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UV PHOTOLYSIS (λ = 185 nm) OF LIQUID *t*-BUTANOL*

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Abstract—The UV photolysis (λ = 185 nm) of liquid t-butanol has been studied. The products have been identified and their quantum yields measured. The products (initial quantum yields) are: hydrogen (0·112), methane (0·265), ethane (0·013), iso-butane (0·015), iso-butene (0·013), neo-pentane (0·005), iso-butenoxide (0·08), acetone (0·205), iso-propanol (0·057), t-amylalcohol (0·05), 2,3,3-tri-methyl-2-butanol (0·003), 1-t-butoxy-2-methyl-2-propanol (0·03), 2,4,4-trimethyl-2-pentanol (0·012), pinacol (0·015), 2,4-dimethyl-pentene-2,4-diol (0·032), and 2,5-dimethylhexane-2,5-diol (0·044). The quantum yield of water formation has been estimated to be 0·05. The products are formed by both molecular fragmentation and radical processes. A detailed decomposition scheme is given in Fig. 4.

INTRODUCTION

Two papers have been published on the UV photolysis of t-butanol. Leuschner and Pfordte[1] suggested that a trimer is formed. Yang *et al.*[2] report a more detailed investigation, but due to the high degree of conversion (2–3 %), they were not able to distinguish between primary and secondary products. As in this study, excitation was by a low pressure mercury arc. The major lines emitted by this are the wavelengths λ = 254 nm and λ = 185 nm. The intensity of the latter is only about 10 % of the λ = 254 nm emission. The decomposition of the alcohol at λ = 254 nm is rather low ($\phi < 10^{-3}$) but the products, especially the carbonyl compounds, have a comparatively high extinction at this wavelength and in addition their quantum yields of product formation approach unity. For this reason the conversion in this study has been kept as low as possible (<0·01 %) in order to exclude secondary product formation.

RESULTS AND DISCUSSION

In the UV photolysis (λ = 185 nm) of t-butanol 16 products have been isolated and their quantum yields determined (see Table 1). The quantum yields of nearly all products are independent of the dose within the range measured (Figs 1–3).

At a dose of 3×10^{19} $\text{quanta}_{185\ \text{nm}}$/5 ml sample, three products start to deviate: acetone, dimethylpentanediol (DMP) and ethane. Under our experimental conditions, the absorbed dose of 3×10^{19} quanta corresponds to a conversion of 0·03 % and the concentration of acetone has reached approx 3×10^{-3} mol/l. At this concentration acetone might absorb light of wavelength λ = 254 nm and will react with t-butanol to give DMP. The decrease in quantum yield of acetone is not completely

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[*] Nr. XI of the series: Strahlenchemie von Akoholen; Nr. X: C. von Sonntag, Z. physik. Chem. N.F. **69**, 292 (1970)

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TABLE 1. UV PHOTOLYSIS (185nm) OF t-BUTANOL IN THE LIQUID PHASE (25°)
Quantum yield of the products formed.

Product	Quantum yield
Hydrogen	0·112 ± 5%
Methane	0·265 ± 5%
Ethane*	0·013 ± 15%
Isobutane	0·015 ± 15%
Isobutene	0·013 ± 15%
Neopentane	0·005 ± 15%
Methyl-t-butyl-ether	no (<0·001)
Isobuteneoxide	0·08 ± 10%
Acetone*	0·205 ± 5%
Isopropanol	0·057 ± 10%
Di-t-butyl-ether	no (<0·001)
t-Amyl alcohol	0·05 ± 10%
2,3,3-Trimethyl-2-butanol	0·003 ± 10%
1-t-Butoxy-2-methyl-2-propanol	0·030 ± 5%
2,4,4-Trimethyl-2-pentanol	0·012 ± 5%
Pinacol	0·015 ± 10%
2,4-Dimethylpentane-2,4-diol*	0·032 ± 10%
2,5-Dimethylhexane-2,5-diol	0·044 ± 10%
Water (estimated)	0·05

* These quantum yields are dose dependent
The values given represent the initial quantum yields

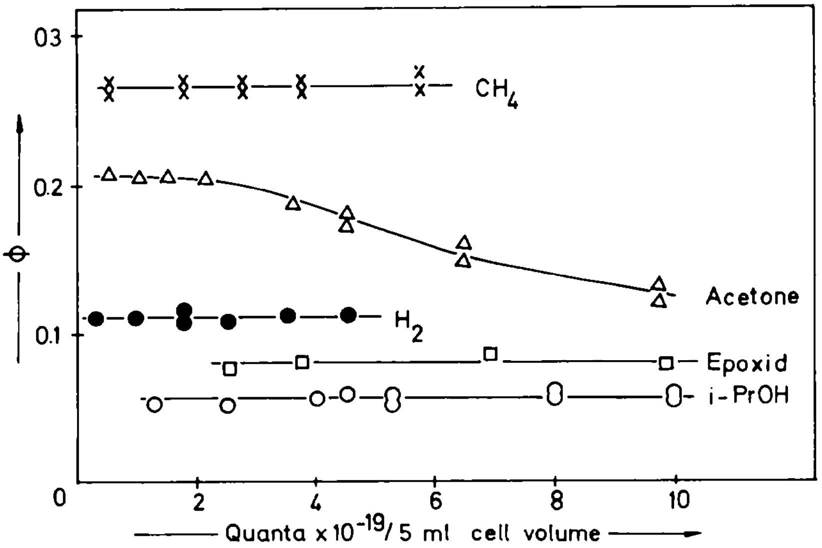


FIG 1. 185 nm photolysis of liquid t-butanol. O_2-free. 25°. The dependence of the quantum yields of methane, acetone, isobuteneoxide (epoxide) and isopropanol (i-PrOH) from the number of 185 nm quanta absorbed in the cell (5 ml).

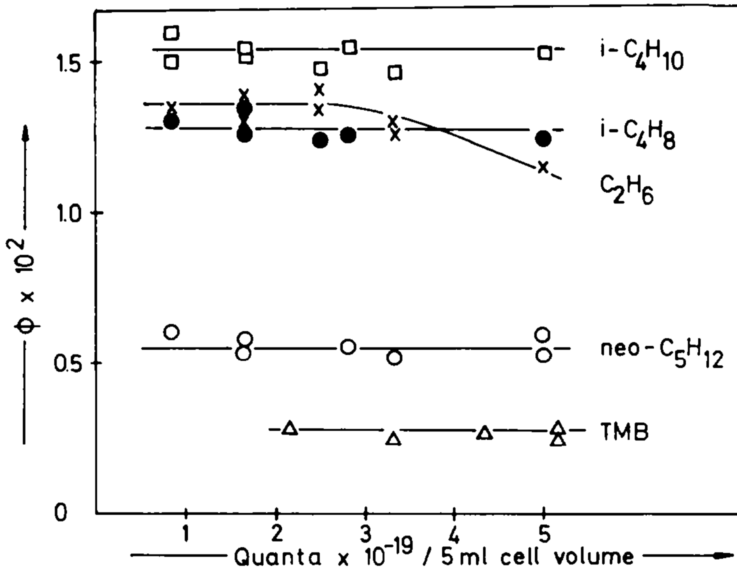


FIG 2. 185 nm photolysis of liquid t-butanol. O_2-free. 25°. The dependence of the quantum yields of isobutane, isobutene, ethane, neopentane and 2,3,3-trimethyl-2-butanol (TMB) from the number of 185 nm quanta absorbed in the cell (5 ml).

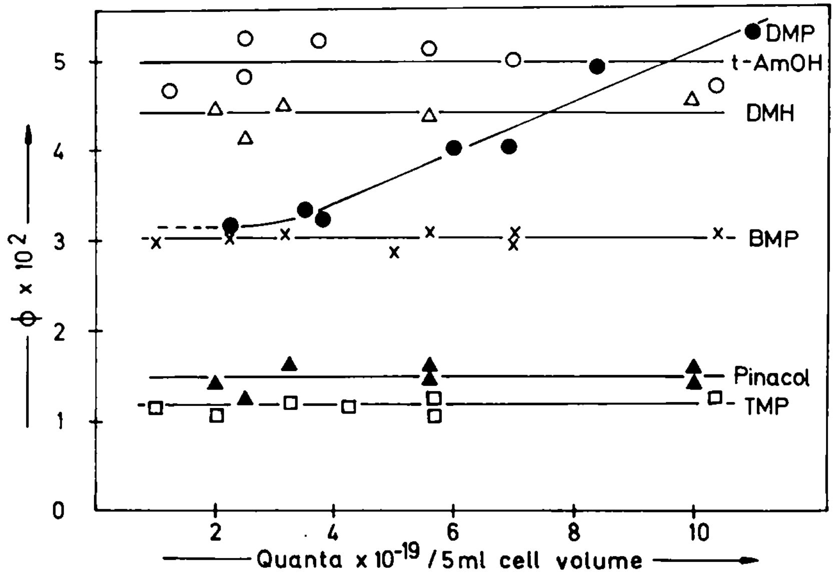


FIG 3. 185 nm photolysis of liquid t-butanol. O_2-free. 25°. The dependence of the quantum yields of 2,4-dimethyl-pentane-2,4-diol (DMP), tert-amyl alcohol (t-AmOH), 2,5-dimethylhexane-2,5-diol (DMH), 1-tertbutoxy-2-methyl-2-propanol (BMP), pinacol and 2,4,4-trimethyl-2-pentanol (TMP) from the number of 185 nm quanta absorbed in the cell (5 ml).

matched by an increase in DMP, but further products such as diacetone alcohol have beeen found at higher doses. The decrease in the ethane yield with increasing dose cannot be explained without much speculation.

Possible primary reactions

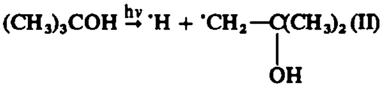
The quantum energy of the 185 nm radiation is equivalent to 155 kcal/mole and exceeds the dissociation energy of every single bond in the t-butanol molecule. The C—C bond, with a dissociation energy of 63 kcal/mole,[3] is by far the weakest compared to the C—O, C—H, and O—H bonds with energies of 91,[4] 98,[4] and 104[5] kcal/mole resp.

Because the difference between the energy of the exciting quantum and the dissociation energy of even the O—H bond is as large as 50 kcal/mole, splitting into radicals is quite possible (reactions 1 to 4).

bond dissociation energy

$(CH_3)_3COH \xrightarrow{h\nu} (CH_3)_2\dot{C}OH\,(I) + {}^{\cdot}CH_3$ 63 kcal/mole (1)

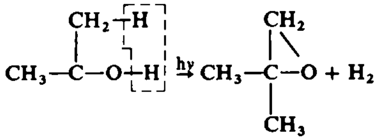
$(CH_3)_3COH \xrightarrow{h\nu} (CH_3)_3C^{\cdot} + {}^{\cdot}OH$ 91 kcal/mole (2)



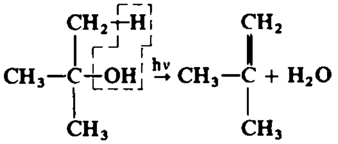
$(CH_3)_3COH \xrightarrow{h\nu} {}^{\cdot}H + {}^{\cdot}CH_2{-}\underset{\displaystyle OH}{\underset{|}{C}}(CH_3)_2\,(II)$ 98 kcal/mole (3)

$(CH_3)_3COH \xrightarrow{h\nu} (CH_3)_3CO^{\cdot} + H^{\cdot}$ 104 kcal/mole (4)

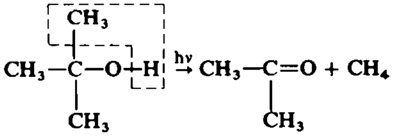
Parallel to the splitting into radicals, molecular fragmentation processes may occur (reactions 5 to 8).



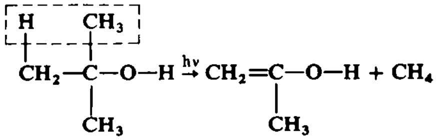
$$CH_3{-}\overset{\displaystyle CH_2{-}H}{\overset{|}{C}}{-}O{-}H \xrightarrow{h\nu} CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_2}{\overset{|\diagdown}{C}}}}{-}O + H_2 \qquad (5)$$



$$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_2{-}H}{\overset{|}{C}}}}{-}OH \xrightarrow{h\nu} CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_2}{\overset{\|}{C}}}} + H_2O \qquad (6)$$

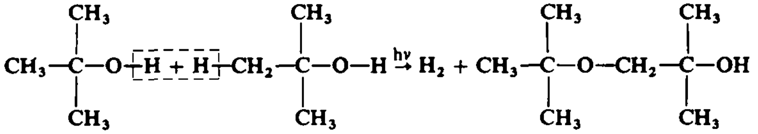


$$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}{-}O{-}H \xrightarrow{h\nu} CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}O + CH_4 \qquad (7)$$



$$\overset{\displaystyle H}{\overset{|}{C}}H_2{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}{-}O{-}H \xrightarrow{h\nu} CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}O{-}H + CH_4 \qquad (8)$$

It will be shown in detail[6] that a reaction of an excited t-butanol molecule with a neighbouring t-butanol (reaction 9) must also be considered.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O\boxed{H + H}CH_2-\underset{CH_3}{\overset{CH_3}{C}}-O-H \xrightarrow{h\nu} H_2 + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-OH \qquad (9)$$

III

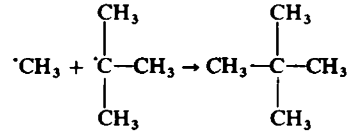
The quantum yield of total decomposition is 0·49. Therefore a deactivation to the ground state (reaction 10), in addition to cage effects, may play an important role.

$$(CH_3)_3COH^* \rightarrow (CH_3)_3COH + \text{energy} \qquad (10)$$

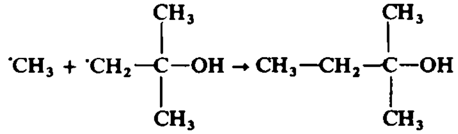
Product formation

***Products involving radicals from reactions* 1 *and* 2.** Methyl radicals (from reaction 1) dimerize to give ethane and add to t-butyl radicals and 2-hydroxy-2-methylpropyl radicals (II) yielding the products neopentane and t-amylalcohol (reactions 11 to 13).

$$^{\cdot}CH_3 + {^{\cdot}CH_3} \rightarrow CH_3CH_3 \qquad (11)$$

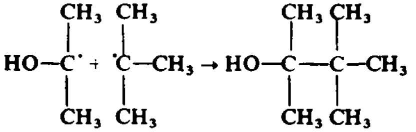


$$^{\cdot}CH_3 + {^{\cdot}\underset{CH_3}{\overset{CH_3}{C}}}-CH_3 \rightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \qquad (12)$$

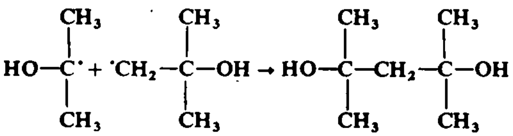


$$^{\cdot}CH_3 + {^{\cdot}CH_2}-\underset{CH_3}{\overset{CH_3}{C}}-OH \rightarrow CH_3-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-OH \qquad (13)$$

The other radicals from reaction (1), the 2-hydroxyisopropyl radicals (I), add to t-butyl radicals and to 2-hydroxy-2-methylpropyl radicals (II), trimethylbutanol (TMB) and dimethylpentanediol (DMP) being the products (reactions 14 and 15).

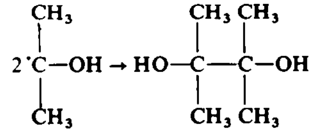


$$HO-\underset{CH_3}{\overset{CH_3}{C}}{^{\cdot}} + {^{\cdot}\underset{CH_3}{\overset{CH_3}{C}}}-CH_3 \rightarrow HO-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \qquad (14)$$

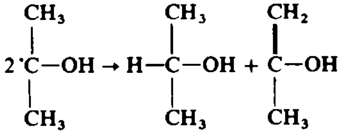


$$HO-\underset{CH_3}{\overset{CH_3}{C}}{^{\cdot}} + {^{\cdot}CH_2}-\underset{CH_3}{\overset{CH_3}{C}}-OH \rightarrow HO-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-OH \qquad (15)$$

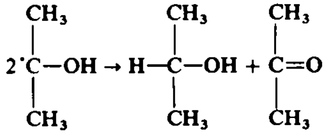
The 2-hydroxyisopropyl radicals (I) either dimerize to pinacol (reaction 16) or disproportionate to isopropanol and acetone (reaction 17). It has been shown[7] that the disproportionation does not follow reaction (18), but rather reaction (17) by which the enol-form of acetone is formed. Therefore the disproportionation of a Me radical with a 2-hydroxyisopropyl radical will also preferentially take place according to reaction (19) and not reaction (20). The addition of a Me radical to a 2-hydroxyisopropyl radical (reaction 21) is the back-reaction of the primary decomposition process (1). Not very much can be said about this reaction.



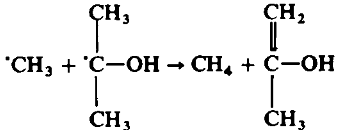
$$2\,{}^{\cdot}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{-OH} \rightarrow \mathrm{HO-}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{-}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{-OH} \qquad (16)$$



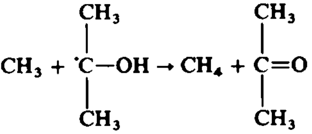
$$2\,{}^{\cdot}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{-OH} \rightarrow \mathrm{H-}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{-OH} + \underset{\mathrm{CH_3}}{\overset{\mathrm{CH_2}}{\mathrm{C}}}\mathrm{-OH} \qquad (17)$$



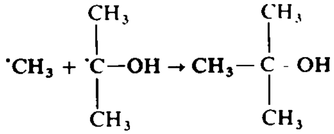
$$2\,{}^{\cdot}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{-OH} \rightarrow \mathrm{H-}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{-OH} + \underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{=O} \qquad (18)$$



$${}^{\cdot}\mathrm{CH_3} + {}^{\cdot}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{-OH} \rightarrow \mathrm{CH_4} + \underset{\mathrm{CH_3}}{\overset{\mathrm{CH_2}}{\overset{\|}{\mathrm{C}}}}\mathrm{-OH} \qquad (19)$$

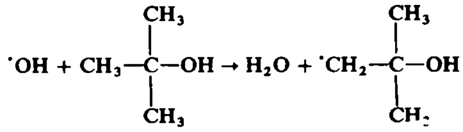


$${}^{\cdot}\mathrm{CH_3} + {}^{\cdot}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{-OH} \rightarrow \mathrm{CH_4} + \underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{=O} \qquad (20)$$

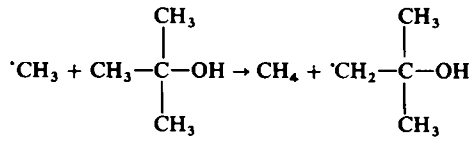


$${}^{\cdot}\mathrm{CH_3} + {}^{\cdot}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{-OH} \rightarrow \mathrm{CH_3-}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{-OH} \qquad (21)$$

The OH radicals formed in reaction (2) will abstract from t-butanol to give water and 2-hydroxy-2-methylpropyl radicals (II) (reaction 22). The rate constant of this reaction has been measured in water and determined to be 2·5 × 10^8 l/moles.[8] Me radicals are less reactive than OH radicals but will still abstract from t-butanol (reaction 23), especially if they contain some excess energy from the decomposition process.



$${}^{\cdot}\mathrm{OH} + \mathrm{CH_3-}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{-OH} \rightarrow \mathrm{H_2O} + {}^{\cdot}\mathrm{CH_2-}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{-OH} \qquad (22)$$

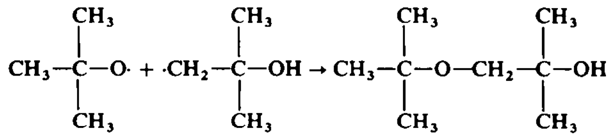


$$\cdot CH_3 + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH \rightarrow CH_4 + \cdot CH_2-\underset{CH_3}{\overset{CH_3}{C}}-OH \qquad (23)$$

Hydrogen formation

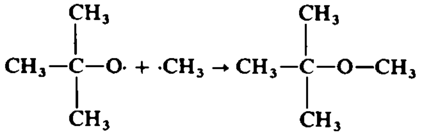
Proofs for absence of reactions 3 *and* 4, *importance of reactions* 5 *and* 9. Reactions (3) and (4) do not appear to occur. Free H atoms and t-butoxy radicals are not formed. This can be proved by the following facts:

The hydrogen yield (ϕ = 0·11) is balanced by the yield of the molecular fragmentation product isobuteneoxide (ϕ = 0·08) and the ether 1-t-butoxy-2-methyl-2-propanol (III) (ϕ = 0·03). The ether (III) is formed by an intermolecular concerted reaction (reaction 9) and not by a radical-radical combination process involving free t-butoxy radicals (reaction 24).

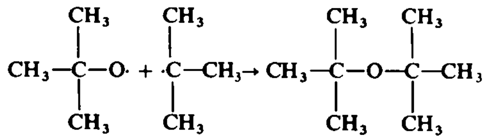


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O\cdot + \underset{(II)}{\cdot CH_2-\underset{CH_3}{\overset{CH_3}{C}}-OH} \rightarrow \underset{(III)}{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-OH} \qquad (24)$$

Although there are free Me and t-Bu radicals generated during photolysis which might react with t-BuO radicals to give ethers, neither methyl-t-butylether (ϕ < 0·001) (reaction 25) nor di-t-butylether (ϕ < 0·001) (reaction 26) has been found.



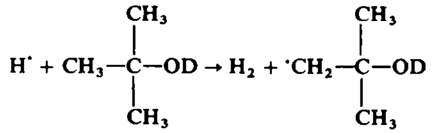
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O\cdot + \cdot CH_3 \rightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_3 \qquad (25)$$



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O\cdot + \cdot\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \rightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \qquad (26)$$

Furthermore radical scavengers such as O_2, benzophenone, naphthalene or isopropanol inhibit the formation of all products containing the structural unit (II) except the yield of the ether which is not influenced at all.

Reaction (3) does not play an important role either, as is shown by the photolysis of O-deuterated t-butanol, where 95% of the hydrogen formed appears as HD. Hydrogen radicals formed in reaction (3) should predominantly abstract the hydrogen from a Me group (reaction 27) yielding H_2 and not HD in O-deuterated t-butanol.



$$H^{\cdot} + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OD \rightarrow H_2 + \cdot CH_2-\underset{CH_3}{\overset{CH_3}{C}}-OD \qquad (27)$$

Isobuteneoxide is not formed by a sequence of radical reactions because the radical scavenger O_2 has no effect on the isobuteneoxide yield. The most probable mechanism is the molecular fragmentation process (5). A mechanism by which two H atoms (one from the Me and one from the OH group) are split off is rather unlikely. Abstraction of these H radical from t-butanol should give rise to a higher hydrogen yield than has been found. The high yield of HD in the photolysis of O-deuterated t-butanol could not be explained either. A third mechanism, the elimination of a H_2 molecule from the Me group (carben mechanism) as has been found in the photolysis of alkanes[9] can also be excluded because of the low H_2 yield of O-deuterated t-butanol.

The molecular processes 6, 7 *and* 8. There is not sufficient proof for the occurence of reaction (6), the fragmentation into water and isobutene, because we are not able to separate this process clearly from process (2). t-Bu radicals might disproportionate to give isobutene and isobutane. The isobutene yield is, therefore, an upper limit for this reaction.

The fact, that methane is formed in a molecular process according to reaction (7) is indicated by the photolysis of t-butanol-OD. 20 % of the methane formed appears as CH_3D. Me radicals, like other radicals, are expected to abstract predominantly at the Me groups and not at the OD-group, where high isotopic effects will even further hinder the abstraction.[10] The importance of reaction (8), the fragmentation into molecular methane and the enol-form of acetone, will be shown by the material balance given below. In the UV photolysis of isopropanol, it has been demonstrated that about 26 % of the methane formed stems from an analogous fragmentation route.[11]

Material balance and decomposition scheme. An overall material balance (quantum yields of the products multiplied by the C, H and O content of the products) gives $C_4H_{10,05}O_{0,94}$. This appears to be sufficiently good to draw some further conclusions.

Having shown that the primary reactions (3) and (4) do not occur to a significant extent, primary processes involving radicals will be restricted to reactions (1) and (2). The molecular processes (5) and (9) can be regarded separately, while reaction (6), which induces some uncertainties about the contribution of reaction (2), has at the most a quantum yield of 0·013.

We are, therefore, left with reactions (1), (2), (7) and (8). The contribution of reaction (1) is given by the products with the structural unit (I):

$$\begin{aligned}\phi(\mathrm{Me_2COH(I)}) &= 2\phi(\mathrm{i{-}PrOH}) + \phi(\mathrm{TMB}) + 2\phi(\mathrm{Pinacol}) + \phi(\mathrm{DMP})\\ &= 0{\cdot}114 + 0{\cdot}003 + 0{\cdot}03 + 0{\cdot}032 = 0{\cdot}179\end{aligned} \tag{28}$$

The yield of all C—C-bonds broken in reactions (1), (7) and (8) is given by:

$$\begin{aligned}\phi(\mathrm{C{-}C\ breaks}) &= \phi(\mathrm{Me_2COH(I)}) + \phi(\mathrm{acetone}) - \phi(\mathrm{i{-}PrOH})\\ &= 0{\cdot}179 + 0{\cdot}205 - 0{\cdot}057 = 0{\cdot}327\end{aligned} \tag{29}$$

The value of ϕ (i-PrOH) has to be substracted, because the disproportionation reaction (17) gives both isopropanol and acetone and it has already been accounted for in ϕ ($Me_2COH(I)$).

It follows from Eqs (28) and (29) that reaction (1) accounts for 55 % of all breaks in C—C bonds. The material balance of combining Me radicals is given by Eq (30):

$$\begin{aligned}\phi(^{\cdot}\mathrm{CH}_{3\,\mathrm{comb}}) &= 2\phi(\mathrm{ethane}) + \phi(\mathrm{neopentane}) + \phi(\mathrm{t{-}AmOH})\\ &= 0{\cdot}027 + 0{\cdot}005 + 0{\cdot}05 = 0{\cdot}082\end{aligned} \tag{30}$$

The yield of abstracting Me radicals (reaction 23) results from the difference in the total yield of Me radical formation (reaction 1, Eq 28) and the yield of combining Me radicals:

$$\phi(^{\cdot}\mathrm{CH}_{3\ \mathrm{abstr}}) = (28) - (30) = 0{\cdot}179 - 0{\cdot}082 = 0{\cdot}097 \tag{31}$$

The contribution of molecular fragmentation processes is equal to the difference of the total methane formed and the methane formed by abstracting methyl radicals (Eq 31):

$$\phi(\mathrm{CH}_{4\ \mathrm{mol}}) = \phi(\mathrm{CH}_{4\ \mathrm{total}}) - (31) = 0{\cdot}265 - 0{\cdot}097 = 0{\cdot}168 \tag{32}$$

From the CH_3/CH_4 balance (30 to 32) it can be calculated that reaction (1) accounts for 52% of the C—C bond breaks, while a value of 55% has been calculated from Eq (28) and (29), which is in fairly good agreement. Therefore, we can deduce that 35% of the methane produced by 185 nm photolysis of t-butanol have Me radicals as precursors while 65% stem from the molecular fragmentation processes (7) and (8). However a contribution of reaction (19) cannot be separated from these molecular fragmentation processes. Assuming that all CH_3D of the photolysis of O-deuterated t-butanol is formed according to (7) and not by radical processes (see above), then 30% of the molecular methane will have taken route (7) and 70% route (8). This 70% is an upper limit because of the uncertainties induced by the possibility of reaction (19).

The yield of reaction (2), the splitting into a t-Bu radical and a OH radical, can be estimated (Eq 33).

$$\begin{aligned}\phi(\mathrm{Me_3C}^{\cdot}) &= \phi(\text{neopentane}) + 2\phi(\text{isobutane}) + \phi(\text{TMB}) + \phi(\text{TMP})\\ &= 0{\cdot}005 + 0{\cdot}031 + 0{\cdot}003 + 0{\cdot}012 = 0{\cdot}051\end{aligned} \tag{33}$$

In this caculation it has been assumed that isobutane is formed by the disproportionation of two t-Bu radicals. If there are further routes of isobutane formation, the quantum yield of reaction (2) might be as low as 0·035. These figures are not very accurate, because the quantum yields of some products used for this calculation are only accurate to about 15%.

Summarising, we can say that in the primary decomposition ($\phi = 0{\cdot}49$) C—C breaks ($\phi = 0{\cdot}33 = 67\%$) are the most important events in the photolysis of t-butanol. In other alcohols e.g. methanol,[12] ethanol[13] and isopropanol[14] the splitting of the O—H and C—H bonds is by far the major process ($>90\%$ of total primary decomposition), whereas it only contributes 23% in the case of t-butanol. Reactions involving the break of the C—O bond are of minor importance (*ca* 10%). 55% of the primary decomposition occurs by molecular fragmentation, 31% of which yield methane, 23% hydrogen and *ca* 2% water, together with their corresponding products. A detailed decomposition scheme is given in Fig 4.

EXPERIMENTAL

Materials. t-BuOH (p.a.), isopropanol (p.a.), acetone (p.a.), naphthalene (p.a.) have been supplied by Merck, Darmstadt. Neopentane, t-amylalcohol (puriss), pinacol (puriss), 2,5-dimethylhexane-2,5-diol and 2-hydroxy-2-methyl-3-butanone (pract) were available (Fluka). The O-deuterated t-BuOH was prepared by Roth-Chemie (Karlsruhe). Isobutane and isobutene (inst. grade) were obtained from Matheson (Newark, U.S.A.). Methane, ethane, carbon monoxide and the carrier gases nitrogen (3-Ring), argon (2-Ring) and helium (3-Ring) were supplied by Messer (Griesheim).

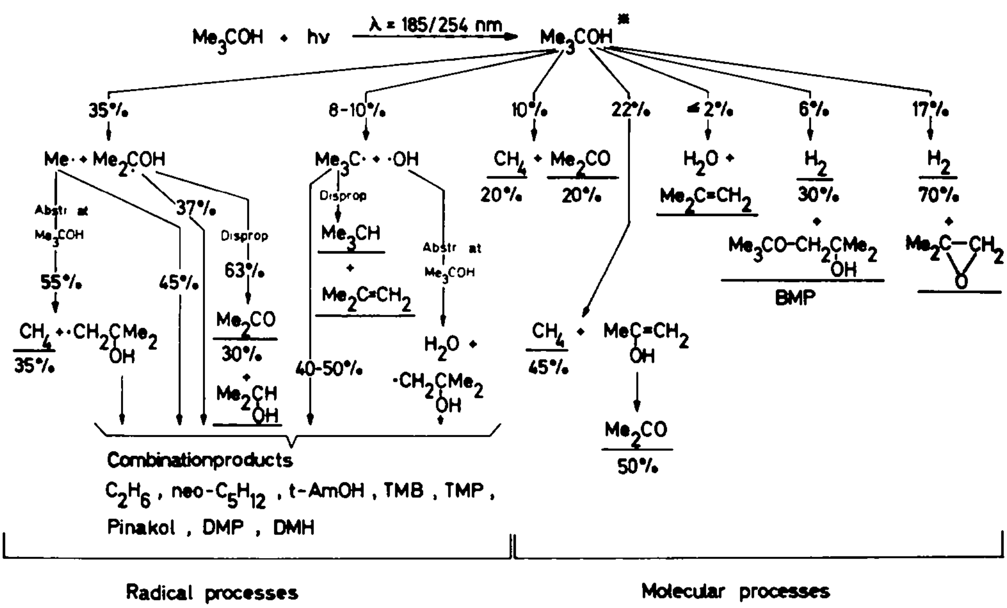


FIG 4. 185 nm photolysis of liquid t-butanol. O_2-free. 25°. Proposed reaction scheme.

t-BuOH contains traces of BuOH (< 0·1 %) as well as isobutylene. The BuOH could not be removed by fractionation, but it was proved, that it did not influence the photolysis of t-BuOH, because its concentration remained constant during photolysis. Bubbling a stream of N_2 through the t-BuOH successfully freed it from isobutylene. However, this process had to be repeated before every run, because traces of isobutylene were formed during storage. The quantum yields were not altered by using t-BuOH (Fluka) instead of t-BuOH (Merck). The other materials were used without further purification.

Irradiation and actionometry. A mercury low-pressure arc (Suprasil window, Gräntzel, Karlsruhe) was used for the UV photolysis. The apparatus is represented in Fig 5. The low pressure arc had a sigmoidal light tube in order to spread the UV light evenly over the entire surface area of the quartz cell. The temp of the cell was kept constant by contact with a thermostated brass block (25°). In order to prevent absorption of the $\lambda = 185$ nm light by atmospheric O_2, the distance between the quartz cell and the lamp was kept small (approx 3 mm). Because the light intensity ($1{\cdot}5$–$2{\cdot}0 \times 10^{18}$ quanta$_{185\ \mathrm{nm}}$/5 ml sample × min) was sufficient, it was not necessary to flush the slit with N_2. To prevent the photolysis of products in the light absorbing zone, the content of the quartz cell was stirred magneticly. To study photolysis at 254 nm separately, a Vycor quartz filter was placed in-between the low-press arc and the quartz cell. The Vycor quartz absorbs light at 185 nm but is transparent at 254 nm.

Two different irradiation vessels were used. One consisted of a quartz cell (Suprasil, Hellma, Mülheim/Baden) equipped with a 3-tap system and an inlet tube to flush the soln with N_2 or carrier gas in order to remove O_2. The other vessel had a 30 ml bulb attached to the quartz cell. The samples were degassed in the bulb by the freeze-pump technique. A cooling finger inserted in the bulb prevented sample contamination by tap grease during the thawing process.

For actinometry at 185 nm, the 5 molar EtOH/water actimometer[15–20] was used. A value of 0·4 was taken for the quantum yield of H_2 formation.[17] Carbonyl compounds were removed from EtOH by boiling with dinitrophenylhydrazine[16] and subsequent fractionation.

The emission of the low-press arc was constant over the period of an experiment but decreased linearily from $2{\cdot}6 \times 10^{18}$ to $1{\cdot}4 \times 10^{18}$ quanta$_{185\ \mathrm{nm}}$/5 ml sample × min over one year. The light intensity was checked weekly and it was confirmed that the quantum yields did not differ within the range of intensities used.

The intensity of the 254 nm line was measured with the $K_3(Fe(C_2O_4)_3)$ actinometer[4, 21] taking $\phi(Fe^{2+}) = 1{\cdot}24$[4]. The flux of the 254 nm quanta was about 10 times that of the 185 nm quanta.

Identification of the products. The products have been determined by gas chromatography (116 E, F 7, Bodenseewerke Perkin Elmer and G–C–M, Beckman).

Hydrogen, methane and ethane were determined by using the method of Kecki and Wincel.[22] Carrier gas was bubbled through the irradiated soln transporting the gases into the gas chromatograph, where they were separated on an activated carbon column. For hydrogen and methane the column temp was raised to 45°. The more soluble and less volatile gases, isobutane, isobutene and neopentane, were driven by a gentle stream of carrier gas into another vessel which was cooled with liquid N_2 and filled with glass beads to enlarge the cooling surface. The trapping vessel was then quickly heated above room temp and the gases were measured on a tetra-isobutylene column kept at room temp.

Most of the liquid products have been separated on a Ucon column Perkin Elmer) operated isothermally at 80° or temp-programmed (2·5° min) starting at the t-BuOH-peak up to an end-temp of 180°. Some products which could not be separated on the Ucon column were determined on a Poropak R column (Perkin Elmer) (either at 180° or 240°) or a β,β′-oxi-di-propioinitrile column at 70°. To exclude the formation of possible products such as hexamethyl-ethane, t-butyl methyl ether and di-t-butyl ether, and to prove the formation of water (which however could not be determined quantitatively) a Poropak Q column (Perkin Elmer) (at 120° and at 180°) and a silicone grease DC column (Perkin Elmer) have been used. Figs 6 and 7 show the gaschromatogramms of UV-irradiated t-BuOH on Ucon and Poropak R columns.

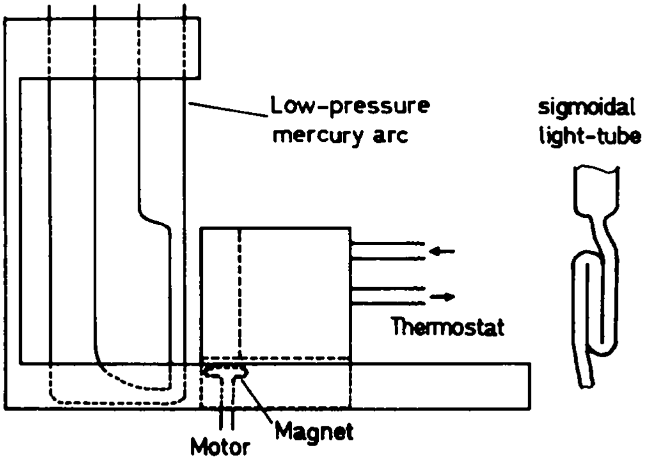


FIG 5. Apparatus for the 185 nm irradiation.

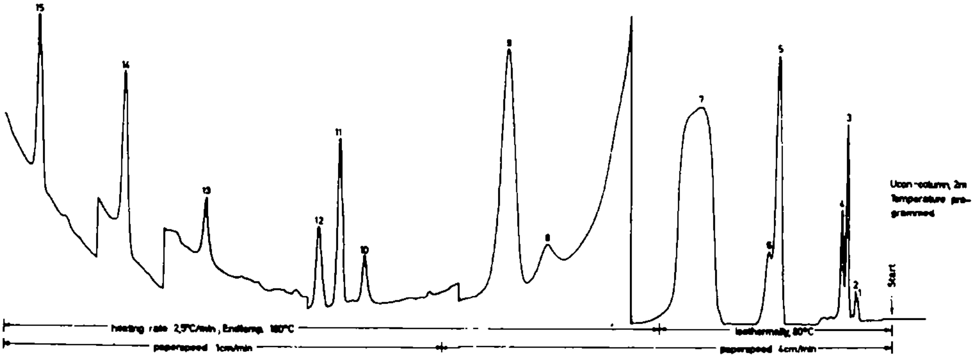


FIG 6. Gaschromatogram of 185 nm irradiated t-butanol. 2 m Ucon column, temperature programmed. (1) Methane, (2) ethane, (3) isobutane, (4) isobutene, (5) acetone, (6) isobuteneoxide, (7) t-butanol, (8) sec-butanol (impurity of t-butanol), (9) t-amyl alcohol, (10) 2,3,3-trimethyl-2-butanol, (11) 1-t-butoxy-2-methyl-2-propanol, (12) 2,4,4-trimethyl-2-pentanol, (13) pinacol, (14) 2,4-dimethylpentane-2,4-diol, (15) 2,5-dimethylhexane-2,5-diol.

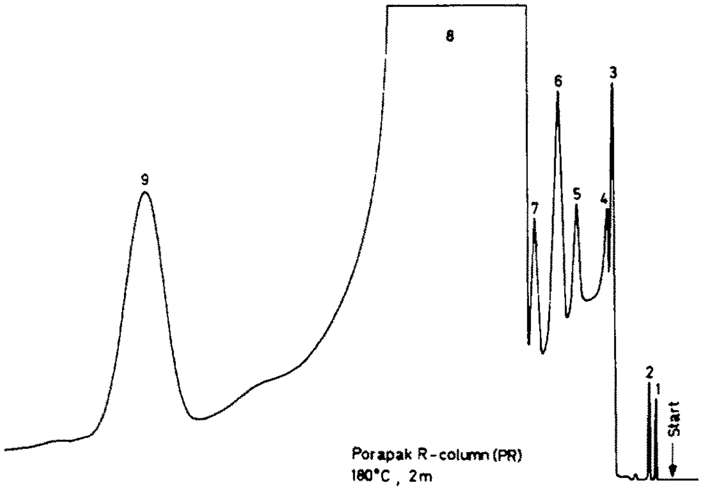


Fig 7. Gaschromatogram of 185 nm irradiated t-butanol. 2 m Poropak R column at 180°. (1) Methane, (2) ethane, (3) isobutane, (4) isobutene, (5) neopentane, (6) acetone, (7) isopropanol, (8) t-butanol, (9) t-amyl alcohol.

The products t-amylalcohol (Ucon-9), 2,3,3-trimethyl-2-butanol (Ucon-10), 1-t-butoxy-2-methyl-2-propanol (Ucon-11), 2,4,4-trimethyl-2-pentanol (Ucon-12), pinacol (Ucon-13), 2,4-dimethylpentane-2,4-diol (Ucon-14), and 2,5-dimethylhexane-2,5-diol (Ucon-15) have been isolated by collecting the fractions corresponding to the GC peaks. The trapping procedure was repeated several times in order to obtain sufficient material for IR and NMR analysis. The tailing of t-BuOH led to traces of this compound in the other fractions collected. This fact had been taken into account in the analysis of the spectra. The NMR spectra were improved by using a time average computer.

The tertiary alcohols, t-amylalcohol, 2,3,3-trimethyl-2-butanol and 2,4,4-trimethyl-2-pentanol give a positive reaction with Deniges-reagent.[23] The specific colouration given by these alcohols appeared on heating, after bubbling the carrier-gas through the Deniges-reagent solution. Dinitrophenylhydrazones were prepared from the irradiated soln but no carbonyl compounds are formed except acetone (TLC test). After an irradiation 10 times as long as for the ordinary experiment diacetone alcohol has been detected presumably a secondary product.

For quantitative determination of the liquid products 10^{-3} molar solutions of reference substances in t-BuOH were used as gas chromatographic standards. The gaseous products were determined quantitatively by comparing the areas of the GC peaks with those of standard volumes.

Preparation of reference-compounds. 2,3,3-Trimethyl-2-butanol (colourless liquid b.p. 131–132°) was prepared by a Grinard-reaction of pinacon with MeMgI[24].

1-t-Butoxy-2-methyl-2-propanol (colourless liquid, b.p. $_{13\ \mathrm{mm}}$ 40–42°). The nitrate of this alcohol has been considered to be a by-product of the electrolysis of a mixture of trimethyl-acetic-acid and sodium nitrate leading to the alcohol[25] by reduction with Zn dust. However, its b.p. (165°) does not follow the series of homologes described by other authors.[26–29]

In this work the compound was prepared by the reaction of chloracetic-acid-methyl-ester with potassium-t-butylate in absolute t-BuOH. By adding 2 mole equivs of Me_3MgI the β-hydroxy-ether is obtained.

Method. In a 3-necked flask, equipped with stirrer, reflux condensor and dropping funnel, 25 g (0·22 mole) potassium-t-butylate are dissolved in 150 ml abs t-BuOH. While stirring, 22 g (0·20 mole) chloracetic acid methyl ester dissolved in 50 ml abs t-BuOH are added over 1 hr. A white salt slowly precipitates. The mixture is refluxed for another 10–15 hr. Care must be taken to exclude moisture. The precipated KCl is filtered off and the soln is concentrated. By distillation 15 g t-butoxyacetic acid methyl ester (I; b.p.: 155–156°) were obtained. A Grignard reagent is prepared from 3·65 g (0·15 mole) Mg and 21·3 g (0·15 mole) MeI in 50 ml ether (abs). 7·3 g (0·05 mole) of I dissolved in 50 ml abs ether are added to the Grignard reagent during 1 hr. The soln is then refluxed for 3 hr and decomposed with cold conc NH_4Cl aq. The product is extracted with ether, the soln concentrated and distilled *in vacuo*, yield: 3·7 g (mol. weight: Calc. 146·2, Found 144; Calc.: C, 65·7, H, 12·3. Found: C, 65·3, H, 12·7%).

The NMR spectrum shows 3 singlets with intensities 2:9:6 at 3·06, 1·18 and 1·10 ppm. These protons are to be attributed to the $-CH_2-O$, t-butoxy and $(CH_3)_2-C-OH$ protons respectively. The IR spectrum shows a strong line at 1080 cm^{-1}, which is typical for aliphatic ethers.[30]

2,4,4-Trimethyl-2-pentanol (colourless liquid, b.p. 146–147°) has been prepared by adding water to diisobutene with 92% H_2SO_4 in acetonitrile.[31]

2,4-Dimethyl-2,4-pentane-diol (colourless liquid, b.p.$_{10}$: 95°) has been prepared by a Grignard reaction of diacetone alcohol with MeMgI.[32]

Isobuteneoxide (colourless liquid, b.p. 51–52°) has been prepared by reacting diazomethane with an aqueous soln of acetone[33] or by splitting off HCl from 1-chloro-2-methyl-2-propanol.[34]

Hexamethylethane (colourless cristalls, m.p. 100°, b.p. 105°) has been prepared from t-BuCl and t-BuMgCl.[35]

Methyl-t-butyl ether (colourless liquid b.p. 55°) has been prepared from t-BuOH and MeOH,[36] and di-t-butyl-ether (colourless liquid, b.p. 106°) by reacting t-BuCl with silver carbonate.[37]

IR and NMR spectra were run on all synthesized products for further confirmation and also for the comparison with products isolated from UV photolysis.

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