

## INTERMOLECULAR ELIMINATION OF SMALL MOLECULES IN THE PHOTOLYSIS ( $\lambda = 185$ nm) OR *t*-BUTANOL AND *t*-BUTYL METHYL ETHER IN CYCLOHEXANE\*

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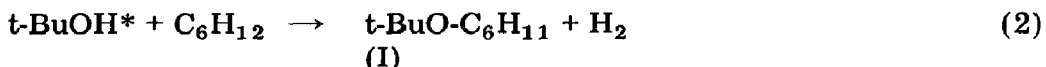
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### Summary

In the 185 nm photolysis of *t*-butanol and *t*-butyl methyl ether in cyclohexane the formation of *t*-butyl cyclohexyl ether is observed. It is not formed *via* a free radical combination process since its quantum yield does not depend on the steady state radical concentration which has been varied by changing either dose rate or substrate concentration. It is concluded that *t*-butyl cyclohexyl ether is formed in an intermolecular reaction of excited *t*-butanol or *t*-butyl methyl ether with the solvent cyclohexane or in a hot reaction in the cage under the elimination of hydrogen or methane respectively. This view is supported by the results of some 254 nm di-*t*-butyl peroxide photolysis experiments.

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In the 185 nm photolysis of *t*-butanol (*t*-BuOH) in cyclohexane as solvent we have observed the formation of *t*-butyl cyclohexyl ether (I):



The quantum yield for the production of (I) is 0.06 at a *t*-BuOH concentration of 0.0465 mol/l (Table 1). The details of the experimental procedure are given elsewhere [1]. Reaction (2) may be truly intermolecular, or else a "hot" cage reaction such that homolytic O-H bond scission and immediate hydrogen abstraction from the solvent cage by the hot H atom is followed by the cage combination of *t*-BuO $\cdot$  and *c*-C<sub>6</sub>H<sub>11</sub> $\cdot$ . With this qualification process (2) is termed "intermolecular". The evidence for the occurrence of process (2) is as follows.

The extinction coefficient of *t*-BuOH at 185 nm is larger than that of

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\*Part XIX of the series: Strahlenchemie von Alkoholen. Part XVIII: D. Schulte-Frohlinde, D. Sanger and C. von Sonntag, Z. Naturforsch. 27 b (1971) 205.

TABLE 1

Quantum yields as a function of light intensity. Concentration 0.0465 mol/l. t-BuOH in cyclohexane; 15 °C.

	Flux $\times 10^{-18}$ (quanta/min)				
	0.16	0.36	0.56	0.69	0.84
$\Phi$ (cyclohexene)	0.306	0.264	0.268	0.261	0.264
$\Phi$ (bicyclohexyl)	0.256	0.244	0.234	0.242	0.250
$\Phi$ (t-butyl cyclohexyl ether) (I)	0.059	0.065	0.059	0.057	0.057
$\Phi$ (acetone)	0.031	0.031	0.037	0.029	0.024
$\Phi$ (isobutene oxide)	0.026	0.022	0.025	0.020	0.019
$\Phi$ (cyclohexanol)	0.0044	0.0041	0.0030	0.0049	0.0033
$\Phi$ (methylcyclohexane)	0.0010	0.0018	0.0017	0.0018	0.0015

cyclohexane by more than two orders of magnitude, at the same wavelength. Thus, at 0.0465 mol/l, the 185 nm u.v. light is absorbed preferentially by t-BuOH.

In the 185 nm photolysis of neat alcohols [2 - 5] and ethers [6 - 8] one of the primary steps gives rise to alkoxy radicals:



Alkoxy radicals are highly reactive and undergo H abstraction reactions (reaction 4). They have been found [2 - 8] to participate to a small extent only in radical combination reactions. If (I) was formed by a combination reaction of the t-BuO $\cdot$  and cyclohexyl radicals (reaction 5) one would expect the quantum yield of (I) to increase with radical density because a pseudo first order process (reaction 4) competes with a second order process (reaction 5). Changes in the cyclohexene and bicyclohexyl quantum yields are not expected since these products arise from second order reactions only, and their quantum yields are large compared to those of other possible radical-radical reaction products. Changes in radical density can be achieved by changing the light intensity or the concentration of the light-absorbing species, in this case t-BuOH. Table 1 gives the yield of several products as a function of light intensity. As can be seen from Table 1 the yield of the ether (I) does not change with light intensity. Equally well, there is no change of its quantum yield over a wide range of concentrations (Table 2).

Further, to test the molecular nature of the formation of (I), di-t-butyl peroxide (DTBP) was photolyzed at 254 nm in cyclohexane. In this system the excited di-t-butyl peroxide dissociates into two t-butoxy radicals. The concentration of the peroxide was chosen such that the t-BuO $\cdot$  radical density was similar to that in a 185 nm t-BuOH photolysis experiment. The cyclo-

TABLE 2

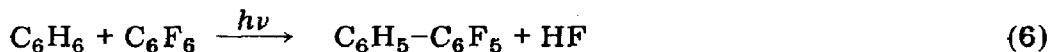
Quantum yield of t-butyl cyclohexyl ether (I) as a function of t-butanol concentration in cyclohexane. Flux of 185 nm quanta  $0.84 \times 10^{18}$ /min; 15 °C.

C(mol/l)	$\Phi$
0.0465	0.057
0.0721	0.057
0.313	0.058
0.638	0.059
0.910	0.058
1.158	0.059

hexyl radical concentrations will then be similar too in both experiments since in the first case t-BuO $\cdot$  and H $\cdot$ , in the second case two t-BuO $\cdot$  are available to abstract hydrogen from the solvent cyclohexane. From the equations below it follows that these conditions are fulfilled when the molar concentration of the di-t-butyl peroxide is about one-third of the t-BuOH concentration. The rate of t-BuO $\cdot$  formation is  $r(\text{t-BuO}\cdot) = 2.3 \cdot \epsilon \cdot \Phi \cdot (\text{t-BuO}\cdot) I \cdot c/N_L$ . For the di-t-butyl peroxide,  $\epsilon_{254} \approx 8$  l/mol cm (as determined on a Cary 17 instrument from a dilute solution in cyclohexane),  $\Phi(\text{t-BuO}\cdot) \approx 2$ , and  $I_{254} = 6.36 \times 10^{18}$  quanta/min per sample. For the t-BuOH [1],  $\epsilon_{185} \approx 300$  l/mol cm in dilute cyclohexane solution,  $\Phi(\text{t-BuO}\cdot) \approx 0.5$ , and  $I_{185} = 0.84 \times 10^{18}$  quanta/min per sample. So,  $r_{254}/r_{185} \approx 0.8 c_{\text{DTBP}}/c_{\text{t-BuOH}}$ . The results are compared in Table 3. The much lower ether yield in the di-t-butyl peroxide photolysis argues in favour of the hypothesis that in the t-BuOH photolysis formation of (I) occurs by the intermolecular elimination reaction (2) and not by reaction (5).

It is of interest that in the photolysis of t-butanol neat and diluted with water, isopropanol and n-hexane, the compound  $(\text{CH}_3)_3\text{C-O-CH}_2\text{-C}(\text{CH}_3)_2\text{OH}$  has been observed [5, 9]. There is evidence [9] that this compound is also formed in a molecular elimination process.

An example of a reaction where a small molecule other than H $_2$  is eliminated intermolecularly seems to have been furnished [10] by the 254 nm photolysis of a mixture of benzene and hexafluorobenzene. This produces pentafluorobiphenyl and HF, apparently *via*:



There is now evidence that even a larger molecule such as methane can be intermolecularly eliminated as well. A case in point is the formation of (I) and methane in the photolysis of t-butyl methyl ether in cyclohexane (reaction 7). t-Butyl methyl ether at concentrations of 0.002 and 0.16 mol/l in cyclohexane was irradiated at 185 nm ( $0.75 \times 10^{18}$  quanta/min per sample). The molar extinction coefficient of the ether in the 0.16 mol/l mixture at 185 nm was found equal to that of the neat t-butyl methyl ether [7], 220

TABLE 3

Relative quantum yields of cyclohexene and t-butyl cyclohexyl ether in the photolysis of t-BuOH ( $\lambda = 185$  nm) and of di-t-butyl peroxide ( $\lambda = 254$  nm) in cyclohexane.

	$\Phi(\text{bicyclohexyl})_{\text{rel}}$	$\Phi(\text{cyclohexene})_{\text{rel}}$	$\Phi(\text{t-butyl cyclohexyl ether})$
t-BuOH photolysis in cyclohexane ( $\lambda = 185$ nm)*	1	1.14	0.242
DTBP photolysis in cyclohexane ( $\lambda = 254$ nm)**	1	1.28	0.012

\*t-BuOH concentration 0.638 mol/l; flux  $0.84 \times 10^{18}$  quanta/min; 15 °C.

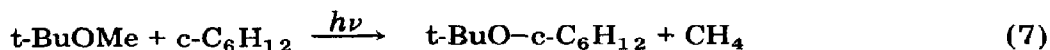
\*\*Di-t-butyl peroxide concentration 0.79 mol/l; flux  $6.36 \times 10^{18}$  quanta/min; 15 °C.

TABLE 4

Quantum yields of bicyclohexyl and t-butyl cyclohexyl ether in the 185 nm photolysis of t-butyl methyl ether/cyclohexane mixtures. Flux  $0.75 \times 10^{18}$  185 nm quanta/min; 15 °C.

	$C_{\text{t-BuOMe}}$ (mol/l)	
	0.0020	0.1615
$\Phi(\text{bicyclohexyl})$	0.051	0.055
$\Phi(\text{t-butyl cyclohexyl ether})$	0.0027	0.0027

l/mol cm. This shows that only the t-butyl methyl ether absorbs light at  $\lambda = 185$  nm, and not the cyclohexane. Quantum yields of t-butyl cyclohexyl ether and bicyclohexyl are listed in Table 4. The interesting fact is that the ratio of the quantum yields is the same at both t-butyl methyl ether concentrations which differ by a factor of about a hundred. As explained above the rate of radical formation is proportional to the concentration of the absorbing molecules. This means that the steady-state concentration of the abstractive t-BuO $\cdot$  must rise in about constant proportion with the t-butyl methyl ether concentration. One would expect, therefore, a pronounced decline, with concentration, of the t-butyl cyclohexyl ether yield compared to that, e.g. of bicyclohexyl, if the product ether was indeed a radical combination product. It seems thus justified to propose the intermolecular elimination process:



## References

- 1 H.-P. Schuchmann, C. von Sonntag and D. Schulte-Frohlinde, to be published.
- 2 C. von Sonntag, *Tetrahedron*, 25 (1969) 5853.
- 3 C. von Sonntag, *Z. Phys. Chem.* [Frankfurt] N. F., 69 (1970) 292.

- 4 C. von Sonntag, Z. Naturforsch., 27 b (1972) 41.
- 5 D. Sanger and C. von Sonntag, Tetrahedron, 26 (1970) 5489.
- 6 C. von Sonntag, H.; P. Schuchmann and G. Schomburg, Tetrahedron, 28 (1972) 4333.
- 7 H.; P. Schuchmann and C. von Sonntag, Tetrahedron, 29 (1973) 1811.
- 8 H.; P. Schuchmann and C. von Sonntag, Tetrahedron, 29 (1973) 3351.
- 9 D. Sanger and C. von Sonntag, Z. Naturforsch., 25 b (1970) 1491.
- 10 D. Bryce-Smith, A. Gilbert and P. J. Twitchett, J. C. S. Chem. Commun., (1973) 457.