

THE U.V. PHOTOLYSIS ($\lambda = 185$ nm) OF *t*-BUTANOL/CYCLO-HEXANE MIXTURES*

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Summary

Dilute solutions of *t*-butanol (0.04 to 1.16 mol/l) in cyclohexane were photolyzed at 185 and 193 nm. At 185 nm and a concentration of 0.91 mol/l the following quantum yields were measured: hydrogen, 0.60; cyclohexene, 0.28₀; bicyclohexyl, 0.24₆; *t*-butyl cyclohexyl ether, 0.058; methane, 0.076; acetone, 0.070; isobutene oxide, 0.029; cyclohexanol, 0.0030; methylcyclohexane, 0.0073; cyclohexyl dimethyl carbinol, 0.0053; ethylene, 0.0010; ethane, 0.0004; isobutene, 0.006; isobutane, 0.001. The quantum yields of methane, acetone, methylcyclohexane, and cyclohexyl dimethyl carbinol increase with increasing *t*-BuOH concentration while those of ethylene and ethane decline and those of the other products are essentially unaffected in the concentration range investigated. The quantum yields increase slightly with temperature. Photolysis at 193 nm leads to the same H₂/CH₄ ratio as is obtained at 185 nm. A reaction scheme is developed which in conjunction with material balance considerations leads to the quantum yields of the primary fragmentation steps of the excited *t*-butanol molecule.

Extinction coefficients of *t*-BuOH/cyclohexane mixtures have been measured and found to increase with falling *t*-BuOH concentration, from 90 l mol⁻¹ cm⁻¹ in neat *t*-BuOH to a value of about 450 l mol⁻¹ cm⁻¹ (at 185 nm) at very low concentrations. This behaviour reflects the existence of different states of association of the BuOH molecules in the solutions, which are believed to be the cause of the concentration dependence of the quantum yields.

Introduction

The 185 nm photolysis of neat liquid *t*-butanol (*t*-BuOH) preferentially leads to C—C bond cleavage [1]. In particular, homolytic O—H bond

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splitting is not observed. However, with *t*-BuOH dissolved in *n*-hexane the quantum yield of the C—C bond cleavage is strongly reduced and the splitting of the O—H bond is drastically enhanced [2]. Furthermore, the u.v. absorption spectrum of *t*-BuOH changes on dilution with *n*-hexane [2].

It has been recognized that besides the monomer there may be linear (and cyclic) oligomers present in the neat alcohols and in their hydrocarbon solutions owing to hydrogen bonding [3 - 8]. Monomers and small oligomers must be relatively more abundant in dilute solutions than in the neat alcohols. The proportion of non-hydrogen-bonded *t*-BuOH molecules in dilute solutions must thus be high, but low in the neat alcohol. It is reasonable to assume that the photochemical findings [2] are causally related to this fact. The present work was undertaken to explore in more detail the lower concentration range of *t*-BuOH/cyclohexane mixtures in an attempt to correlate the photochemical and the associative behaviour of *t*-BuOH.

Experimental

Cyclohexane (Merck) was purified by fractional distillation followed by column chromatography on basic Al_2O_3 (W 200, Woelm) to remove olefinic impurities such as cyclohexene. No cyclohexene could be detected gas-chromatographically in the solvent so treated even after having been stored for several months without special precautions. *t*-Butanol (Merck) was purified by zone-melting (two sweeps) after which it was found gas-chromatographically to be free of impurities, in particular isobutene.

The optical density of the *in vacuo* deaerated solutions was measured in the wavelength region from 186 nm to 200 nm using a Perkin-Elmer Cary 17 spectrograph. The Suprasil QS optical cell of 0.100 cm width could enclose a liquid layer of a thickness of 0.010 cm. This was effected by inserting a 0.090 cm Suprasil QS platelet into the cell. Both cell and insert were obtained from Hellma, Müllheim.

In the 185 nm experiments mixtures with concentrations ranging from 0.4 to 21% w/w of *t*-BuOH were irradiated with a low pressure Hg arc (Graentzel, Karlsruhe) which could be used without filtering the 254 nm line as the latter was found to be photolytically inactive. This was tested when a 1.5 mm Vycor plate shutting off the 185 nm line was interposed between the lamp and the cell ($\Phi_{254}/\Phi_{185} < 10^{-3}$). The amount of 185 nm quanta absorbed was 0.84×10^{18} per minute as determined by the ethanol actinometer [9 - 11]. The concentration range was chosen such that total absorption of the 185 nm light within a 1 cm layer of the solution was in all cases assured. The photolyses were carried out in a Suprasil QS cell (Hellma). 1.5 g of solution were thermostated and stirred by means of a Teflon coated magnetic bar. Photolysis times extended up to 15 min. Most runs were performed at 15 °C and a few at 60 °C. In the 60 °C experiments a hot air gun mounted in an appropriate position was employed to prevent the condensation of sample vapours in the cell superstructure. Before photolysis the sample was degassed in a Hg-free greaseless high vacuum system where it

was repeatedly frozen and pumped, evaporated, and reprecipitated. In those cases where volatile products such as H_2 , CH_4 , C_2H_4 , and C_2H_6 were to be determined the sample was not degassed on the vacuum line but was purged for 20 min by a stream of argon to remove traces of oxygen. The latter procedure must be applied with care since excessive scrubbing may lead to a selective removal of *t*-BuOH from the cyclohexane solutions. Product analysis was done by gas chromatography (g.c.) using Perkin-Elmer F20, F 30, 900, and Varian 1700 instruments. A full description of some gas chromatographic procedures and instrumental modifications employed in this work has been published [12]. The volatile products were determined by scrubbing the sample with the carrier gas and transferring them either totally or in part into the gas chromatograph. The rest of the products was determined through liquid sample injection. Details on the analysis are given in Table 1.

A carbon lamp [14] was the light source in the 193 nm experiments where only hydrogen and methane were measured at *t*-BuOH concentrations ranging from 2.0 to 8.6% w/w. A microwave discharge in a mixture of helium with about 1% of methane gives rise to excited carbon atoms emitting at 193, 166, and 156 nm. Only the 193 nm line penetrates into the photolysis cell while the shorter wavelengths are largely removed by absorption in the lamp and cell silica windows. The gas mixture is pumped continually so that a pressure of about 1 Torr is maintained in the discharge zone and decomposition products of the methane are carried off.

Results

U.v. absorption of *t*-BuOH becomes intensive below 200 nm. The extinction coefficient of *t*-BuOH in cyclohexane exceeds that of the neat alcohol. Figure 1 shows the molar extinction coefficient of *t*-BuOH as a function of wavelength at various concentrations. Table 2 shows quantum yields of the major and of some minor 185 nm photolysis products from liquid *t*-BuOH/cyclohexane mixtures as a function of concentration. At a cyclohexane consumption quantum yield of about 0.8 (Table 2) the degree of cyclohexane conversion is about 0.1% after 15 min. The product quantum yields are independent of the dose within the dose range employed. The hydrogen quantum yield which is constant over the concentration range studied balances that of the dehydrogenated products (Table 3). Methane plus methylcyclohexane which increase with concentration give a fair balance against products such as acetone and cyclohexyl dimethyl carbinol (Table 3). An apparent slight disbalance in this second group of products may be due to isopropanol which could not be measured because of the g.c. peak overlap with the solvent cyclohexane.

At 193 nm the ratio of the methane to hydrogen yields was determined at several *t*-BuOH concentrations. As is seen from Fig. 2 this ratio essentially equals the ratio measured at 185 nm for the same concentrations.

Most experiments were carried out at 15 °C. Raising the photolysis

TABLE 1

Relative retention times of products and reactants and sources of reference compounds.

Compound	Relative retention time			Source
Hydrogen	2.5 ^a			
Methane	1.1 ^b			L'Air Liquide
Ethylene	2.3 ^b			L'Air Liquide
Ethane	2.9 ^b			L'Air Liquide
Isobutene	0.07 ^c			Chem. Werke Hüls
Isobutane	0.04 ^c			Phillips
Cyclohexane	1.00 ^c	1.0 ^d	1.00 ^e	Merck
Cyclohexene	1.53 ^c		1.37 ^e	BASF
Methylcyclohexane	1.84 ^c		1.61 ^e	Fluka
Bicyclohexyl	4.5 ^f	68.5 ^d	4.1 ^g	Fluka
Acetone	0.48 ^c		0.48 ^e	Merck
t-Butanol	1.59 ^c			Merck
Cyclohexanol			2.6 ^g	Fluka
Cyclohexyl dimethyl carbinol	5.6 ^f			h
Isobutene oxide	0.55 ^c		0.69 ^e	Bayer
t-Butyl cyclohexyl ether	1.0 ^f	11.0 ^d	1.0 ^g	i

^a Elution time, in minutes. Column: active coal, 4 m, 5 mm i.d., 23 °C, 38 ml Ar/min.

^b Elution time, in minutes. Column: Porapak Q (100 - 120 mesh), 2 m stainless steel, 1/8 in., 80 °C, 18 ml Ar/min.

^c Capillary column: Perkin-Elmer 7G3 (100 m stainless steel, 0.5 mm i.d., polypropylene glycol), room temp., ~ 2 ml N₂/min.

^d 110 °C; otherwise as under c.

^e Capillary column: Perkin-Elmer 7G3 (100 m stainless steel, 0.5 mm i.d., polypropylene glycol), 60 °C, ~ 2.5 ml He/min, used in combination with a precolumn: 20% Ucon-50 LB 550 X on Chromosorb P (60 - 80 mesh), 2 m glass, 1/8 in. The injected sample is first analyzed on the precolumn such that the interesting parts of the ensuing gas chromatogram can be collected while the rest is discarded. The frozen-out fractions are then flash heated and swept into the main analyzing column [12].

^f Column: 15% P 4000 on Chromosorb P (60 - 80 mesh, KOH treated), 3 m stainless steel, 1/8 in., 150 °C, 20 ml Ar/min.

^g Column: 5% Marlophen 87 (heptaglycolmonoisobutyl phenyl ether) on Chromosorb G (60 - 80 mesh), 2 m glass, 1/8 in., temperature programmed to 6 min at 85 °C, rise 3 °C/min, final temperature 123 °C, 20 ml Ar/min.

^h Synthesized from cyclohexylmagnesium bromide and acetone.

ⁱ Synthesized [13] in the autoclave from cyclohexanol and isobutene.

temperature to 60 °C brings about a slight increase in the quantum yields (Table 4). This effect is more readily apparent for hydrogen and its corresponding products than it is for methane and its group.

Discussion

Formation of products

The absorption of a 185 nm quantum by a saturated compound

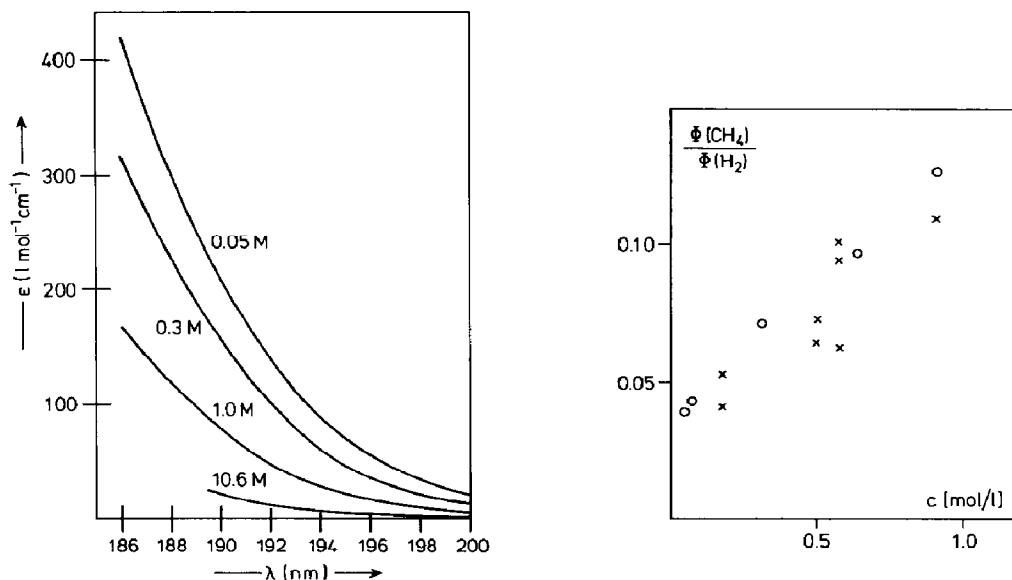
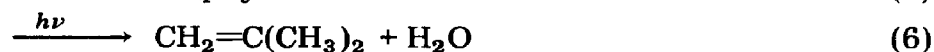
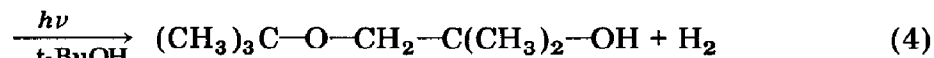
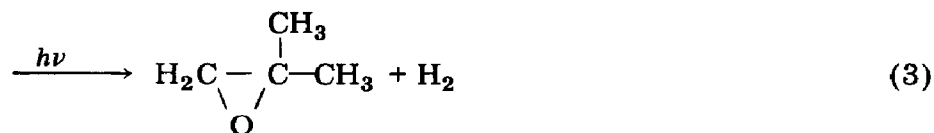
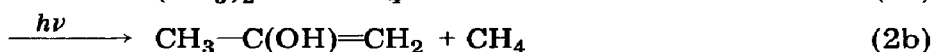
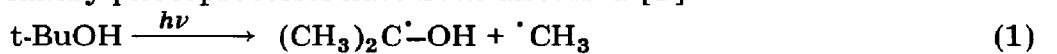


Fig. 1. The molar extinction coefficient of t-BuOH/cyclohexane mixtures at different t-BuOH concentrations.

Fig. 2. The ratio of $\Phi(\text{CH}_4)/\Phi(\text{H}_2)$ at $\lambda = 185 \text{ nm}$ (O) and 193 nm (X), at different t-BuOH concentrations.

molecule containing a hetero atom, such as t-BuOH, brings about a transition of largely $n-\sigma^*$ type [14]. (However, the terminating orbital could also be a $3s$ Rydberg orbital [15].) Barring deactivation, the excited t-BuOH molecule will fragment in a variety of ways, or interact with a neighbouring molecule, leading to photolysis products. In the photolysis of neat t-BuOH the following primary photoprocesses have been discussed [1]:



In the presence of cyclohexane as a solvent two additional primary steps have to be considered:

TABLE 2

Concentration dependence of quantum yields of some t-BuOH/cyclohexane mixture photolysis products*,
Flux 0.84×10^{18} quanta/min per sample (15 °C)

	$C_{t\text{-BuOH}}$ (mol/l)							
	0.0465	0.0721	0.313	0.638	0.910	1.158	2.29	
1 Φ (hydrogen)	0.62	0.63	0.63	0.61	0.60	0.61		
2 Φ (cyclohexene)	0.264	0.268	0.270	0.278	0.280	0.270		
3 Φ (bicyclohexyl)	0.250	0.250	0.244	0.244	0.246	0.246		
4 Φ (t-butyl cyclohexyl ether)	0.057	0.057	0.058	0.059	0.058	0.059		
5 Φ (methane)	0.024	0.027	0.045	0.062	0.076	0.081	0.107	
6 Φ (acetone)	0.024	0.032	0.043	0.064	0.070	0.078		
7 Φ (isobutene oxide)	0.019	0.021	0.026	0.030	0.029	0.026		
8 Φ (cyclohexanol)	0.0033	0.0033	0.0029	0.0033	0.0030	0.0029		
9 Φ (methylcyclohexane)	0.0015	0.0025	0.0044	0.0061	0.0073	0.0098		
10 Φ (cyclohexyl dimethyl carbinol)	0.0016	0.0019	0.0030	0.0040	0.0053	0.0063		
11 Φ (ethylene)	0.0026	0.0021	0.0013	0.0010 ₇	0.0010 ₂	0.0009 ₅	0.0006 ₆	
12 Φ (ethane)	0.0007 ₇	0.0006 ₉	0.0006 ₀	0.0005 ₂	0.0004 ₄	0.0004 ₈	0.0003 ₆	
13 Φ (isobutene)			0.004	0.006	0.006			
14 Φ (isobutane)			0.001	0.001	0.001			

*Isopropanol could not be determined as its gas chromatographic signal is overlain by that of cyclohexane.

TABLE 3

Hydrogen and methane/methyl material balances in the 185 nm photolysis of t-BuOH/cyclohexane mixtures at 185 nm. Flux 0.84×10^{18} quanta/min per sample (15 °C)

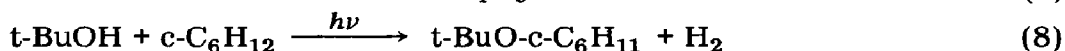
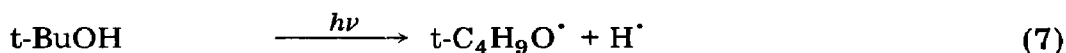
	$C_{t\text{-BuOH}}$ (mol/l)					
	0.0465	0.0721	0.313	0.638	0.910	1.158
Φ [1]*	0.62	0.63	0.63	0.61	0.60	0.61
Φ [2+3+4+7+8] + $\frac{1}{2}\Phi$ [9+10]	0.60	0.60	0.60	0.62	0.62	0.61
Φ [5+9] + 2Φ [12]	0.027	0.031	0.051	0.069	0.084	0.092
Φ [6+10]	0.026	0.034	0.046	0.068	0.075	0.084

*Product numbers refer to Table 2.

TABLE 4

Quantum yields of some t-BuOH/cyclohexane mixture photolysis products as a function of temperature. Flux 0.75×10^{18} quanta/min. Concentration 8.6% w/w (0.910 mol/l)

	Temperature (°C)	
	15	60
Φ (hydrogen)	0.60	0.71
Φ (methane)	0.076	0.08
Φ (ethylene)	0.0010	0.0007
Φ (ethane)	0.0004	0.0004
Φ (cyclohexene)	0.280	0.34
Φ (methylcyclohexane)	0.0073	0.011
Φ (bicyclohexyl)	0.246	0.35
Φ (isobutene oxide)	0.029	0.024
Φ (acetone)	0.070	0.08
Φ (t-butyl cyclohexyl ether)	0.058	0.05

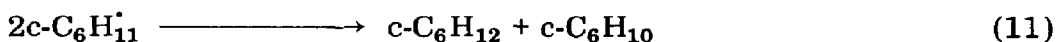
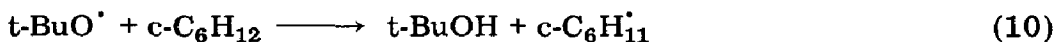
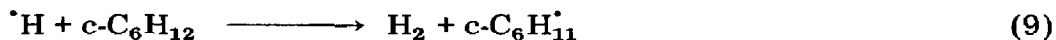


The absence of process (7) in the photolysis of neat t-BuOH is remarkable since in the case of the lower homologous alcohols the corresponding reaction is important [16 - 19]. In the neat t-BuOH the amount of hydrogen produced is equivalent to the sum of the products isobutene oxide (process 3) and 1-t-butoxy-2-methylpropanol-(2) (process 4). The latter compound was shown to arise from the non-radical process 4 [1, 20]. In cyclohexane solution, however, the hydrogen yield is largely matched by the yield of cyclohexene and bicyclohexyl which are formed in the termination of cyclohexyl radicals (reactions 11 and 12) generated by the reactive radicals H^\bullet and $t\text{-BuO}^\bullet$ ($t\text{-BuO}^\bullet$ is considerably more reactive than, e.g., CH_3 [21]). The latter radicals arise in process (7). Cyclohexene and bicyclohexyl are formed in the ratio of 1.1, in good agreement with the reported value of 1.1 for k_d/k_c for the cyclohexyl radical [22]. The fact that more than 90%

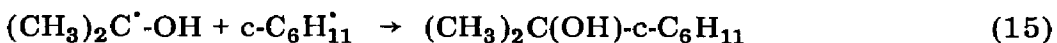
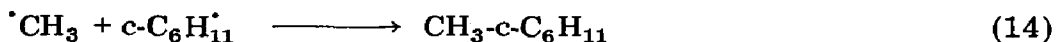
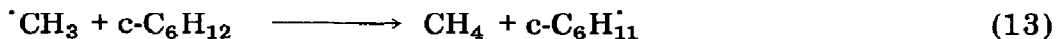
of the hydrogen produced in the photolysis of O-deuterated t-butanol in n-hexane [2] is HD indicates that the hydrogen atoms largely come from the hydroxyl group, and not from the methyl group.

Process (8) is similar to process (4). The t-butyl cyclohexyl ether quantum yield was found to be independent of the radical density which was varied by changing t-BuOH concentration (Table 2), or light intensity [23]. If, on the other hand, this ether was formed through combination of t-BuO[•] and [•]C₆H₁₁ its yield would depend on the steady-state radical concentration since such a process (second order in radicals) would have to compete with the hydrogen abstraction process (10; first order in radicals). A more detailed reasoning leading to the formulation of process (8) is given elsewhere [23].

Since neither H[•] nor t-BuO[•] combine with other radicals under these conditions they are quantitatively converted into cyclohexyl radicals, molecular hydrogen, and t-butanol (reactions 9 and 10). Hence the quantum yields of hydrogen, cyclohexene, and bicyclohexyl remain constant as long as the primary photochemical processes do not change with concentration.



Some further radical reactions of minor importance are:

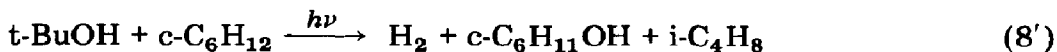


In dilute solutions such as dealt with in this work process (4) as well as reactions of the type:



are expected to be unimportant, the former on account of the quadratic dependence of its rate on [t-BuOH] [cf. 20], the latter especially because cyclohexane is a better hydrogen donor than t-BuOH.

With the exception of cyclohexanol and ethylene all the products found can be accounted for in terms of the above mechanism. While it is not clear how ethylene is formed, the cyclohexanol could arise in a side reaction to (8):



with the newly formed t-butyl cyclohexyl ether molecule having a tendency towards breaking up because of sterical strain before being fully thermalized.

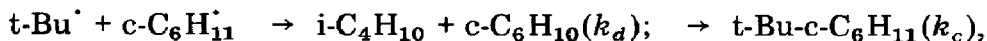
(For example, the strain energy of di-*t*-butyl ether is 7.6 kcal/mol [24]; using Benson's method of thermochemical group increments [25] one estimates 7.2 kcal/mol for di-*t*-butyl ether, and 6.8 kcal/mol for *t*-butyl isopropyl ether relative to dimethyl ether.)

Calculation of primary process quantum yields

On the basis of the product quantum yields and the mechanism given above the quantum yields of several primary bond split modes can be calculated (Table 5). The mechanism shows that $\Phi(\text{H}_2) = \Phi(3) + \Phi(7) + \Phi(8)$, $\Phi(\text{isobutene oxide}) = \Phi(3)$, and $\Phi(\text{t-butyl cyclohexyl ether}) = \Phi(8)$, from which $\Phi(7)$ can be obtained.

A complete calculation of the C—C bond homolysis quantum yield $\Phi(1)$ cannot be carried out because one of the corresponding products, isopropanol, has not been measured, since its g.c. signal is swamped by that of the solvent cyclohexane. The sum of primary CH_3 and CH_4 production, $\Phi(1) + \Phi(2a) + \Phi(2b)$ is equal to $\Phi(\text{CH}_4) + \Phi(\text{CH}_3\text{-c-C}_6\text{H}_{11}) + 2\Phi(\text{C}_2\text{H}_6)$. However, judging by the acetone yields of runs carried out at different light intensities [23] it appears that most of the C—C split is of a molecular nature which would imply the formation of but little isopropanol. This is also borne out by the fact that the discrepancy in the C—C bond scission material balance is only slight.

The C—O bond split (reactions 5 and 6) is of minor importance. Since water was not determined an estimate could only be made on the basis of products containing the C_4 moiety: isobutane, isobutene, and *t*-butylcyclohexane. Of these, isobutane and isobutene were measured while *t*-butylcyclohexane was not identified for lack of reference material. This compound arises from the combination of *t*-butyl with cyclohexyl radicals whose concentration is the highest of all the radicals in this system. Assuming that all the isobutane comes from disproportionation, and taking a k_d/k_c ratio of unity for the reactions:

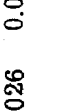


$\Phi(\text{t-butylcyclohexane}) \approx 10^{-3}$ is estimated. (For $t\text{-Bu}^\cdot + s\text{-Pr}^\cdot$, the gas phase value of k_d/k_c is 0.7 [22].) Finally, $\Phi(\text{C—O split}) = \Phi(5) + \Phi(6) = \Phi(\text{isobutane}) + \Phi(\text{t-butylcyclohexane}) + \{\Phi(\text{isobutene}) - \Phi(8')\}$. $\Phi(8') = \Phi(\text{cyclohexanol})$. The quantum yields of primary processes thus obtained are listed in Table 5 as functions of *t*-BuOH concentration. There is a strong concentration dependence of all quantum yields going from dilute solution to 100% *t*-BuOH.

Possible reasons for the concentration dependence of the primary quantum yields

t-BuOH molecules form a variety of H-bonded aggregates in their hydrocarbon solutions, the relative concentration of which changes with total alcohol content [3 - 8]. We assume that the concentration dependence of the quantum yields is a consequence of this phenomenon.

TABLE 5
Primary photoprocesses quantum yields as functions of *t*-BuOH concentration in cyclohexane at 15 °C

		<i>C_t</i> -BuOH (mol/l)						
		0.0465	0.0721	0.313	0.638	0.919	1.158	10.6 [1] (neat)
+ RH*	→ <i>t</i> -BuO [•] + H [•]	0.54	0.55	0.54	0.52	0.51	0.53	0.00
	→ <i>t</i> -BuOR + H ₂	0.057	0.057	0.058	0.059	0.058	0.059	0.03**
→ c-C ₆ H ₁₁ OH + <i>i</i> -C ₄ H ₈ + H ₂	→ CH ₂ -C(CH ₃) ₂ + H ₂	0.003	0.003	0.003	0.003	0.003	0.003	0.003
	→ 	0.019	0.021	0.026	0.030	0.029	0.026	0.08
→ CH ₃ + [•] C(CH ₃) ₂ OH	→ CH ₄ + CH ₃ -CO-CH ₃	0.027	0.031	0.051	0.069	0.084	0.092	0.33
	→ <i>i</i> -C ₄ H ₈ + H ₂ O							
	→ <i>t</i> -Bu [•] + [•] OH							

* R = *c*-C₆H₁₁.

** R = CH₂-C(CH₃)₂-OH.

*** Φ(*c*-C₆H₁₁[•] + *t*-Bu[•] → comb.) estimated at 0.001 from Φ(*i*-C₄H₁₀).

Since excitation of alcohols in the region of the first u.v. absorption band between 160 and 200 nm is due to a promotion of an electron from the lone pair of the oxygen to an antibonding orbital it is fair to assume that H bond formation has a considerable influence on alcohol photochemistry. The H bond formation leads to a shift in the absorption spectrum of t-BuOH as shown in Fig. 1. The question arises whether it is merely the shift in energy caused by H bonding which modifies the pattern of primary reactions. This does not seem to be the case as the CH_4/H_2 ratios at 185 nm and 193 nm are equal (Fig. 2).

The excited t-BuOH molecules will have different life-times with respect to the different primary processes. If in the H-bonded state the O—H split is retarded but not the C—C split, then the excitation energy could be channelled into the C—C bond. This would explain why at low concentration (high monomer content) the quantum yield for O—H cleavage is high whereas at high concentration (low monomer content) the quantum yield for the C—C bond break predominates. Evidence for the enhancement of the C—C split through hydrogen bonding is also afforded by the observation that the photolysis of t-BuOH in dilute aqueous solutions leads practically only to the C—C split [2]. Since the increase in $\Phi(\text{C—C bond split})$ is not compensated by the decrease in $\Phi(\text{O—H bond split})$ there is a contribution of a radiationless decay or of a cage recombination. Indeed the sum of primary process quantum yields is below unity because deactivation steps which do not lead to product formation are also involved.

No definite conclusions seem possible at this stage as to the effect of temperature on the quantum yields. As Table 4 shows there is at 60 °C an increase in the quantum yields of both hydrogen and methane over those found at 15 °C, the increase perhaps being relatively larger with hydrogen than with methane. Taking note of the cyclohexene, bicyclohexyl, and methylcyclohexane yields it is clear that there is enhancement of the homolytic O—H split. One could attempt to explain this as a consequence of a shift in the association equilibrium towards smaller species, with the amount of monomers rising, the lower oligomers keeping their share, and the larger oligomers diminishing. Concurrently one should expect a decline of the C—C bond split. That, however, is not the case. This fact indicates that the temperature effect is not exclusively due to the shift in the association equilibrium but that the individual primary process quantum yields are themselves temperature dependent. Before the hypothesis concerning the concentration dependence of primary process quantum yields can be further developed a quantitative knowledge about the monomer and oligomer content of the dilute t-BuOH/cyclohexane mixtures is necessary.

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