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THE UV PHOTOLYSIS ($\lambda = 185$ nm) OF LIQUID Di-t-BUTYL ETHER[a]

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Abstract—In the 185 nm photolysis of di-t-butyl ether the following primary products (quantum yields) have been found: isobutene (0·87), t-butanol (0·84), acetone (0·07), isobutane (0·06), the dehydrodimer 2,5-di-t-butoxy-2,5-dimethylhexane (0·04$_5$), methane (0·04), 2-t-butoxy-2,4,4-trimethylpentane (0·03$_1$), t-amyl-t-butyl ether (0·01$_5$), neopentane (0·01), hexamethylethane (0·01), t-butyl isopropenyl ether (0·01), 1,2-di-t-butoxy-2-methylpropane (0·009), isobutene oxide (0·008), hydrogen (0·005), ethane (0·0008), 2,4-di-t-butoxy-2,4-dimethylpentane (0·0005), and t-butyl isopropyl ether (0·0004). The product material balance is $C_8H_{17\cdot90}O_{0\cdot975}$. Conversions did not exceed 0·4%.

Most easily cleaved is the C—O bond, predominantly following the molecular route (72% of the total, including cage disproportionation) to t-butanol and isobutene; the homolytic split into t-BuO$^{\cdot}$ and t-Bu$^{\cdot}$ amounts to a further 19%. The C—C bond rupture is of lesser importance (7%), while the C—H bond is the least affected (0·5%). Acetone is considered to derive from the sequence

$$Me_3C{-}O{-}CMe_3 \xrightarrow[-^{\cdot}Me]{h\nu} Me_3C{-}O{-}C^{\cdot}Me_2 \xrightarrow[-t\text{-}Bu^{\cdot}]{} Me_2CO$$

There is some decomposition of di-t-butyl ether by 254 nm radiation into t-BuOH and isobutene in a reaction entirely molecular, amounting to about 2% of the total decomposition.

INTRODUCTION

Aliphatic ethers are transparent in the near UV. Absorption increases rapidly as wavelength decreases below 200 nm, and the first absorption bands, due to n-σ^* transitions, show maxima in the vicinity of 185 nm.[1] It has been demonstrated that liquid-phase photolysis at 185 nm of diethyl and t-butyl methyl ethers largely occurs by means of a homolytic split of the C—O bond.[2,3] Di-t-butyl ether differs from these ethers in that its molecule is considerably strained and thus remarkably unstable thermally as well as towards hydrolysis.[4] It is conceivable that some strain may also persist in the excited state and lead to an interesting difference in its photolytic behaviour. A further contrast to the two ethers already investigated lies in the fact that di-t-butyl ether has no C—H bonds α to the O atom. If spatial proximity to this photochemical "center of action" implies a comparatively high probability of involvement in the subsequent primary reactions, then di-t-butyl ether should show a rather small hydrogen quantum yield.

RESULTS AND DISCUSSION

Those photolysis products which have been identified are listed in Table 1, the major products being uncertain to about ± 5%. Five minor products with quantum yields estimated at about 10^{-3} or less were not identified. A material balance of $C_8H_{17\cdot90}O_{0\cdot975}$ was obtained. The relative importance of the primary photolytic steps (Fig 1) was determined from the product quantum yields (Table 1) as summarized in Table 2 which represents a detailed balance for key products and the radical species. For instance, t-Bu arises (see mechanism) in steps 2 and 10, and is consumed in steps 12, 13, and 15 to 20. The quantum yields of all steps except step 2 are known from product quantum yields, and from disproportionation/combination ratios. In the case of t-BuOH, the total quantum yield is the sum of those of steps 1, 7, and 17. The latter are unknown except for that of step 17. In this manner a system of several equations is obtained with 4 unknowns which is fulfilled if the unknowns are given the values $w \approx 0\cdot70$, $x \approx 0\cdot16$, $y \approx 0\cdot02$, and $z \approx 0\cdot19$, as can be verified from the table. Owing to the fact that in this system the number of equations exceeds the number of the unknowns the latter are not quite sharply determined. This leads to an uncertainty margin regarding the primary processes.

$$t\text{-}BuO\text{-}t\text{-}Bu \xrightarrow{h\nu} i\text{-}C_4H_8 + t\text{-}BuOH \tag{1}$$

$$\xrightarrow{h\nu} t\text{-}Bu^{\cdot} + t\text{-}BuO^{\cdot} \tag{2}$$

$$\xrightarrow{h\nu} t\text{-}BuO\text{-}C^{\cdot}(CH_3)_2(r^{\cdot}) + {}^{\cdot}CH_3 \tag{3}$$

$$\xrightarrow{h\nu} t\text{-}BuO\text{-}i\text{-}C_3H_6 + CH_4 \tag{4}$$

$$\xrightarrow{h\nu} \text{isobutene oxide} + i\text{-}C_4H_{10} \tag{5}$$

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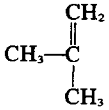
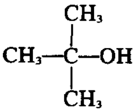
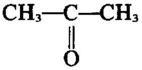
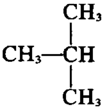
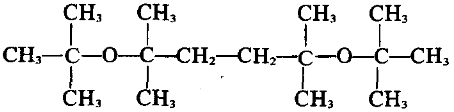
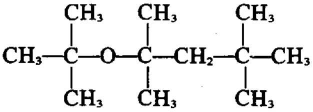
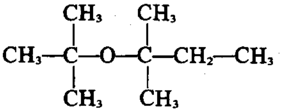
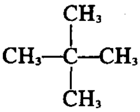
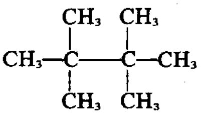
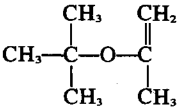
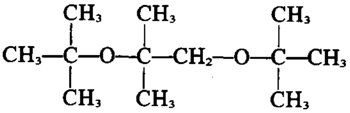
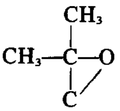
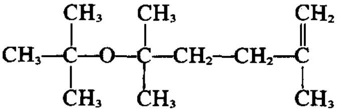
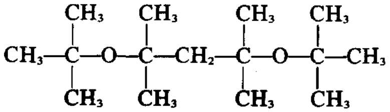
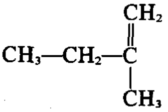
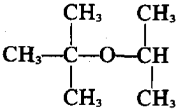
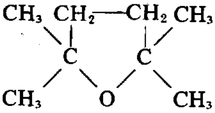
[a] Part III of the series: Strahlenchemie von Äthern. Part II is the Ref 3.

Table 1. 185 nm Photolysis product quantum yields in oxygen-free liquid di-t-butyl ether at 15°, conversion ≤0·4%

Product	Quantum yield
 $CH_3-C(=CH_2)-CH_3$	0·87
 $(CH_3)_3C-OH$	0·84
 $CH_3-C(=O)-CH_3$	0·07
 $CH_3-CH(CH_3)_2$	0·06
 $(CH_3)_3C-O-C(CH_3)_2-CH_2-CH_2-C(CH_3)_2-O-C(CH_3)_3$	0·04$_5$
CH_4	0·04
 $(CH_3)_3C-O-C(CH_3)_2-CH_2-C(CH_3)_3$	0·03$_1$
 $(CH_3)_3C-O-C(CH_3)_2-CH_2-CH_3$	0·01$_5$
 $C(CH_3)_4$	0·01
 $(CH_3)_3C-C(CH_3)_3$	0·01
 $(CH_3)_3C-O-C(=CH_2)-CH_3$	0·01
 $(CH_3)_3C-O-C(CH_3)_2-CH_2-O-C(CH_3)_3$	0·009
	0·008
H_2	0·005
 $(CH_3)_3C-O-C(CH_3)_2-CH_2-CH_2-C(=CH_2)-CH_3$	0·003*
CH_3-CH_3	0·0008
 $(CH_3)_3C-O-C(CH_3)_2-CH_2-C(CH_3)_2-O-C(CH_3)_3$	0·0005
 $CH_3-CH_2-C(=CH_2)-CH_3$	0·0005*
 $(CH_3)_3C-O-CH(CH_3)_2$	0·0004
	0(<0·0001)

*Secondary product; average quantum yield after 10 minutes, at a dose rate of 0·95×10^{18} quanta/min.

$\xrightarrow{h\nu}$ t-BuO-C$(CH_3)_2CH_2(R^{\cdot})+H^{\cdot}$ (6)

t-BuO$^{\cdot}$+t-BuO-t-Bu $\longrightarrow$ t-BuOH+R$^{\cdot}$ (7)

$^{\cdot}CH_3$+t-BuO-t-Bu $\longrightarrow$ $CH_4+{}^{\cdot}R$ (8)

H$^{\cdot}$+t-BuO-t-Bu $\longrightarrow$ $H_2+{}^{\cdot}R$ (9)

$^{\cdot}$r $\longrightarrow$ t-Bu$^{\cdot}$+acetone (10)

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

$^{\cdot}CH_3$+t-Bu$^{\cdot}$ $\longrightarrow$ CH_4+i-C_4H_8 (12)

$\longrightarrow$ neo-C_5H_{12} (13)

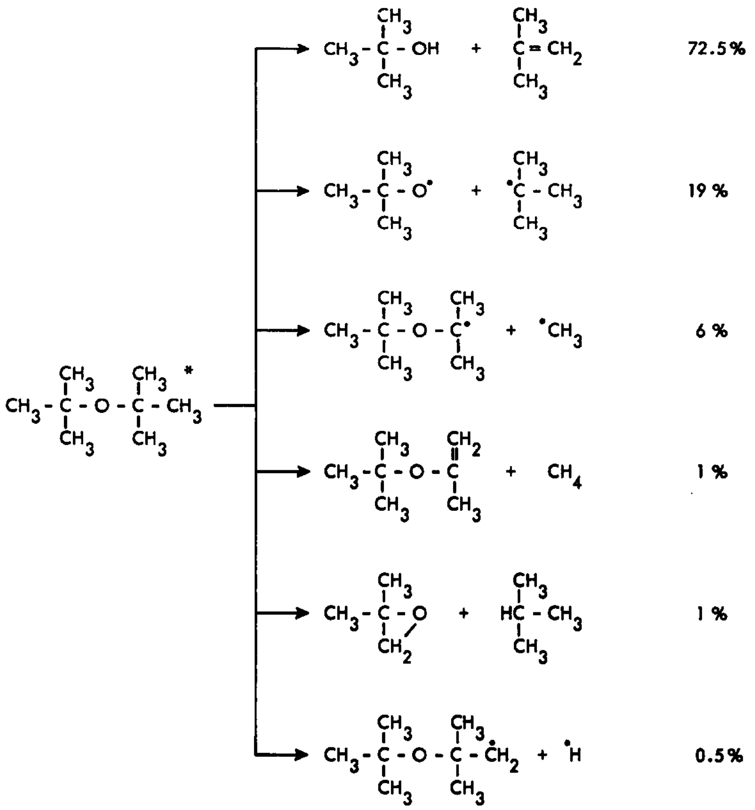


Fig. 1. 185 nm Photolysis of liquid di-t-butyl ether. Φ (primary processes) = 0·97.

$$^{\cdot}CH_3 + {}^{\cdot}R \longrightarrow CH_3\text{-}R \qquad (14)$$

$$2\,\text{t-Bu}^{\cdot} \longrightarrow \text{i-}C_4H_{10} + \text{i-}C_4H_8 \qquad (15)$$

$$\longrightarrow (\text{t-Bu})_2 \qquad (16)$$

$$\text{t-Bu}^{\cdot} + \text{t-BuO}^{\cdot} \longrightarrow \text{i-}C_4H_8 + \text{t-BuOH} \qquad (17)$$

$$\longrightarrow \text{t-BuO-t-Bu} \qquad (18)$$

$$\text{t-Bu}^{\cdot} + {}^{\cdot}R \longrightarrow \text{i-}C_4H_8 + \text{t-BuO-t-Bu} \qquad (19)$$

$$\longrightarrow \text{t-Bu-R} \qquad (20)$$

$$\text{t-BuO}^{\cdot} + {}^{\cdot}R \longrightarrow \text{t-BuO-R} \qquad (21)$$

$$r^{\cdot} + {}^{\cdot}R \longrightarrow r\text{-}R \qquad (22)$$

$$2R^{\cdot} \longrightarrow R\text{-}R \qquad (23)$$

Reaction 10 must be considered the major source of acetone because the rate constant of the t-BuO· fragmentation

$$\text{t-BuO}^{\cdot} \longrightarrow CH_3\text{—}CO\text{—}CH_3 + {}^{\cdot}CH_3 \qquad (24)$$

is much too small ($\log A_{24} = 13{\cdot}5$, $E_{24} = 16{\cdot}5$ kcal/mol.[6] If one assumes, for reaction 7, $\log A_7 = 11{\cdot}8$ and $E_7 = 7{\cdot}3$ kcal/mol which are the Arrhenius parameters quoted by Trotman–Dickenson[5] for the reaction CH_3O + neopentane ⟶ MeOH + neopentyl, then a ratio $v_7/v_{24} \approx 10^3$ is obtained. On the other hand, $v_7/v_{10} = \phi_7/\phi_{10} \approx 3$, therefore $(v_7/v_{24}) \times (v_{10}/v_7) \approx 300$. This is true if essentially all $Me_3C\text{—}O\text{—}CMe_2$ radicals are transformed into acetone (i.e. $v_3 = v_{10}$) which is very likely since their combination product with $Me_3C\text{—}O\text{—}CMe_2\text{—}CH_2$, 2,4-di-t-butoxy-2,4-dimethylpentane, is formed with a very small quantum yield (*ca* $0{\cdot}5 \times 10^{-3}$). It is noted that while the homologous radical $Me_3\text{—}C\text{—}O\text{—}{}^{\cdot}CH_2$ encountered in the photolysis of t-butyl methyl ether is not supposed to undergo fragmentation into t-butyl and formaldehyde, the radical $Me_3C\text{—}O\text{—}{}^{\cdot}CMe_2$ can be expected to decompose rather more readily owing to a higher strain energy content and greater stabilization of the newly-formed double bond in the acetone *vs* the formaldehyde molecule.* The apparent slight imbalance of isobutene as compared to the other products may indicate a small contribution to the primary decomposition from the process

$$\text{t-Bu-O-tBu} \longrightarrow 2C_4H_8 + H_2O \qquad (25)$$

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*Note added in proof.

Table 2. Mechanistic material balance of key species

Species	Source elementary eq. No.	step ϕ	Sink elementary eq. No.	step ϕ	ϕ (total found)
i-C_4H_8	1	w^a			0·87
	12	$0{\cdot}01^b$			
	15	$0{\cdot}07^c$			
	17	$0{\cdot}02^d$			
	19	$0{\cdot}03^e$			
t-BuOH	1	w^a			0·84
	7	x^a			
	17	$0{\cdot}02^d$			
acetone	10	0·07			0·07
i-C_4H_{10}	5	0·008			0·06
	15	$0{\cdot}07^c$			
CH_4	4	0·01			0·04
	8	y^a			
	12	$0{\cdot}01^b$			
neo-C_5H_{12}	13	0·01			0·01
C_2H_6	11	0·0008			0·0008
$CH_3^{\cdot}$	3	$0{\cdot}07^f$	8	y^a	
			11	0·0016	
			12	$0{\cdot}01^b$	
			13	0·01	
			14	0·015	
t-Bu˙	2	z^a	12	$0{\cdot}01^b$	
	10	0·07	13	0·01	
			15	$0{\cdot}14^c$	
			16	0·02	
			17	$0{\cdot}02^d$	
			18	$0{\cdot}003^g$	
			19	$0{\cdot}03^e$	
			20	0·03	
t-BuO˙	2	z^a	7	x^a	
			17	$0{\cdot}02^d$	
			21	0·009	
r^h	3	$0{\cdot}07^f$	10	0·07	
R^i	6	0·005	14	0·015	
	7	x^a	19	$0{\cdot}03^e$	
	8	y^a	20	0·03	
	9	0·005	21	0·009	
			23	0·09	

[a] Unknown elementary step quantum yield to be estimated; [b] $k_{12}/k_{13} \approx 1$; see Trotman-Dickenson,[5] [c] $k_{15}/k_{16} \approx 7$; see Trotman-Dickenson,[5] [d] from ϕ(1,2-di-t-butoxy-2-methylpropane)/ϕ(2-t-butoxy-2,4-dimethylpentane) ≈ 1/3 it is estimated that [t-BuO˙] ≈ 1/3 [t-Bu˙] assuming that t-BuO˙ behaves like t-Bu˙, [e] $k_{19}/k_{20} \approx 1$, in analogy to k_{12}/k_{13}, [f] essentially all radicals $(CH_3)_3C—O—\dot{C}(CH_3)_2$ are assumed to decompose into acetone and t-Bu˙, [g] assumed $k_{17}/k_{18} \equiv k_{15}/k_{16} \approx 7$, [h] $r = (CH_3)_3C—O—\dot{C}(CH_3)_2$; [i] $R = (CH_3)_3C—O—C(CH_3)_2—\dot{C}H_2$.

However, water could not be measured under the conditions of the present work.

As for the hydrogen quantum yield, it is believed that even allowing for an initial isobutene impurity of about 100 ppm together with the isobutene present after irradiation times of up to about 5 minutes the reaction

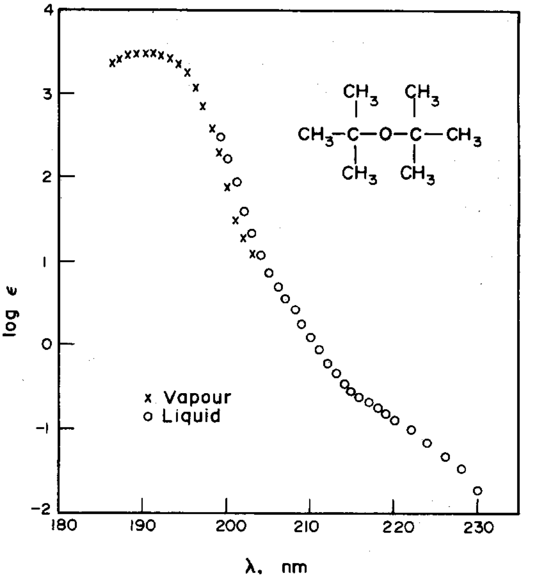

Fig 2. The molar extinction coefficient of di-ti-butyl ether in the range 186 ≤ λ ≤ 230 nm.

$$H + iso\text{-}C_4H_8 \longrightarrow t\text{-}Bu \qquad (26)$$

does not interfere with the process 9. According to Back,[7] for the processes n-C_5H_{12} + H ⟶ H_2 + n-C_5H_{11} (a), C_5H_{10} + H ⟶ C_5H_{11} (b), $k_a/k_b \geq 4{\cdot}5 \times 10^{-3}$ at room temperature. Using the same value for the present system, a rate ratio $v_9/v_{26} \approx 50$ results. This means that H atoms would not be lost to analysis.

A minor photodecomposition of the di-t-butyl ether occurs at 254 nm leading to t-butanol and isobutene. Up to about 2% of the t-butanol which is formed in the 185 nm photolysis was found when using a vycor filter. Under these conditions isobutane is found only in minute traces, its ratio to t-butanol being of the order of 10^{-3}, which means that at 254 nm the t-butanol arises through a molecular split exclusively. The quantum yields of t-butanol and isobutene given in Table 1 are corrected for this and represent the behaviour of the system at "pure" 185 nm irradiation.

CONCLUSIONS

The scheme of primary processes arrived at as indicated above is shown in Fig 1. The predominant feature is the facility of the C—O bond rupture. A C—C bond split is much less probable while a C—H bond split is less likely again by an order of magnitude. Thus, in its 185 nm photolysis, di-t-butyl ether in some ways contrasts remarkably with diethyl and t-butyl methyl ether, as can be seen from Table 3. The fact that there is a high probability of cleavage into isobutene and t-butanol makes it seem likely that the di-t-butyl ether molecule possesses strain energy also in its excited state. Smutny and Bondi[8] find a strain of 7·6 kcal/mol for the ground state. It must be noted, however, that the cage disproportionation reaction could not be distinguished from true molecular fragmentation in this work. Therefore the homolytic C—O bond cleavage may be more important than the results would suggest. The low hydrogen yield is in keeping with the hypothesis that hydrogen α to the oxygen atom is split off more easily than a H atom farther from it.

Table 3. Relative importance of 185 nm photolysis primary split modes in some ethers

Split mode	tBuOtBu $\phi = 0{\cdot}97$[a]	tBuOMe[3] $\phi = 0{\cdot}66$[a]	EtOEt[2] $\phi = 0{\cdot}6$[a]
C—O, molecular[b]	73·5%	10·5%	18·5%
C—O, homolytic	19%	82%	70%
C—C, total	7%	4·5%	0·5%
C—H, total	0·5%	3%	11%

[a] Total quantum yield of primary photoprocesses.
[b] Including cage disproportionation.

Table 4. Relative retention times of products and some other compounds of interest. Sources of reference compounds

Product	Relative retention time			Source
hydrogen	2·5[a]			
methane		0·45[b]		l'Air liquide
ethane		1·40[b]		l'Air liquide
isobutene	0·042[c]	19·9[b]	0·089[d]	Chem. Werke Hüls
isobutane	0·024[c]	0·039[e]	0·050[d]	Phillips
pentene[f]	0·12[c]	0·15[e]		*g*
neopentane			0·069[d]	Fluka
2,4-dimethylpentane	0·35[c]	0·37[e]		Fluka
hexamethylethane	0·82[c]	0·87[e]		*h*
t-butanol	0·69[c]	0·64[e]	2·2[d]	Merck
acetone	0·27[c]	0·30[e]		Merck
isobutene oxide	0·31[c]	0·35[e]		Bayer
t-butyl methyl ether[q]	0·28[c]	0·31[e]	0·49[d]	*i*
t-butyl isopropyl ether	0·56[c]	0·60[e]		*i*
t-butyl isopropenyl ether	0·90[c]	0·91[e]		*g*
di-t-butyl ether	1·0[c,d,e,j]			*k*
2,2,5,5-tetramethyltetrahydrofuran[q]		1·6[e]		*l*
t-amyl-t-butyl ether	2·5[c]	2·3[e]	2·2[j]	*m*
2-t-butoxy-2,4,4-trimethylpentane			7·9[j]	*g*
1,2-di-t-butoxy-2-methylpropane			8·4[j]	*g*
5-t-butoxy-2,5-dimethylhexene[f]			10[j]	*g*
2,3-di-t-butoxy-2,3-dimethylbutane[q]			21[j]	*n*
2,4-di-t-butoxy-2,4-dimethylpentane			24[j]	*o*
2,5-di-t-butoxy-2,5-dimethylhexane			53[j]	*p*

[a] Elution time, in min. Column: active coal, 4 m, 5 mm I. D., 23°, 38 ml Ar/min.
[b] Elution time, in min. Column: Porapak Q, 100–120 mesh, 1·2 m, 2·2 mm I. D., 65°, 20 ml He/min.
[c] Capillary column: Perkin Elmer 7 G3 (100 m s.s., 0·5 mm I. D., polypropylene glycol), 40°, *ca.* 2 ml He/min.
[d] Column combination: P 4000 (15%+KOH on celite, 60–100 mesh), 6 m, 2·2 mm I. D.; plus UCW-98 (5% on Chromosorb W, 60–80 mesh), 1 m, 2·2 mm I. D., 16 ml Ar/min.
[e] 65°; otherwise as under *c*.
[f] Secondary product.
[g] The product was tentatively identified by its mass spectrum.
[h] See Flood and Calingaert.[11]
[i] See Evans and Edlund.[12]
[j] 110°; otherwise as under *c*.
[k] See Erickson and Ashton.[9]
[l] 2,2,5,5-Tetramethyl-tetrahydrofuran was obtained by treating 2,5-dimethylhexanediol (2, 5) with conc. sulfuric acid at 0°.
[m] t-Amyl-t-butyl ether was obtained after the method of Erickson and Ashton[9] from t-amyl chloride and t-butyl chloride.
[n] 185 nm photolysis of t-butyl isopropyl ether and gas chromatography of the products.
[o] 185 nm photolysis of a 1 : 1 mixture of t-butyl isopropyl and di-t-butyl ethers. On gas chromatography, one new peak of moderate size appeared between those assigned to the dehydro dimers of t-butyl isopropyl and di-t-butyl ethers. This new peak was assigned to the mixed dehydro dimer.
[p] 254 nm photolysis of a 3 : 1 mixture of di-t-butyl ether and di-t-butyl peroxide and gas chromatography of the products.
[q] Not formed during photolysis ($\phi < 10^{-4}$).

EXPERIMENTAL

Di-t-butyl ether was synthesized according to the method of Erickson and Ashton[9] from t-butyl chloride and silver carbonate, and purified by preparative gas chromatography on 6 m 40 mm I. D. carbowax 20 M and 4 m 40 mm I. D. PPG 2000 on Chromosorb P-AW-DMCS 60–80 mesh columns, at 80°. Traces of t-BuOH were removed by passing the purified ether through aluminium oxide (basic, WOELM). The main other trace impurity, isobutene, could not be entirely eliminated by treatment with ozone and subsequently, aluminium oxide. This procedure had been successful in the case of t-butyl methyl ether as shown in Part II of this series.[3] Apparently there is slight catalysis by the Al_2O_3 of the decomposition into t-BuOH and isobutene. Thus, the mole fraction of the remaining isobutene was 10^{-4}. It is noted, however, that isobutene being one of the main products on irradiation increases to 5 times this value after 2 min, continuing to increase at the initial rate for irradiation times of up to 10 min. The other major and most of the minor products showed a linear increase with dose for even longer times. It was therefore concluded that the isobutene impurity was sufficiently small so as not to vitiate the results.

The purified ether was degassed and stored in a Hg-free greaseless stopcock high-vacuum line. Samples were prepared, irradiated and analyzed largely as described in Part II,[3] with the difference that isobutene could not be measured along with other volatile products from the vapourized sample owing to the fact that already at 60° there was fairly rapid decomposition of the substrate into isobutene and t-BuOH catalysed by the walls of the flask. (However, liquid injection gas chromatography was possible without noticeable sample decomposition at operating temperatures below 120°). The isobutene was therefore measured together with the other less volatile products through liquid injection. Since the isobutane results from both the vapourized and the liquid samples were in agreement it is concluded that the isobutene measurements are quantitative. For the determinations from liquid samples an internal standard was applied in the following way: a known volume kept at room temperature was filled with 2,4-dimethylpentane vapour in equilibrium with its liquid kept at 0°. The vapour pressure is given by Stull,[10] and at 0° is 28 torr. Subsequently the vapour was condensed into the cell onto the ether. Exact sample sizes were determined by weighing, and ranged between 1·10 and 1·30 g. The flux of 185 nm quanta through an aperture of the appropriate size was $0{\cdot}95 \times 10^{18}$ per minute as determined by the ethanol actinometer. The effect of the 254 nm radiation was checked by means of a vycor filter 1·5 mm thick. The molar extinction coefficient ϵ of di-t-butyl ether was measured on a Cary 17 instrument, the procedure being the same as with the t-butyl methyl ether. Its vapour pressure at 0° is 7·6 torr.[8] At 186 nm $\epsilon \approx 2200 \text{ l mol}^{-1} \text{ cm}^{-1}$ (Fig 2).

The products measured were identified by gas chromatographic comparison with authentic substances, and/or combined gas chromatography and mass spectrometry. Details of the gas chromatography product analysis and sources of reference compounds are given in Table 4.

Note added in proof: Recent ESR work supports the view taken in this paper that fragmentation of the $Me_3C—O—CMe_2^{\bullet}$ radical gives rise to acetone. Hydrogen abstraction from t-butyl isopropyl ether rapidly leads to the appearance of t-Bu$^{\bullet}$, and the precursor radical is not seen. No fragmentation has been observed in the radical derived from t-butyl methyl ether whereas the 1-t-butoxyethyl radical obtained from t-butyl ethyl ether shows some fragmentation so that *it* as well as t-Bu$^{\bullet}$ is being seen (S. Steenken, H.-P. Schuchmann and C. von Sonntag, to be published).

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