

Products of Benzyl Chloride Photolysis in Methanol—Water Mixtures

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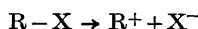
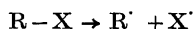
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When benzyl chloride was photolysed in methanol–water mixtures at 0 °C the following reaction products were obtained by GLC: benzyl alcohol, benzylmethyl ether, bibenzyl, β -phenylethyl alcohol and small amounts of benzaldehyde. The changes in the relative amounts of different products with changes in the solvent composition are interpreted in terms of a homolytic bond dissociation of singlet excited benzyl chloride followed by two competing reactions: the abstraction of hydrogen from methanol by chlorine atoms and the oxidation of benzyl radical to carbonium ion by chlorine atoms. The final products are then obtained by radical combination reactions and by nucleophilic reactions of the benzyl carbonium ion with solvent molecules.

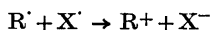
Photolysis of benzyl chloride in gas phase^{1,2} produces benzyl radicals and chlorine atoms. As no toluene has been observed¹ among the products at room temperatures hydrogen abstraction reactions by benzyl radicals are slow compared with radical combination reactions. Chlorine atoms, however, abstract hydrogen atoms forming hydrogen chloride.¹ The benzyl radical has been observed^{3,4} in photolysis of benzyl chloride in solid matrices. Photolysis of benzyl chloride in 1:1 methanol–water mixture⁵ gives products by hydrogen abstraction and combination reactions of the benzyl and chlorine radicals. In addition also benzyl alcohol and methyl benzyl ether were obtained, products which result from photochemical nucleophilic reactions of benzyl chloride with solvent molecules.

A similar competition between two different types of photochemical reactions, radical and nucleophilic reactions, has been observed in photolyses of substituted benzyl acetates^{6–10}

and in photolyses of substituted phenyl esters and phenyl chlorides.^{11,12} These results have been interpreted in terms of two competing primary photodissociation processes, a homolytic and a heterolytic dissociation:



The nucleophiles then react with the carbonium ion R^{+} . In some cases also the excited molecule may react with nucleophiles.¹² It is also possible that the radical X^{\cdot} oxidizes the carbonium radical to a carbonium ion.¹⁰



The quantum yield of photodissociation of benzyl chloride in 1:1 methanol–water mixture is 1.0 and independent of the wavelength of the exciting light and of added oxygen.⁵ The photodissociation is therefore expected to occur from the excited singlet state.

In order to study the mechanism of the photochemical reactions of benzyl chloride we have measured the amounts of different products formed in photolysis of benzyl chloride in methanol–water mixtures.

EXPERIMENTAL

The benzyl chloride, a product of BDH, was purified by vacuum distillation before use.

Non de-aerated benzyl chloride solutions were photolysed with the light of a 100 W medium pressure mercury arc tube in a thermostat at 0 °C. The initial concentration of benzyl chloride was about 4×10^{-2} to 9×10^{-2} mol dm⁻³ except for solutions containing small

Table 1. Products of the photolysis of benzyl chloride in methanol–water mixtures at 0 °C. x is the mol fraction of water in the reaction mixture and c the initial concentration of benzyl chloride.

x H ₂ O	$10^4 c/\text{mol dm}^{-3}$ PhCH ₂ Cl	Mol % of products				
		PhCH ₂ OH	PhCH ₂ OCH ₃	(PhCH ₂) ₂	PhCH ₂ CH ₂ OH	PhCHO
0	766	0	37.8	15.9	44.5	
0.105	806	9.0	38.9	13.0	37.3	
0.197	893	9.5	35.6	13.4	39.8	
0.351	921	11.1	34.3	14.1	38.7	
0.481	920	18.3	32.7	12.3	34.9	
0.585	406	25.6	32.7	11.3	28.8	
0.678	199	34.5	34.5	6.8	22.9	
0.830	42.6	46.2	36.5	7.8	8.9	
0.893	23.2	73.2	15.0	1.3	9.8	0.1
0.950	32.1	87.1	5.2	0.8	5.8	0.9

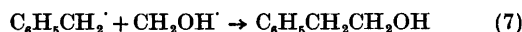
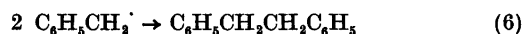
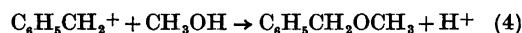
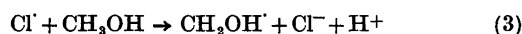
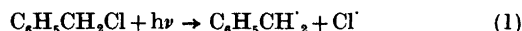
amounts of methanol where lower concentrations of about 1×10^{-3} had to be used. The reaction mixture was analysed by GLC using Carbowax 1540 or 4000 and the products were identified by comparison of their chromatograms with those of known compounds and by mass spectroscopy. A reference sample was kept in the dark at the same temperature and the products of thermal reactions were analysed in the same way and subtracted from the amounts of products obtained in photolysis reactions. These corrections were usually small, of the order of a few per cent of the amounts of products of the photolysis. The results are shown in Table 1.

With different illumination times, which caused from 1 to 16 % of benzyl chloride to decompose, the relative amounts of various products were constant except for a small increase in the relative amount of β -phenylethyl alcohol within the first two per cents of benzyl chloride decomposition. The relative amounts of the products also remained constant as the initial concentration of benzyl chloride was increased from 1.5×10^{-2} to 5.8×10^{-2} mol dm⁻³, except that the amount of β -phenylethyl alcohol increased slightly from 8.2 to 10.2 %. No attempt is made to explain the cause of these small changes. The decreases in the amount of benzyl chloride match well with the sum of the products, and it is therefore likely that all important products of the photolysis of benzyl chloride were detected. The ethylene glycol expected to form in the photolysis could not be detected by GLC, however.

RESULTS AND DISCUSSION

In the present study on the photolysis of benzyl chloride in methanol–water mixtures the following products were obtained: benzyl alcohol, benzylmethyl ether, bibenzyl, β -phenylethyl alcohol and small amounts of benzal-

dehyde (Table 1). In order to explain the observed products we propose the following mechanism:



This mechanism is similar to that proposed by Ichimura and Moi¹ for photolysis of benzyl chloride in gas phase in the presence of an excess of butane. In order to account for the products of nucleophilic reactions we have added the steps 2, 4, and 5.

Chlorine atoms formed by the photodissociation reaction may react in the solvent cage either with methanol by abstracting a hydrogen atom or by oxidizing the benzyl radical to benzyl carbonium ion, reactions 2 and 3, respectively. The relative rates of these two competing reactions can be determined from the ratio of the sum of twice the amount of bibenzyl and β -phenylethyl alcohol and the sum of the amounts of benzyl alcohol and benzylmethyl ether (Table 1 and Fig. 1). This ratio increases linearly as the mol fraction of methanol in water increases from a value

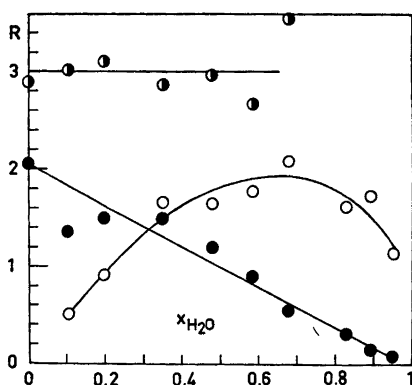
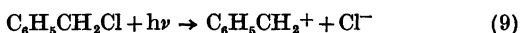


Fig. 1. Relative amounts of products (mol) in photolysis of benzyl chloride in methanol-water mixtures. Half-filled circles: (β -phenylethanol)/(bibenzyl); open circles: (methylbenzyl ether) (water)/(benzyl alcohol) (methanol); filled circles: (β -phenylethanol) + 2 (bibenzyl)/(methylbenzyl ether) + (benzyl alcohol). x is the mol fraction of water in the methanol-water mixtures.

of about zero in pure water to about 2 in pure methanol.

In water all the chlorine atoms formed oxidize the benzyl radicals to benzyl carbonium ions whereas in methanol one third of the chlorine atoms formed oxidize the benzyl radicals and two thirds abstract a proton from methanol molecules. If it is assumed that every chlorine atom reacts within the solvent cage and that in addition to the benzyl radical 8 methanol molecules are within the same minimum distance from the chlorine atom the chlorine atoms would react about 4 times faster with benzyl radicals than with methanol molecules.

The linear relationship of the ratio of two different types of products with the mol fraction of methanol indicates that benzyl radicals are produced in a secondary reaction (2) and not in a primary heterolytic photodissociation reaction (9).



A primary heterolytic photodissociation has been proposed in photolysis of substituted benzyl acetates⁶⁻¹⁰ and substituted phenyl esters.^{11,12} However, no proofs have been given in favour of either reaction (9) or reactions (1)

and (2) for photochemical nucleophilic reactions.

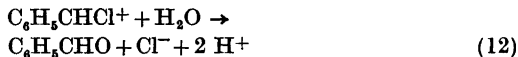
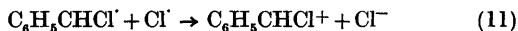
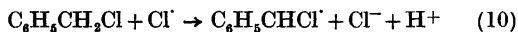
The benzyl radical does not readily abstract hydrogen atoms and if it is not oxidized by chlorine atoms, the benzyl radical combines with another benzyl radical to form bibenzyl or with methanoyl radical to form β -phenylethylalcohol.

The ratio of the two products, β -phenylethyl alcohol and bibenzyl, is approximately constant about 3.0, as shown in Fig. 1. Thus about 60% of the benzyl radicals combine with methanoyl radicals to form β -phenylethyl alcohol, and the rest of the benzyl radicals combine to bibenzyl. If all β -phenylethyl alcohol molecules are formed in the solvent cage this recombination is about 3 times faster than the competing escape of benzyl radicals from the cage in the whole range of methanol-water solvent mixtures. The relatively slow recombination reaction is due to the hydrogen chloride separating the two radicals, benzyl and methanoyl, in the solvent cage.

The benzyl carbonium ion formed in the reaction 2 may react with the nucleophiles chloride ion, water or methanol to form benzyl chloride, benzyl alcohol or benzylmethyl ether. The extent of the re-formation of the starting material, benzyl chloride, cannot be estimated from the present results. The ratio of the two other products, benzylmethyl ether and benzyl alcohol, varies with the solvent composition, as shown in Fig. 1, and a maximum value of about 1.9 is obtained in a solvent mixture where the mol fraction of methanol is about 0.7. The methanolysis reaction of benzyl cation is then about twice as fast as the hydrolysis reaction, whereas the methanolysis of benzyl chloride in the same solvent mixture was found to be about 6.3 times faster than the hydrolysis at 0 °C. There is then less discrimination among the fast nucleophilic reactions of benzyl cation than the slower nucleophilic reactions of benzyl chloride.

In solvent mixtures of low methanol content, small amounts of benzaldehyde were observed in the photolysis of benzyl chloride (Table 1). Small amounts of benzaldehyde has also been observed by electrolytic oxidation of substances which presumably form benzyl radicals as unstable intermediates, e.g. the oxidation of *o*-chlorophenylacetic acid in meth-

anol,¹³ of toluene in acetic acid¹⁴ and of *p*-methoxybenzyl alcohol in methanol.¹⁵ Small amounts of chlorine atoms escaping the cage may oxidize either benzyl chloride or benzyl alcohol to benzaldehyde.



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REFERENCES

1. Ichimura, T. and Moi, Y. *J. Chem. Phys.* 57 (1972) 1677.
2. Boyrakecken, F. and Nicholas, J. E. *J. Chem. Soc. B* (1970) 691.
3. Brockdehurst, B., Porter, G. and Savadotti, M. *Trans. Faraday Soc.* 60 (1964) 2017.
4. Arai, S., Tagawa, S. and Imamura, M. *J. Phys. Chem.* 78 (1974) 519.
5. Ivanov, V. B., Ivanov, V. L. and Kuzmin, M. G. *Zh. Org. Chem.* 9 (1933) 340.
6. Jaeger, D. A. *J. Am. Chem. Soc.* 96 (1974) 6216.
7. Jaeger, D. A. *J. Am. Chem. Soc.* 97 (1975) 903.
8. Jaeger, D. A. *J. Am. Chem. Soc.* 98 (1976) 6401.
9. Saltier, J. *Surv. Prog. Chem.* 2 (1964) 307.
10. Zimmerman, H. E. and Sandel, W. R. *J. Am. Chem. Soc.* 85 (1963) 915, 922.
11. Havinga, E. and Kronenberg, M. E. *Pure Appl. Chem.* 16 (1968) 137.
12. Cornelisse, J. and Havinga, E. *VIII Int. Conference on Photochemistry*, Edmonton 1975.
13. Woolford, R. G. and Liu, W. S. *Can. J. Chem.* 44 (1966) 2783.
14. Ross, S. D., Finkelstein, M. and Petersen, R. C. *J. Am. Chem. Soc.* 89 (1967) 4088.
15. Parker, V. D. and Burgert, B. E. *Tetrahedron Lett.* 20 (1968) 2411.

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