Photochemical Preparation of Trialkyliodoammonium Iodides

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THE photolysis or the uranyl-photosensitized reaction of tetrabutylammonium iodide in an acidified aqueous solution leads to the precipitation of tributyliodoammonium iodide with the overall reaction[1]

$$R_4N^+ + 2I^- + H^+ \xrightarrow[(UO_2^{++})]{h\nu} R_3IN^+I^- + RH \qquad (1)$$

where R is butyl. The hydrocarbon produced can be collected over the aqueous solution for g.l.c. With the butyl compound, the gaseous hydrocarbon produced is mainly butane; small amounts of octane and butylene detected are probably formed from the recombination and disproportionation of butyl radicals.

We have extended the photochemical studies to other tetra-alkylammonium iodides, including methyl, ethyl, propyl, butyl, and isopentyl compounds. The experimental procedures were similar to those previously described,[1] and, except in the case of the methyl compound, photoprecipitation of the corresponding trialkyliodoammonium iodides was observed. The failure to precipitate the trimethyliodoammonium iodide from the acidified aqueous solution may be due to its solubility in water. However, its formation according to reaction (1) was assumed, since a mass spectrometric analysis of the gaseous products showed the formation of methane and a little ethane. All the other trialkyliodoammonium iodide products were checked by elemental and n.m.r. analysis.

U.v. absorption data for the derivatives [λ_{max} (EtOH): Et and Bu, 360, 291, 219; Pr, 258, 293, 220; isopentyl, 360, 293, 219 mμ] indicate that the three absorption bands are not dependent on the alkyl groups. The band at 219 mμ is undoubtedly the charge-transfer-to-solvent band of the iodide ions. The other two absorption bands at 360 and 291 mμ are similar to those exhibited by the tri-iodide ions. A quantitative spectrophotometric measurement of the u.v. absorption of triethyliodoammonium iodide in alcohol was undertaken. The extinction coefficient at 219 mμ was estimated to be 13,200 and, assuming from the literature[2] that the 360 and 291 mμ bands are due to tri-iodide ions, the extinction coefficients of these two absorption maxima were taken as 26,400 and 40,000. The results show that with a 10 μM solution, in which ion association is probably negligible, the concentrations of the iodide and tri-iodide ions are 8·7 and 0·67 μM, respectively. The relative ratio of $[I_3^-]$ to $[I^-]$ increases directly with the solution concentration up to about 10^{-4} M.

One of the possible mechanisms of producing tri-iodide ions when trialkyliodoammonium iodides were dissolved in alcohol, which is consistent with the experimental findings, involves the following steps:

$$R_3IN^+I^- \text{ (dissolved)} = R_3IN^+ + I^- \tag{2}$$

$$R_3IN^+ = R_3N + I^+ \tag{3}$$

$$I^+ + 2I^- = I_3^- \tag{4}$$

A recent e.s.r. investigation of γ-irradiated tetraalkylammonium iodides[3] showed that the primary chemical effect is the breaking of a C–C bond next to the nitrogen atom. In comparison, the present study of solid γ-irradiated trialkyliodoammonium iodides suggests the main chemical reaction is the rupture of the N–I bond leading to broad and unresolved e.s.r. spectra of iodine atoms and R_3N^+ radicals.

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