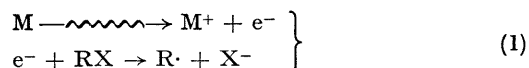# Geminate *Versus* Non-Geminate Recombination in Binary Mixtures of Alkyl Halides

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Summary Non-geminate recombination is shown to occur in liquid-phase photolyses and radiolyses of binary mixtures of alkyl halides.

THE photolysis and radiolysis of pure alkyl halides and of alkyl halides in solution has been studied by many groups.[1-3] Analysis of such systems following radiolysis indicates the role played by dissociative electron attachment reactions [reaction (1)]. Further support for the importance of

$$\left.\begin{array}{l} M \longrightarrow\!\!\!\wedge\!\!\wedge\!\!\wedge\!\!\wedge\!\!\wedge\longrightarrow M^+ + e^- \\ e^- + RX \rightarrow R\cdot + X^- \end{array}\right\} \qquad (1)$$

these reactions is obtained from the investigation of photo-ionization reactions of solutions containing tetramethyl-*p*-phenylenediamine (TMPD) and alkyl halides as solutes

[reaction (2)]. Radical production following photolysis

$$\left.\begin{array}{l} TMPD + h\nu \rightarrow TMPD^+ + e^- \\ e^- + RX \rightarrow R\cdot + X^- \end{array}\right\} \qquad (2)$$
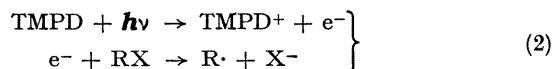
indicates that direct bond cleavage is the major contributing reaction [reaction (3)]. In all cases, the alkyl halide is separated into a so-called geminate pair which is held

$$RX + h\nu \rightarrow R\cdot + X\cdot \qquad (3)$$
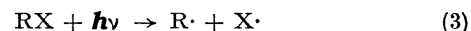
within a cage of surrounding molecules. Confirmation of these processes has been obtained in the solid state *via* e.s.r. studies of the trapped radicals, and it has been demonstrated that similar processes are equally important in the liquid phase by using such indirect techniques as scavenger studies, product analysis, and radio-isotope-tracer methods.

The reaction of original partners R· and X· to give back the same molecule RX is usually referred to as geminate recombination, whereas the reaction of any radical R· with species X· supplied by another pair is referred to as non-geminate recombination. Willard *et al.*[3a] have shown that
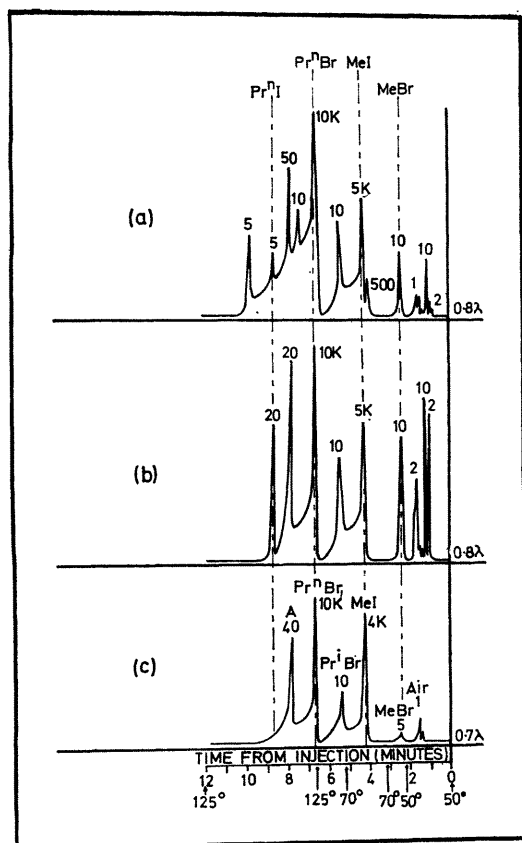

FIGURE. (a) *Radiolysed binary mixture*; (b) *photolysed binary mixture*; (c) *equimolar binary mixture of the two purified components*.

for solutions of alkyl halides in glassy matrices the iso-thermal decay of methyl radicals follows first-order kinetics for more than five half-lives, and that radicals of higher molecular weight obey so-called composite first-order kinetics. Willard *et al.*[4] have also shown that the radical decay rate is independent of the geminate partner, and depends only on the nature of the matrices and radicals involved. These data are interpreted to mean that recombination occurs by a geminate process.

Prior to any non-geminate processes, separation of the geminate pair must take place. It is known that species comprising the geminate pair are able to break out of the solvent cage in liquid-phase radiolyses and photolyses, as demonstrated by scavenger studies, tracer techniques, and general product analyses. Thus it should be possible to detect non-geminate processes in the liquid state, and perhaps in the solid state.

In order to determine the extent of non-geminate pro-cesses, if any, we investigated the radiolysis and photolysis of binary mixtures of alkyl halides in various phases, by

examination of the products formed by radiolysis, or photolysis, of equimolar mixtures of alkyl halides R_1X and R_2Y. In particular, the presence of cross-products R_1Y and R_2X caused by non-geminate recombination was sought, where the two radicals R_1· and R_2· are distinguish-able by either chemical form (*e.g.*, methyl and ethyl) or *via* radioactive tagging (*e.g.*, CH_3· and $^{14}CH_3$·).

Product analyses were carried out by gas chromatography with a modified Bendix ChromaLab 2100 dual-column dual-flame-ionisation detector unit. A 12 ft column packed with 5% w/w di-isodecylphthalate on 100—120 mesh Chromosorb G gave adequate analytical separation of the major products. Radiolyses were performed with a 300 Ci cobalt-60 source (dose rate of 3.55×10^{16} eV g^{-1} as deter-mined by a Fricke dosimeter), and photolyses by an unfil-tered super-pressure mercury lamp (Bausch and Lomb Monochromator source, approximately 5×10^{16} photons per second as determined by potassium ferrioxalate dosi-metry).

Radiolyses were made of samples contained in a cell with a minimum possible vapour space above the liquid so as to reduce any chance of non-geminate processes taking place in the gas phase. The ratio of vapour to liquid did not exceed 1:10 by volume. Photolyses were limited to the liquid phase by careful masking of the quartz reaction cell. Standard vacuum line techniques were employed to prepare binary mixtures of methyl iodide and n-propyl bromide, conventional chemical and physical methods being used for purification.

A typical gas chromatogram for the binary mixture prior to either photolysis or radiolysis is given in the Figure (c), and chromatograms for systems after radiolysis or photolysis are given in the Figure, (a) and (b), respectively. The only impurities found in the binary mixture prior to reaction were methyl bromide, isopropyl bromide, and one unidenti-fied component [peak A, Figure (c)].

Radiolysis at room temperature of the binary mixture (49·6 mole % MeI in Pr^{n}Br) to a dose of 3.02×10^{18} eV g^{-1} exhibited an approximately ten-fold increase in methyl bromide concentration, one of the predicted cross-products, and showed the presence of detectable quantities of the other cross-product, n-propyl iodide [see Figure (a) and (c)]. Photolysis of a similar binary mixture [50·2 mole % MeI in Pr^{n}Br, see Figure (c)] showed an eighteen-fold increase in methyl bromide concentration, and substantial quantities of n-propyl iodide.

The results in the Figure, (a) and (b), demonstrate the presence of the predicted cross-products, and thus the occurrence of non-geminate recombination in this liquid-phase system. It is interesting to consider further the relative yields of cross-product molecules MeBr and Pr^{n}I following radiolysis and photolysis. Quantitatively, the amount of dissociation of each molecular species in the binary mixture during photolysis should be approximately equal, and depend on the optical absorption coefficients for the molecules concerned. Provided that molecular environ-ments for each component are similar, *i.e.*, no solute clump-ing phenomena, and that radical lifetimes are comparable, approximately equal yields of the cross-product molecules would be expected. When corrected for the flame-ioniza-tion detector's sensitivity to carbon content rather than total number of molecules entering the detection zone, the chromatogram following photolysis should show an apparent

mole ratio of Pr^nI to MeBr of greater than unity. The data in the Figure (b) show a ratio of *ca.* 2 : 1. On the other hand, radical production during radiolysis depends on dissociative electron-attachment reactions rather than direct homolytic bond cleavage, and the electron-capture cross-section of a molecule is a marked function of its identity. Willard and his co-workers[3a,4] have shown that the relative efficiencies of radical production in the methyl halides are in the order Cl > Br > I, and that for any one halogen atom the efficiency decreases as the molecular weight of the alkyl group increases. From these data it would be expected that radiolysis of the binary mixture would lead to more decomposition of the MeI relative to the Pr^nBr, and thus to a $MeBr : Pr^nI$ cross-product molecular ratio of greater than unity. The data in the Figure (a) support this hypothesis.

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