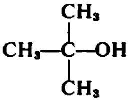
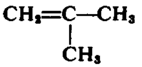
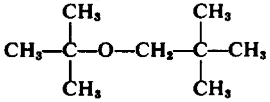
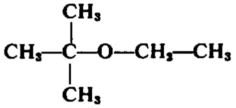
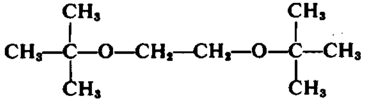
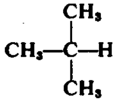
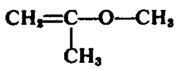
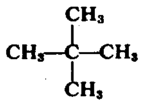
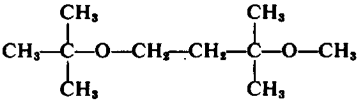
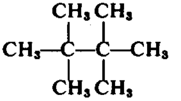
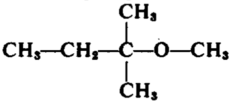
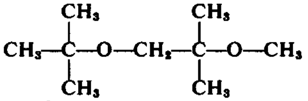
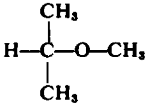
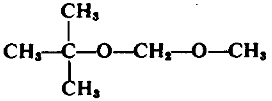
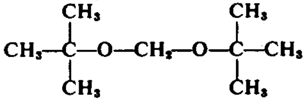
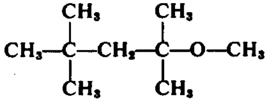
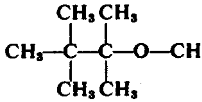
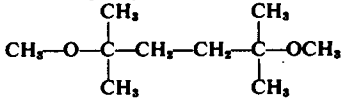
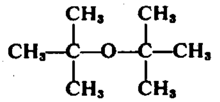
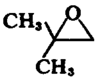
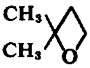
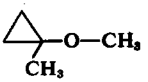
RESULTS AND DISCUSSION

Of the two main spectral lines at 185 and 254 nm which are emitted by the Hg low pressure arc only the 185 nm line is photolytically active in this system. Strong absorption sets in below 200 nm (Fig 1). Vycor transmits the 254 nm line but absorbs the 185 nm one. When a Vycor filter was used, no photolysis occurred. The quantum yields were obtained using the ethanol actinometer.[8–11] Its H_2 quantum yield of 0·4 can be derived[2] taking Dainton and Fowles' value of 1·0 for the N_2 formation in the 185 nm photolysis of N_2O.[9] Since conversions were kept very low (between about 0·03 and 0·1%) the products found (Table 1) are all primary ones, i.e. their quantum yields are all dose-independent. Error limits for the major products such as isobutene, methanol, t-butanol, t-butyl ethyl ether, t-butyl neopentyl ether, and di-t-

---

*Part II of the series: Strahlenchemie von Äthern
Part I is the ref. 6.

Table 1. 185 nm Photolysis Product Quantum Yields in Oxygen Free Liquid t-Butyl Methyl Ether at 15°C, Conversion < 0·1%

product	quantum yield
CH_3OH	0·40$_5$
 $CH_3-C(CH_3)_2-OH$	0·20$_0$
 $CH_2=C(CH_3)-CH_3$	0·17$_8$
 $CH_3-C(CH_3)_2-O-CH_2-C(CH_3)_2-CH_3$	0·14$_2$
 $CH_3-C(CH_3)_2-O-CH_2-CH_3$	0·13$_4$
 $CH_3-C(CH_3)_2-O-CH_2-CH_2-O-C(CH_3)_2-CH_3$	0·09$_7$
CH_4	0·05$_6$
 $CH_3-C(CH_3)_2-H$	0·04$_6$
 $CH_2=C(CH_3)-O-CH_3$	0·03$_0$
H_2	0·019$_5$
 $CH_3-C(CH_3)_2-CH_3$	0·01$_6$
CH_3-CH_3	0·015
CH_2O	0·01$_2$
 $CH_3-C(CH_3)_2-O-CH_2-CH_2-C(CH_3)_2-O-CH_3$	0·005
 $CH_3-C(CH_3)_2-C(CH_3)_2-CH_3$	0·004$_8$
 $CH_3-CH_2-C(CH_3)_2-O-CH_3$	0·002$_7$
 $CH_3-C(CH_3)_2-O-CH_2-C(CH_3)_2-O-CH_3$	0·002
 $H-C(CH_3)_2-O-CH_3$	0·001$_5$
 $CH_3-C(CH_3)_2-O-CH_2-O-CH_3$	0·001
 $CH_3-C(CH_3)_2-O-CH_2-O-C(CH_3)_2-CH_3$	0·001
 $CH_3-C(CH_3)_2-CH_2-C(CH_3)_2-O-CH_3$	0·001
 $CH_3-C(CH_3)_2-C(CH_3)_2-O-CH_3$	0·0003
 $CH_3-O-C(CH_3)_2-CH_2-CH_2-C(CH_3)_2-OCH_3$	0·0002
 $CH_3-C(CH_3)_2-O-C(CH_3)_2-CH_3$	0·00005
	≤ 0·001
$CH_3-CO-CH_3$	0(< 0·0005)
	0(< 0·0001)
	0(< 0·0001)

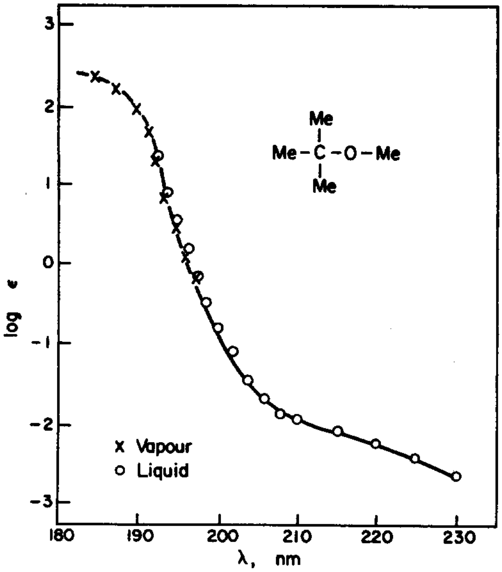


Fig 1. The Molar Extinction Coefficient of t-Butyl Methyl Ether in the Range 185 < λ < 230 nm

butoxy-ethane are *ca* ± 5%. The uncertainties associated with the quantum yields of the minor products in the order of magnitude range from 10^{-3} on down are greater, a realistic estimate being closer to ± 50%. The quantum yield of ether disappearance is 1·12 as calculated from the products, whereas for all primary processes a quantum yield of 0·66 has been estimated from the decomposition scheme given below. The material balance works out to $C_5H_{11\cdot97}O_{1\cdot018}$. Some runs were carried out with deuterated ether ($t{-}C_4H_9{-}O{-}CD_3$). Table 2 shows the deuterium distribution in the hydrogen, methane, and ethane produced. Some pronounced isotope effects are apparent. Whereas ϕ(ethane)/ϕ(methane) decreases slightly from about 0·27 to about 0·20–0·22, ϕ(hydrogen)/ϕ(methane) diminishes to about 1/6 of the value found in the undeuterated photolysis. Similarly, the dehydrodimer quantum yield ratios are strongly affected by deuteration (Table 3).

Table 2. Deuterium Distributions from the 185 nm Photolysis of t-Butyl Methyl-d_3 Ether (in %)

	Ethane		Methane		Hydrogen*	
	run 1	run 2	run 1	run 2	run 1	run 2
d_0		5	40	41		
d_1					40	50
d_2			5		60	50
d_3	26	24	52	55		
d_4			3	4		
d_5	4	4				
d_6	70	67				

*Values somewhat uncertain

Table 3. Dimer Quantum Yield Ratios [R = t-butoxymethyl, r = (2-methoxyisopropyl) methyl]

	Ether-d_0	Ether-d_3
ϕ_{R-r}/ϕ_{R-R}	0·05	0·15
ϕ_{r-r}/ϕ_{R-r}	0·04	0·16

The energized (185 nm ≙ 155 kcal/mol) t-BuOMe molecule can undergo fragmentation in different ways. Multiple fragmentation leading to three or more particles being very unlikely the molecule will break up into either two radicals (reactions 1–5) or two molecules (reactions 6–8).

$$\text{t-BuOMe} \xrightarrow{h\nu} \text{t-Bu}^{\cdot} + {}^{\cdot}OCH_3 \quad (1)$$
$$\text{t-BuOMe} \xrightarrow{h\nu} \text{t-BuO}^{\cdot} + {}^{\cdot}CH_3 \quad (2)$$
$$\text{t-BuOMe} \xrightarrow{h\nu} (CH_3)_2\dot{C}{-}OMe + {}^{\cdot}CH_3 \quad (3)$$
$$\text{t-BuOMe} \xrightarrow{h\nu} \text{t-BuO}{-}\dot{C}H_2 + H^{\cdot} \quad (4)$$
$$\text{t-BuOMe} \xrightarrow{h\nu} {}^{\cdot}CH_2{-}C(CH_3)_2{-}OMe + H^{\cdot} \quad (5)$$
$$\text{t-BuOMe} \xrightarrow{h\nu} \text{i-}C_4H_8 + MeOH \quad (6)$$
$$\text{t-BuOMe} \xrightarrow{h\nu} \text{i-}C_4H_{10} + CH_2O \quad (7)$$
$$\text{t-BuOMe} \xrightarrow{h\nu} CH_2{=}C(CH_3){-}OMe + CH_4 \quad (8)$$
$$\text{t-BuOMe} \xrightarrow{h\nu} \text{t-BuO}{-}\underline{C}H + H_2 \quad (9)$$
$$\text{t-BuOMe} \xrightarrow{h\nu} \underline{C}H{-}C(CH_3)_2{-}OMe + H_2 \quad (10)$$
$$\text{t-BuOMe} \xrightarrow{h\nu} \text{i-PrOMe} + \underline{C}H_2 \quad (11)$$
$$\text{t-BuOMe} \xrightarrow{h\nu} \text{t-BuOH} + \underline{C}H_2 \quad (12)$$

All the products which have been found can be rationalized in terms of these primary processes, there being evidence (see below) against carbene formation (reactions 9–12). It also becomes clear from the product list that several conceivable molecular eliminations do not take place, such as cyclisation reactions accompanied by the elimination of molecular hydrogen or methane. It remains to be seen whether such reactions are disfavoured with t-BuOMe since here they must lead to 3- and 4-membered rings, or whether they are unlikely with ethers in general. In fact tetrahydrofuran has not been detected as a product in the diethyl ether photolysis.

The fragment radicals produced interact with the substrate as well as with each other. By H abstractions (reactions 13–15) mainly the t-butoxymethyl radical (subsequently called R) is generated. Its isomer, 2-methoxy-isobutyl (r), plays a minor role. When the OMe group is deuterated abstraction becomes more difficult, and therefore the isomer radical concentration is enhanced with respect to that of t-butoxymethyl (Table 3). OMe, t-BuO and the H atom are highly reactive radicals so that their stationary concentration in this system is low and their involvement in radical-radical reactions is slight as is demonstrated by the low yield of products such as formaldehyde t-butyl methyl and di-t-butyl acetals ($\phi = 10^{-3}$, Table 1). The reactivity of the Me radical is lower, its activation energies for

H abstraction on the average being about 3 kcal/mol higher than the corresponding ones of the OMe radical[12]. Hydrogen abstraction does still occur as the results of the deuterated ether experiments show, but a variety of Me radical reaction products is formed as well, e.g. ethane, t-butyl ethyl ether, and neopentane (reactions 17–21). t-Butyl and 2-methoxyisopropyl are not expected to abstract from t-BuOMe, and will mainly undergo combination and disproportionation reactions (e.g. reactions 22–28). The following radical processes determine the features of the material balance ($R = \text{t-BuO—CH}_2$):

$$\text{t-BuOMe} + \mathrm{CH_3O^{\cdot}} \longrightarrow {}^{\cdot}\mathrm{R} + \mathrm{CH_3OH} \tag{13}$$
$$\text{t-BuOMe} + \text{t-BuO}^{\cdot} \longrightarrow {}^{\cdot}\mathrm{R} + \text{t-BuOH} \tag{14}$$
$$\text{t-BuOMe} + \mathrm{H^{\cdot}} \longrightarrow {}^{\cdot}\mathrm{R} + \mathrm{H_2} \tag{15}$$
$$\text{t-BuOMe} + {}^{\cdot}\mathrm{CH_3} \longrightarrow {}^{\cdot}\mathrm{R} + \mathrm{CH_4} \tag{16}$$
$${}^{\cdot}\mathrm{CH_3} + {}^{\cdot}\mathrm{CH_3} \longrightarrow \mathrm{C_2H_6} \tag{17}$$
$${}^{\cdot}\mathrm{CH_3} + {}^{\cdot}\mathrm{R} \longrightarrow \text{t-BuOEt} \tag{18}$$
$${}^{\cdot}\mathrm{CH_3} + \text{t-Bu}^{\cdot} \longrightarrow \text{neo-}\mathrm{C_5H_{12}} \tag{19}$$
$$\longrightarrow \mathrm{CH_4} + \text{i-}\mathrm{C_4H_8} \tag{20}$$
$${}^{\cdot}\mathrm{CH_3} + \mathrm{(CH_3)_2C^{\cdot}}\text{—OMe} \longrightarrow \mathrm{CH_4} + \mathrm{CH_2{=}C(CH_3)}\text{—OMe} \tag{21}$$
$$\text{t-Bu}^{\cdot} + \mathrm{R^{\cdot}} \longrightarrow \text{t-BuO-neo-}\mathrm{C_5H_{11}} \tag{22}$$
$$\longrightarrow \text{t-BuOMe} + \text{i-}\mathrm{C_4H_8} \tag{23}$$
$$\text{t-Bu}^{\cdot} + \text{t-Bu}^{\cdot} \longrightarrow (\text{t-Bu})_2 \tag{24}$$
$$\longrightarrow \text{i-}\mathrm{C_4H_8} + \text{i-}\mathrm{C_4H_{10}} \tag{25}$$
$$\mathrm{(CH_3)_2C^{\cdot}}\text{—OMe} + \mathrm{R^{\cdot}} \longrightarrow \mathrm{CH_2{=}C(CH_3)}\text{—OMe} + \text{t-BuOMe} \tag{26}$$
$$\mathrm{(CH_3)_2\dot{C}}\text{—OMe} + \text{t-Bu}^{\cdot} \longrightarrow \mathrm{CH_2{=}C(CH_3)}\text{—OMe} + \text{i-}\mathrm{C_4H_{10}} \tag{27}$$
$$\longrightarrow \text{i-PrOMe} + \text{i-}\mathrm{C_4H_8} \tag{28}$$
$$\mathrm{R^{\cdot}} + \mathrm{R^{\cdot}} \longrightarrow \mathrm{R_2} \tag{29}$$

Other radical-radical combination reactions occur, accounting for several of the minor products listed in Table 1.

In the UV photolysis of hydrocarbons carbene formation is quite often observed. Reactions 11 or 12, however, can occur only to a quite unimportant extent in this system. Treating t-BuOMe with diazomethane in the presence of CuCl leads to the methylene insertion products t-amyl methyl ether and t-butyl ethyl ether in the ratio of about 2 : 1.[13] Thus even if most of the t-amyl methyl ether found in the present system arose in this way the quantum yield of reaction 12 could not exceed about 0·003. Thermal fragmentation of the t-BuO$^{\cdot}$ radical ($E = 16{\cdot}5$ kcal/mol, $\log A = 13{\cdot}5$[14], reaction 30) proves to be unimportant in this system as no acetone has been found. Similarly, reaction 31 cannot occur since its activation energy is expected to be about 20 kcal/mol.[15,16]

$$\text{t-BuO}^{\cdot} \longrightarrow \mathrm{CH_3COCH_3} + {}^{\cdot}\mathrm{CH_3} \tag{30}$$
$$\mathrm{R^{\cdot}} \longrightarrow \text{t-Bu}^{\cdot} + \mathrm{OCH_2} \tag{31}$$

Given the product quantum yields of the undeuterated t-BuOMe photolysis, as well as the results obtained with the deuterated compound conclusions see below) it is possible to estimate the relative importance of the different primary decomposition paths if use is made of disproportionation/combination ratios[12] of pairs of radicals playing a role in the present system. With $k_{25}/k_{24} = 7{\cdot}4$[12] one can calculate the isobutane yield corresponding to the hexamethylethane yield. Allowing for a small contribution from reaction 27 the remaining isobutane must have come from the molecular decomposition reaction 7, in fair agreement with the formaldehyde yield. Assuming the ratio k_{23}/k_{22} equal to that of $\mathrm{C_2H_5}$/t-Bu (= 0·53[12]), and $k_{20}/k_{19} = 0{\cdot}85$,[12] one can on the basis of the t-BuO-neo-$\mathrm{C_5H_{11}}$ and neopentane yields estimate the isobutene yield of reactions 23 and 20. Reaction 25 yields as much isobutene as isobutane. The remaining isobutene is expected to derive from the molecular split (reaction 6) where methanol is the other product Substracting this from the methanol total the yield of the homolytic scission 1 is obtained, essentially all methoxy radicals being converted into methanol through H abstraction.

The sequence of the reactions 2 and 14 leads to the formation of t-butanol. Since reaction 12 has been shown not to occur and coupling products of the t-BuO radical are of minor importance the yield of t-butanol represents the yield of the primary reaction 2. The C—C bond scission mainly represented by the products isopropenyl methyl ether and i-PrOMe is of minor importance. An estimate similar to that above shows that the major part of the C—C bond split reactions is due to the elimination of molecular methane (reaction 8), a conclusion which is confirmed by the results of the deuterated t-BuOMe photolysis as discussed below. Regarding hydrogen it is expected that the major contribution comes from the homolytic scission of the OMe group C—H bond (reaction 4). This is borne out by the fact that in the OMe-deuterated photolysis no $\mathrm{H_2}$ has been found. However, the hydrogen results are not sufficiently reliable to strictly exclude a small contribution from reaction 5.

The deuterium distribution in the products ethane, methane, and hydrogen resulting from the photolysis of t-$\mathrm{C_4H_9}$—O—$\mathrm{CD_3}$ was determined. From the material balance considerations it was concluded that in the undeuterated ether the Me—O bond is homolytically broken with a quantum yield of $\phi_2 = 0{\cdot}2$, as against a value for ϕ_3 of about 0·008 for the Me—C bond, leading to a ratio for ϕ_3/ϕ_2 of about 0·04. The ethane results from the photolysis of the deuterated ether yield a ratio of $\phi_3/\phi_2 = 0{\cdot}16$, indicating that in the deuterated ether the scission of the O—$\mathrm{CD_3}$ bond is disfavoured with respect to the scission of the O—Me bond in the undeuterated one. An even more pronounced isotopic effect appears to operate in the hydrogen formation, whose quantum yield in the deuterated ether is reduced to about 1/6 of that with the undeuterated ether.

Making the reasonable assumption (*cf* 17) that $^{\cdot}CH_3$ and $^{\cdot}CD_3$ abstract hydrogen equally well, and taking ϕ_3/ϕ_2 as obtained via the deuterated ethane yields one may draw some conclusions regarding the methane formation, as follows.

Methane can be formed by five different routes (reactions a–e).

$$\begin{array}{rl} \text{t-BuOCD}_3 & \xrightarrow{a} CH_4 + CH_2{=}C(CH_3){-}OCD_3 \\ \text{t-BuOCD}_3 + {}^{\cdot}CH_3 & \xrightarrow{b} CH_4 + r \\ & \xrightarrow{c} CH_3D + R \\ \text{t-BuOCD}_3 + {}^{\cdot}CD_3 & \xrightarrow{d} CD_3H + r \\ & \xrightarrow{e} CD_4 + R \end{array}$$

Thus $v_b/v_c = v_d/v_e$ and $v_b + v_c = 0{\cdot}16(v_d + v_e)$, i.e. $v_c \doteq 0{\cdot}16 \cdot v_e$. This is in agreement with the experiment in so far that whereas a small amount of CD_4 was found (3–4%) no CH_3D was detected, i.e. the amount of CH_3D could at best have been marginal, v_{CH_3D}/v_{CD_4} equalling 0·16.

Furthermore, $v_c/v_e = 0{\cdot}16 = v_b/v_d$. Experiment gives $v_d(= v_{CD_3H})$, corresponding to 55%. Thus $v_b(= v_{CH_4,\text{radical}})$ corresponds to 9%. Since the sum $v_a + v_b$ $(= v_{CH_4})$ corresponds to 40%, it follows that v_a $(= v_{CH_4,\text{molecular}})$ corresponds to 31%, and the homolytic to molecular C—C bond split ratio equals 9/31 = 0·29. For the non-deuterated ether ϕ_3 has been estimated* at about 0·008, ϕ_8 being about 0·026†. Their ratio is 0·31, in fair agreement with the value of 0·29. While it must be borne in mind that the unusually large isotope effect on the split yielding t-butoxy and methyl may well mean that other bonds will be affected too, though mostly to a much lesser extent, this agreement can be taken as an indication that methoxy deuterium substitution affects the C—C bond split but little.

A large isotope effect on hydrogen formation is, of course, to be expected. By deuterating the OMe group the hydrogen quantum yield is reduced to about 1/6 of its value in the undeuterated ether. This and the fact that no H_2 has been detected, indicates that the OMe hydrogens are mainly involved. These results also exclude t-BuOMe $\xrightarrow{h\nu} H_2 + \underline{C}H{-}C(CH_3)_2{-}OMe$ (10), and the sequence t-BuOMe $\xrightarrow{h\nu} {}^{\cdot}H + {}^{\cdot}r$ (5), $H^{\cdot} + \text{t-BuOMe} \xrightarrow{h\nu} H_2 + {}^{\cdot}r$ (15a).

The high yield of HD shows that the analogous reaction (15a) occurs with $D^{\cdot}$ atoms. The molecular process (32) cannot be entirely excluded:

$$\text{t-BuOCD}_2{-}\boxed{DH}{-}CH_2{-}C(CH_3)_2{-}OCD_3 \xrightarrow{h\nu} HD + Rr \quad (32).$$

An intermolecular hydrogen elimination process has been observed in 185 nm photolysis of t-butanol.[5, 18] It must be concluded however that the hydrogen mainly comes from the methoxy group (via reaction (4), and possibly to a quite small extent reaction (9)).

In this manner a scheme of the primary reactions emerges as shown in Fig 2. It is evident that by far the major process (82%) is the homolytic scission of the C—O bond, the split into $t\text{-}Bu^{\cdot}$ and $MeO^{\cdot}$ being favoured over that leading to $t\text{-}BuO^{\cdot}$ and Me. Molecular processes (including cage reactions[6]) involving the C—O bond amount to about 10·5%. The process giving isobutene and methanol, exclusively followed in the thermal decomposition, contributes only 8·5% in the 185 nm photolysis. Even less important is the split into isobutane and formaldehyde (2%).

As stated above t-BuOH is exceptional among a series of alcohols in that it decomposes, on UV excitation, largely through scission of the C—C bond,[5] rather than the O—H bond. An analogous behaviour in case of t-BuOMe has not been found. The C—C link is broken with a probability of 4·5% only, insignificantly larger than the 0·5% found in the UV photolysis of diethyl ether[6]. With t-BuOMe the elimination of molecular methane appears to be the major process by which the C—C bond is cleaved. The low yield of H_2(3%) reflects the fact that molecular elimination processes involving the formation of a double bond, as is possible with diethyl ether (H_2-formation 10%), cannot occur in t-BuOMe.

EXPERIMENTAL

t-BuOMe was synthesized from isobutene and methanol in the autoclave.[19] High purity of the product after the usual work-up was achieved by treating it with a trace of O_3 at −50°. After a few min the O_3 was driven off by scrubbing with argon, and the ether was passed through a column filled with activated basic aluminia (Woelm). This procedure resulted in the removal of the t-BuOH, MeOH, and isobutene which are the main impurities, down to amounts of less than 0·1 ppm (for comparison, photolytic conversions ranged from *ca* 0·03% to *ca* 0·1%, after 15 min). The ether so purified was stored in a Hg-free high-vacuum line and photolized in the manner described pre-

---

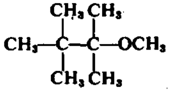
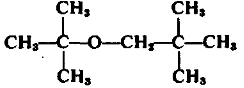
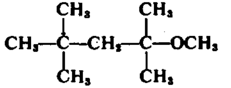
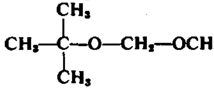
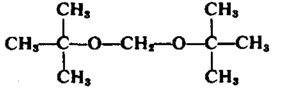
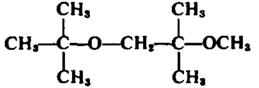
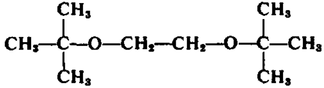
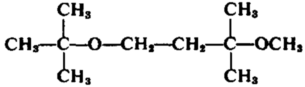
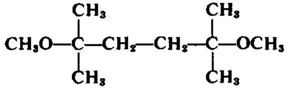
*This split leads to the radical $(CH_3)_2\dot{C}{-}OMe$ which reacts in the following ways:

$$\begin{array}{rlll} (CH_3)_2\dot{C}{-}OMe + t\text{-}Bu^{\cdot} & \longrightarrow CH_2{=}C(CH_3){-}OMe & & \\ & & \phi = 0{\cdot}0015 & (27) \\ & \longrightarrow \text{i-Pr OMe} & \phi = 0{\cdot}0015 & (28) \\ & \longrightarrow \text{comb.} & \phi = 0{\cdot}0003 & (28a) \\ + \text{t-BuO}{-}\dot{C}H_2 & \longrightarrow CH_2{=}C(CH_3){-}OMe & & \\ & & \phi = 0{\cdot}002 & (26) \\ & \longrightarrow \text{comb.} & \phi = 0{\cdot}002 & (26a) \\ + {}^{\cdot}CH_3 & \longrightarrow CH_2{=}C(CH_3){-}OMe & & \\ & & \phi = 0{\cdot}0003 & (21) \\ & \longrightarrow \text{comb.} & \phi = 0{\cdot}0003 & (21a) \end{array}$$

$k_{27} = k_{28}$ and $k_{26} = k_{26a}$ are assumed. Also $[CH_3]/[\text{t-BuO-}CH_2]$ has been estimated at about 0·1 to 0·15, and $k_{26} = k_{21}$ has been assumed.

†$\phi[CH_4, \text{ molecular}] = \phi[CH_2 = C(CH_3){-}OMe] - \phi[CH_2 = C(CH_3){-}OMe, \text{ radical}]$; $\phi[CH_2 = C(CH_3){-}OMe, \text{ radical}] = \phi[27 + 26 + 21] \approx 0{\cdot}004$, $\phi[CH_2 = C(CH_3){-}OMe] \approx 0{\cdot}030$.

Table 4. Relative Retention Times of Products and of Some Similar Compounds. Sources of Reference Compounds

Compound	Relative retention time			Source^{a}
Hydrogen	2·5^{b}			
Methane	3·8^{c}	0·02^{d}	0·04^{e}	L'Air liquide
Ethane	18·6^{c}	0·08^{d}	0·12^{e}	L'Air liquide
Iso-butene	0·11^{f}	1·00^{d}	1·00^{e}	Chem. Werke Hüls
Iso-butane	0·07^{f}	0·84^{d}	0·92^{e}	Phillips
Neopentane	0·11^{f}		2·04^{e}	Fluka
Hexamethylethane		1·97^{g}	3·51^{i}	20
Methanol		0·84^{d}	0·47^{e}	Merck
t-Butanol	3·14^{f}	1·46^{g}	0·73^{i}	Merck
Formaldehyde		0·25^{d}		Formalin 35%, Merck
Acetone	0·92^{f}		0·51^{i}	Merck
Isobutene oxide	1·09^{f}		0·85^{i}	Bayer
α,α-Dimethyloxetane	2·45^{f}			21
1-Methylcyclopropyl methyl ether	1·68^{f}			*k*
Dimethyl ether		0·52^{d}		Matheson
Isopropenyl methyl ether	0·65^{f}	0·51^{g}	0·67^{i}	22
Isopropyl methyl ether	0·46^{f}			23
t-Butyl methyl ether	1·00^{f}		1·00^{i}	19
t-Butyl ethyl ether	1·51^{f}	1·00^{g}	1·62^{i}	19
t-Amyl methyl ether		1·78^{g}		19
Di-t-butyl ether		2·27^{g}		24
 $CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}\overset{CH_3}{\underset{CH_3}{C}}{-}OCH_3$			1·29^{h}	19
 $CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}O{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3$	5·57^{f}	2·81^{g}	1·00^{h}	19
 $CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}OCH_3$			2·64^{h}	19
 $CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}O{-}CH_2{-}OCH_3$		3·36^{i}	1·00^{h}	25
 $CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}O{-}CH_2{-}O{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3$			2·71^{h}	25
 $CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}O{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}OCH_3$			4·39^{h}	*l*
 $CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}O{-}CH_2{-}CH_2{-}O{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3$			5·45^{h}	19
 $CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}O{-}CH_2{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}OCH_3$			7·86^{h}	*l*
 $CH_3O{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_2{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}OCH_3$			14·15^{h}	19

[a] Numbers refer to bibliography. [b] Elution time, in min. Column: active coal, 4 m, 5 mm I.D., 23°, 38 ml Ar/min. [c] Elution time, in min. Column: active coal, 2 m, 5 mm I.D., 60°, 25 ml He/min. [d] Column: Porapak N, 2 m, 2·2 mm I.D., 100°, 47 ml He/min. [e] Column: Porapak Q, 1·5 m, 2·2 mm I.D., 100°, 47 ml He/min. [f] Capillary column: Perkin Elmer 7G3 (100 m s.s., 0·5 mm I.D., propylene glycol), room temp, *ca* 2 ml He/min. [g] 65°; otherwise as under *f*. [h] 110°; otherwise as under *f*. [i] Capillary column: OV 101 (dimethyl silicone oil), 100 m glass, 0·25 mm I.D., 70°, *ca* 1 ml Ar/min. [k] A sample of α-methylcyclopropyl methyl ether, prepared from isopropenyl methyl ether and diazomethane in the presence of CuCl, was provided by Mr. G. Dielmann and Dr. G. Schomburg of this institute. [l] A mixture (*ca* 3 : 1) of t-BuOMe and di-t-butyl peroxide was photolysed with 254 nm light and the products separated gas-chromatographically.

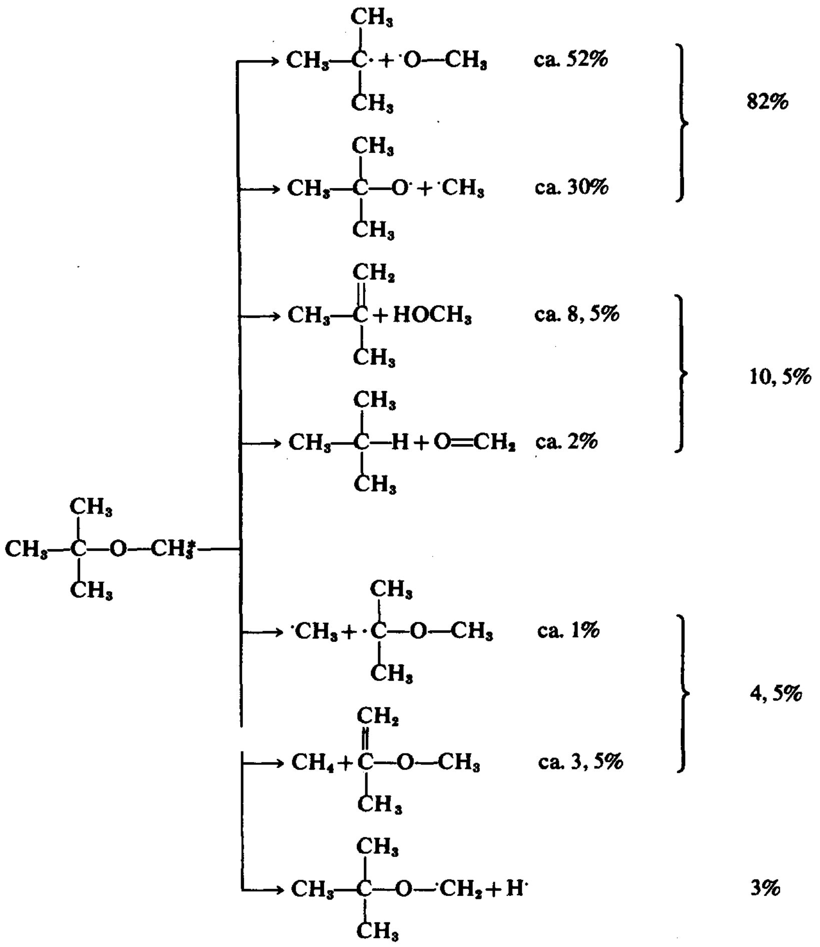


Fig 2. 185 nm photolysis of liquid t-butyl methyl ether Φ(primary processes) = 0·66

viously.[6] The flux of 185 nm quanta was 1·4 · 10^{18} min^{-1}, as determined by the ethanol actinometer.[8–11] The products identified by means of VPC and MS, were quantitatively analysed by VPC, using a Perkin Elmer 900 instrument equipped with both FID and TCD, and a Perkin Elmer F20 instrument equipped with an FID. 5 μl samples were injected to measure all products except the gaseous and very volatile ones such as the hydrocarbons up to neopentane, and formaldehyde. To measure these the contents of the cell were transferred into an evacuated 2 l bulb. Aliquot parts of the vapour, about 2 ml, were introduced into the gas chromatograph from the bulb which was thermostatted at 60°. Hydrogen, methane, and ethane were further determined in another way also described previously.[6] Details on the gas-chromatographic columns and conditions employed are found in Table 4 where elution times of some relevant compounds are listed. Also indicated therein are the sources of the reference compounds.

The molar extinction coefficient ε of t-BuOMe was measured in the vapour phase using a Cary 17 and found to be ε (185 nm) = 220 l/mol · cm (Fig 1). A 1 cm quartz cell, kept at an ambient temp of 20°, was evacuated, and ether vapour was then admitted into the cell from a small bulb where pure ether was kept at 0°. Under these conditions the vapour pressure was 82 mm Hg, and the vapour concentration in the cell was 4·4 · 10^{-3} mol/l. t-BuOMe absorbs so strongly in the frequency region of interest that the extinction of a 0·01 cm liquid layer is too high, making a quantitative determination of ε from the liquid phase impossible. The extinction coefficient of the liquid has been determined at higher wavelengths (230 to 192 nm, Fig 1), using SUPRASIL (HELLMA) quartz cells of 1 cm, 0·1 cm, and 0·01 cm widths (In a similar manner the extinction coefficient of diethyl ether has been redetermined as a function of the wavelength, and we report here that the value for ε given in Part I[6] of this series is probably in error and much nearer to the gas phase value of $\approx$ 1·5 . 10^4 l mol^{-1} cm^{-1}. This error, however, does not affect our conclusions as to the mechanism of the liquid diethyl ether photolysis).

Deuterated t-BuOMe ($C_4H_9OCD_3$) was synthezised from MeOH-d_3 by the same method.[17] After photolysis hydrogen, methane, and ethane were drawn off into a bulb and toeplered through a trap kept at − 160° so that the collected volatiles were free of isobutene and ether. Mass spectrometry of the mixture was done on a CEC MS 103 instrument.

Acknowledgement—We are grateful to Dr. D. Henneberg and Mr. H. Damen for their valuable help with the preparation and interpretation of the mass spectra. Special thanks are due to Dr. G. Schomburg who has generously supported the gas-chromatographic side of the present work, and to the staff of the gas chromatography analytical lab.

REFERENCES

[1] C. v. Sonntag, *Tetrahedron* **25**, 5853 (1969)

[2] C. v. Sonntag, *Z. phys. Chem.*, N.F., **69**, 292 (1970)

[3] C. v. Sonntag, *Z. Naturforsch.* **27b**, 42 (1972)

[4] H. J. van der Linde and C. v. Sonntag, *Photochem. Photobiol.* **13**, 147 (1971).

[5] D. Sänger and C. v. Sonntag, *Tetrahedron* **26**, 5489 (1970)

[6] C. v. Sonntag, H.-P. Schuchmann, and G. Schomburg, *Ibid.* **28**, 4333 (1972)

[7] N. J. Daly and C. Wentrup, *Aust. J. Chem.* **21**, 2711 (1968)

[8] L. Farkas and Y. Hirshberg, *J. Am. Chem. Soc.* **59**, 2450 (1937)

[9] F. S. Dainton and P. Fowles, *Proc. Roy. Soc.* **287A**, 295 (1965)

[10] U. Sokolov and G. Stein, *J. Chem. Phys.* **44**, 2189, 3329 (1966)

[11] N. Getoff and G. O. Schenck, *Photochem. Photobiol.* **8**, 167 (1968).

[12] A. F. Trotmann-Dickenson and G. S. Milne, NSRDS-NBS 9, U.S. Dept. of Commerce, Washington, D.C., (1967)

[13] G. Schomburg, private communication (1972)

[14] S. W. Benson and H. E. O'Neal, NSRDS-NBS 21, U.S. Dept. of Commerce, Washington, D.C., (1970)

[15] L. F. Loucks and K. J. Laidler, *Canad. J. Chem.* **45**, 2767 (1967)

[16] J. A. Kerr, *Chem. Rev.* **66**, 465 (1966)

[17] P. Gray and A. A. Herod, *Trans. Faraday Soc.* **64**, 1568 (1968)

[18] D. Sänger and C. v. Sonntag, *Z. Naturforsch.*, **25b**, 1491 (1970)

[19] T. W. Evans and K. R. Edlund, *Ind. Eng. Chem.* **28**, 1186 (1936)

[20] D. T. Flood and G. Calingaert. *J. Am. Chem. Soc.* **56**, 1211 (1934)

[21] G. M. Bennett and W. G. Philip, *J. Chem. Soc.* 1938 (1928)

[22] L. Claisen, *Ber. Dtsch. Chem. Ges.* **31**, 1019 (1898)

[23] J. F. Norris and G. W. Rigby, *J. Am. Chem. Soc.* **54**, 2088 (1932)

[24] J. L. E. Erickson and W. H. Ashton, *Ibid.* **63**, 1179 (1941)

[25] G. Parc, M. Davidson, M. Hellin, and F. Coussemant, *Bull. Soc. Chim., Fr*, 1325 (1964)