

Photochemical Dehalogenation of Halogenobenzenes in Alkaline Alcoholic Solution

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Summary Free radicals generated photochemically in alkaline propan-2-ol bring about chain dehalogenation of dissolved bromobenzene and iodobenzene but chlorobenzene is non-reactive.

It has been shown that certain inorganic and organic substrates undergo ready dissociative electron transfer in solution with the ionized form of the dimethylhydroxymethyl radical, $(\text{CH}_3)_2\dot{\text{C}}\text{O}^-$ (I).¹⁻³ Criteria have been suggested for predicting the kind of substrates which will undergo this reaction.^{2,3} We present results on the reaction of chlorobenzene, bromobenzene, and iodobenzene in propan-2-ol solution with the radical anion (I). The latter was produced by reaction of radicals generated photochemically by absorption of light in the near-u.v. (>3000 Å) either by the substrate itself, in the case of

iodobenzene, or by dissolved di-t-butyl peroxide (DTBP) in the case of bromobenzene and chlorobenzene.

Solutions contained in Pyrex tubes were deaerated (freeze-pump-thaw cycles under vacuum or flushing with argon which had been presaturated with solvent) and exposed to a high-pressure mercury lamp. The reaction products were then analysed by gas chromatography. In the absence of base, benzene and acetone were produced in approximately equal amounts from each halogenobenzene solution. In the presence of potassium hydroxide the stoichiometry remained the same but the yield per unit exposure time increased for the bromobenzene and iodobenzene solutions, reaching maximum values when potassium hydroxide concentrations exceeded *ca.* 10^{-2}M . The yields for chlorobenzene solutions were essentially insensitive to the presence of potassium hydroxide. Since the optical density in the absorbing region is not changed

significantly by the presence of potassium hydroxide, increase in yields must reflect a chain process. Equating the rate of formation of benzene from neutral solutions with the rate of production of primary photolytic radicals, then chain length in alkaline solution may be defined as the observed rate of benzene formation divided by the rate of its formation from neutral solutions. For comparison, the effect of potassium hydroxide on reaction rate for all three halogenobenzenes are presented in terms of chain length in Figure 1.

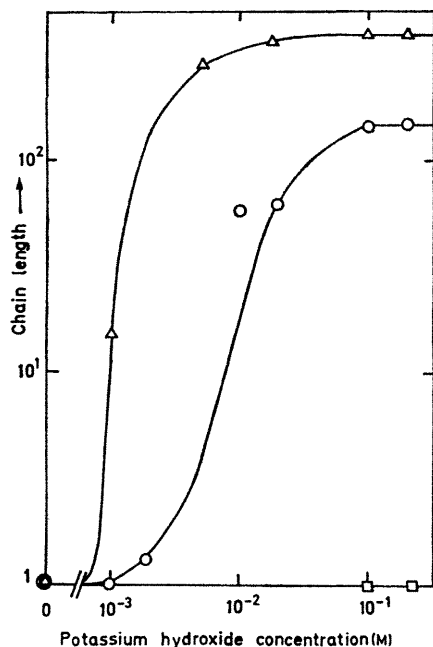
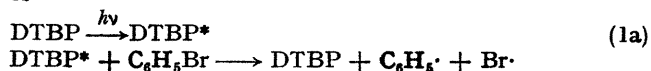


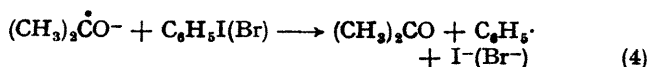
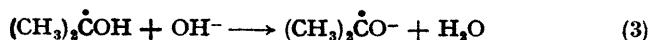
FIGURE 1. Dehalogenation yield as a function of potassium hydroxide concentration. (See text for definition of chain length.) Chlorobenzene —□—, bromobenzene —○—, iodobenzene —△—.

The observed chain dehalogenation of bromobenzene and iodobenzene may be explained by the following sequence:

Initiation



Propagation



The greatly reduced chain lengths observed when photolysis was carried out in the presence of dissolved molecular

oxygen is consistent with the free-radical nature of the initiation and propagation steps.

At any given halogenobenzene concentration, the dependence of product yield on time was linear up to ca. 50% consumption of halogenobenzene. This indicates that the rate-determining slow step in chain propagation is reaction 2 rather than 4. However, rather complex behaviour is observed in the dependence of chain length on the initial concentration of both bromobenzene and iodobenzene (Figure 2). While the decrease in chain length

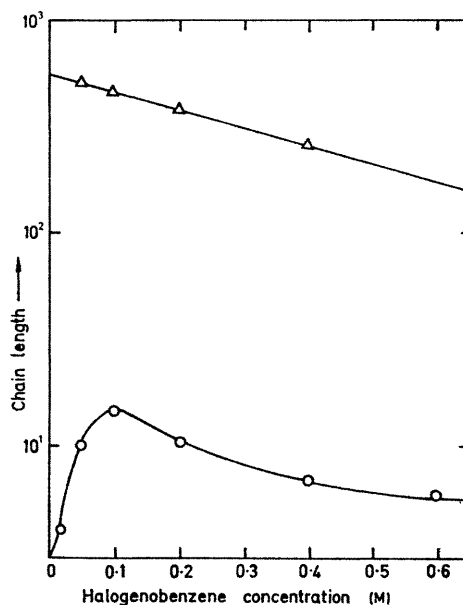


FIGURE 2. Dehalogenation yield as a function of halogenobenzene concentration. Bromobenzene —○—, iodobenzene —△—.

with increasing halogenobenzene concentration is consistent with the halogenobenzene itself acting as a chain terminator, this conclusion does not fit in with the linear yield-time dependence mentioned above. A possible explanation is that chain termination is *via* reaction between a chain carrier and an impurity (so far undetected) initially present in the halogenobenzene. This point is being investigated.

The reactions described above offer a new efficient method for dehalogenation of aryl bromides and iodides. The method is selective insofar as it offers a means of dehalogenation in the presence of aryl chlorides without the latter undergoing reduction. In addition, preliminary results indicate that when bromine and/or iodine atoms are attached to an aryl group which also contains a chlorine substituent, the former are removed selectively (*p*-chlorobromobenzene and *p*-chloriodobenzene are both reduced to chlorobenzene *via* a chain reaction in alkaline propan-2-ol).

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² W. V. Sherman, *J. Amer. Chem. Soc.*, 1968, 90, 6773.

³ W. V. Sherman, *J. Phys. Chem.*, 1968, 72, 2287.