

## Mechanism of Photolysis of Benzyltrimethylammonium Salts in Hydroxylic Solvents

By DAVID C. APPLETON, DAVID C. BULL, RICHARD S. GIVENS, VERONICA LILLIS, JAMES MCKENNA,\*  
JEAN M. MCKENNA, and ANDREW R. WALLEY

(Chemistry Department, The University, Sheffield S3 7HF)

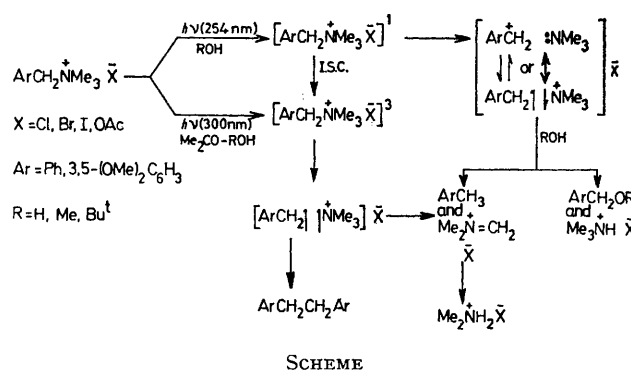
**Summary** Photolysis of benzyltrimethylammonium bromide in aqueous t-butyl alcohol gives benzyl t-butyl ether and some toluene by a singlet pathway with more toluene and bibenzyl by a triplet pathway, in each case *via* a reactive intermediate geminate pair (or pairs); analogous mechanisms are suggested for photolysis of a range of benzyltrimethylammonium salts in water or methanol.

PREVIOUS work<sup>1</sup> on the photolysis of benzylammonium salts and related systems has not disclosed the detailed mechanistic features of the decompositions. Our recent results are of interest in this respect, particularly since they provide an especially clear-cut differentiation between singlet and triplet pathways, and information on reaction intermediates. Anion, solvent, and nuclear-substituent variations in our work are indicated in the proposed reaction scheme, which is based on the following evidence.

(a) Products. Benzyltrimethylammonium bromide in aqueous t-butyl alcohol (10% water) gave benzyl alcohol, benzyl t-butyl ether, toluene, and bibenzyl. The iodide salt gave little toluene, no bibenzyl, and > 90% of benzyl methyl ether on photolysis in methanol. 3,5-Dimethoxybenzyltrimethylammonium iodide gave a similar product distribution, but more typically (*cf.* ref. 1) lower yields of benzyl methyl ether or benzyl alcohol were obtained (30–60% based on salt decomposed) together with the toluene and the bibenzyl on photolysis of the various salts (see Scheme) in methanol or water. Di- and tri-methylamine were also identified in the product mixtures as their protonated salts.

(b) Multiplicity. Toluene and bibenzyl were obtained from the acetone-sensitised photolysis of benzyltrimethylammonium bromide in aqueous t-butyl alcohol. Quenching by piperylene in the corresponding direct photolysis gave a linear Stern–Volmer plot ( $\tau = 4.1 \times 10^{-8}$  s) for bibenzyl

but a non-linear plot for toluene: evidently some (we estimate *ca.* 40%) of this product is also produced *via* the singlet pathway. Piperylene also quenched the phosphorescence of the quaternary bromide in mixed alcohol glasses at  $-170^\circ\text{C}$ . The conclusions drawn from these results



have been extrapolated to cover photolyses of all the salts examined in all the solvents (see Scheme). The short triplet lifetime explains the observed lack of sensitivity of product quantum yields (usually *ca.* 0.2–0.5 overall) to traces of oxygen.

(c) Intermediates. The stereochemical results reported in the following communication<sup>2</sup> imply at least one reactive intermediate between photoactivated quaternary salt and products in the ionic photolysis. This is represented in the Scheme as a geminate (ground-state) ion-pair; it is not presently clear whether the additionally required singlet radical-pair is a separate species or whether this is a case of resonance hybridisation.<sup>3</sup> For simplicity, any successive additional geminate pairs with differing degrees of solvation

are omitted from the Scheme. Part return to quaternary salt with retention of configuration at carbon and at nitrogen is not excluded on present evidence.

A species with  $\lambda_{\max}$  302 and 313 nm, and  $\tau$  ca. 100  $\mu$ s was observed in the flash photolysis of benzyltrimethylammonium iodide or bromide in methanol. The peak positions agree with those in the published<sup>4</sup> spectrum of the benzyl radical in alcohols, but since the quaternary iodide yields no bibenzyl we feel that in our work the observed spectrum

is associated in whole or in part with geminate radical pairs. Curiously, no analogous transients were observed in photolyses of well degassed methanolic solutions of 3,5-dimethoxybenzyltrimethylammonium iodide or 1-phenylethyltrimethylammonium bromide.

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<sup>1</sup> T. D. Walsh and R. C. Long, *J. Amer. Chem. Soc.*, 1967, **89**, 3943; M. A. Ratcliff, Jr. and J. K. Kochi, *J. Org. Chem.*, 1971, **36**, 3112.

<sup>2</sup> V. Lillis, J. McKenna, J. M. McKenna, and I. H. Williams, following communication.

<sup>3</sup> Cf. C. Walling, H. P. Waits, J. Milovanovic, and C. J. Pappiaonnou, *J. Amer. Chem. Soc.*, 1970, **92**, 4927.

<sup>4</sup> R. L. McCarthy and A. McLachlan, *Trans. Faraday Soc.*, 1960, **56**, 1187; T. O. Meiggs, L. I. Grossweiner, and S. I. Miller, *J. Amer. Chem. Soc.*, 1972, **94**, 7981, 7986.