A Radiation-induced Iodine Exchange Reaction

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ABUNDANT information on the reactivity of organic compounds towards the hydrated electron has recently become available.[1] In particular, aromatic compounds are the largest group for which a unified theory of reactivity could be developed.[2] However, this knowledge has not been applied extensively to preparative chemistry. Elias and his co-workers[3] have recently reported radiation-induced exchanges between aromatic iodine compounds and elementary iodine in organic solvents. The use of radioactive iodine in the elemental state gives rise to a number of practical difficulties. We report here a γ-radiation-induced exchange between *p*-iodobenzoate ion and iodide ion in aqueous solution which may be used to label the aromatic molecules with radioactive iodine, and suggest a mechanism involving the hydrated electron. The cæsium salt of iodobenzoic acid was employed because of its solubility in water.

An aqueous solution 0·5 molar in both cæsium *p*-iodobenzoate and cæsium [^{125}I]iodide gave, on irradiation (6·6 megarads of Co-60 γ-radiation), an organic acid labelled with ^{125}I. No incorporation of activity was observed in the absence of radiation. Analysis of this product as the methyl ester, using preparative scale g.l.c., gave only one component which was isolated and corresponded to methyl *p*-iodobenzoate (m.p. 114°, lit.,[4] 114°). Cæsium *p*-[^{125}I]iodobenzoate, prepared *via* the diazonium compound, was irradiated under similar conditions in the presence of inactive iodide. The specific activity of the acid was found to decrease on irradiation. These two experiments show that a genuine isotopic iodine exchange is being observed.

In order to incorporate a significant fraction of the active iodide into the organic molecule using moderate radiation doses (say up to 10 megarads), it is necessary to use solute concentrations lower than about 10^{-1} molar. In a typical experiment an aqueous solution equimolar (0·01 M) in cæsium [^{125}I] iodide and cæsium *p*-iodobenzoate gave, on irradiation (1·8 megarads of γ-radiation), an incorporation equal to 32% of the theoretical maximum.

We have studied in a preliminary manner the effect of varying pH, solute concentration, and the presence of thiosulphate on the yield of exchange. Some results are shown in the Table [G(exchange) = molecules exchanged per 100 e.v. energy observed]. Experiments 7–10 show the effect of added KOH on the exchange yield, and it is evident that the yield is lowered at pH > 9. The addition of thiosulphate (*cf.*, experiments 8, 11) similarly decreases the yield. These observations suggest that the formation of molecular iodine is important in the exchange process. Hydroxyl radicals produced by the action of radiation on water will oxidise the iodide to iodine as shown in reactions (1)—(3).

TABLE

Expt.	[I⁻] mole l.$^{-1}$	[*p*-iodobenzoate] mole l.$^{-1}$	G(exch.)
1	0·05	0·02	2·73
2	0·05	0·05	2·06
3	0·05	0·2	1·84
4	0·5	0·2	3·05
5	0·2	0·2	2·75
6	0·02	0·2	0·43
7	0·01	0·01	2
8	0·01	0·01	2[a]
9	0·01	0·01	0·5[b]
10	0·01	0·01	0·2[c]
11	0·01	0·01	0·2[d]

[a] 10^{-5} M in KOH; [b] 10^{-3} M in KOH; [c] 10^{-1} M in KOH; [d] 10^{-5} M in KOH and 10^{-3} M in thiosulphate.

$$\cdot\mathrm{OH} + \mathrm{I}^- \rightarrow \mathrm{OH}^- + \cdot\mathrm{I} \tag{1}$$

$$\cdot\mathrm{I} + \mathrm{I}^- \rightarrow \cdot\mathrm{I}_2^- \tag{2}$$

$$2\,\cdot\mathrm{I}_2^- \rightarrow \mathrm{I}_2 + 2\mathrm{I}^- \tag{3}$$

$$\mathrm{R{-}I} + e^-_{\mathrm{aq}} \rightarrow (\mathrm{R{-}I})^- \rightarrow \cdot\mathrm{R} + \mathrm{I}^- \tag{4}$$

$$\cdot\mathrm{R} + \mathrm{I}_2 \rightarrow \cdot\mathrm{I} + \mathrm{RI} \tag{5}$$

$$\cdot\mathrm{R} + \cdot\mathrm{I}_2^- \rightarrow \mathrm{R{-}I} + \mathrm{I}^- \tag{6}$$

$$\mathrm{R{-}I} + \cdot\mathrm{OH} \rightarrow \text{Phenolic products} \tag{7}$$

However exchange between *p*-iodobenzoate and elemental iodine does not occur in the absence of radiation. Thus some other radiation-induced process is involved in the exchange mechanism.

Iodoaromatic compounds react very rapidly with hydrated electrons ($k > 10^9$ mole litre^{-1} sec.$^{-1}$), giving iodide and an organic radical,[2] by reaction (4). Organic radicals are efficiently scavenged by iodine, and in our system this would lead to exchange (reaction 5).

We note that the maximum observed G(exchange) is approximately equal to G_e. At the solute concentrations used (*i.e.*, $\geqslant 10^{-2}$ M in acid), dissolved oxygen will not compete significantly for e_{aq}^-, and essentially all the hydrated electrons will react according to (4) above.

The observation that G(exchange) does not fall to zero in experiments 10 and 11 leads us to suggest that in addition reaction (6) may contribute to the exchange. The effect of varying solute concentration, seen in the Table, may be understood qualitatively by considering reaction (7) which will not lead to an exchange. The competition for OH radicals between iodobenzoate ion and iodide would lead to a dependence of G(exchange) on solute concentration qualitatively similar to that seen in the Table. Thus G(exchange) increases with iodide concentration at constant *p*-iodobenzoate concentration (experiments 3—6), but decreases at constant iodide concentration as the *p*-iodobenzoate concentration is increased (experiments 1—3).

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