96. *Some (n, γ) Effects in Iodobenzene.*

By P. F. D. Shaw.

Some of the factors affecting the reproducibility of extractions (by an aqueous reagent) of radio-iodine from neutron-irradiated iodobenzene have been studied. In the presence of iodine extractions are easily reproducible, but without iodine the amount of extractable radio-iodine is variable because of the variable formation of aliphatic radio-iodine compounds which are probably produced by the " rupture " of benzene rings by the energetic recoiling radio-iodine atoms.

The low value (about 40%) for the efficiency of extraction of radio-iodine from iodobenzene compared with that for other organic monohalides is probably caused by the formation of a stabilised " iodonium " radical, Ph_2I^-. The chief evidence for this is that phenyl radicals (produced by photolysis) in iodobenzene give compounds containing the Ph–I–Ph structure, and that the presence of nitric oxide during the neutron-irradiation of iodobenzene increases the efficiency of extraction; no similar effect could be observed in bromobenzene or ethyl iodide where it is assumed that no stabilised radicals are produced.

DURING investigation (Shaw and Collie, preceding paper) of the reproducibility of extraction (by an aqueous reagent) of radio-halogens from neutron-irradiated organic halides, the Szilard–

Chalmers effect in iodobenzene was studied. Although the efficiency of extraction had previously been reported to be lower than that for other monohalides, the independence of this quantity of the presence of iodine (Lu and Sugden, *J.*, 1939, 1273) indicated that extractions of this substance might be easily reproducible and that no " exchange " corrections would be necessary (cf. McKay, *Nature*, 1937, **139**, 283).

The reproducibility of extractions of neutron-irradiated iodobenzene containing a trace of free iodine is shown in Table I (*a*) and was better than 1%. Under these conditions no exchange between the extractable species and the bulk of the iodobenzene was observed after the irradiated liquid had been heated at 100° for 30 minutes before extraction.

TABLE I.

(*a*) Concn. of I (mg./l.).	Activity/min.*	(*b*) Concn. of Br (mg./l.).†	Activity/min.*
50	2315 ± 20	100	2325 ± 20
100	2295 ± 20	100	2305 ± 20
100	2320 ± 20		
100	2300 ± 20		
100	2320 ± 20		

* Corrected to saturation-irradiation and to time of removal from source.

† Extracting agent: sodium sulphite–potassium iodide solution.

In the absence of iodine, extractions were variable, the activities obtained being as much as 9% lower than those from iodine–iodobenzene solutions irradiated under the same conditions. Heating at 100° for 30 minutes before extraction caused a small variable decrease in the activity extracted. This did not appear to be caused by exchange between the extractable species and the iodobenzene since increasing the time of heating to 60 minutes did not further significantly lower the activity (corrected for radioactive decay). Possibly some of the extractable radio-iodine compounds add slowly to olefinic impurities produced by the recoiling atoms (see below).

The rôle of added iodine in stabilising the activities extractable seemed analogous to that of bromine in bromobenzene (Shaw and Collie, *loc. cit.*) and accordingly experiments, summarised in Table II, were performed to test the amount of aliphatic radio-iodine present: extracted neutron-irradiated specimens of iodobenzene were heated under reflux with silver acetate in alcohol. The quantity (extracted + aliphatic radio-iodine) was independent of the presence of iodine within experimental error; this indicates that, in the absence of iodine, the loss of activity from the extractable species may be caused by addition of elementary radio-iodine, etc., to compounds containing double bonds. The latter might be produced by disruption of benzene rings (as outlined for bromobenzene); the stabilising action of added iodine could then be explained by assuming that it added to such compounds, leaving the radio-iodine produced available for subsequent extraction. Confirmatory evidence was obtained from extractions of neutron-irradiated iodobenzene which contained a small quantity of added bromine [Table I (*b*)]. This bromine should saturate olefinic molecules present, and it can be seen that the activities extracted are consistent with this view since they are the same as those from iodine–iodobenzene solutions.

TABLE II.

(All activities corrected to saturation-irradiation, and to time of removal from neutron source.)

Initial state of iodobenzene.	Extracting agent.	Activity/30 mins. ($\times 10^{-6}$) (extracted).	Activity/30 mins. ($\times 10^{-6}$) (1st refluxing).	Activity/30 mins. ($\times 10^{-6}$) (2nd refluxing).	Total activity/30 mins. ($\times 10^{-6}$).
I present	Na_2SO_3	2·380 ± 0·022	0·310 ± 0·009	0·124 ± 0·010	2·814 ± 0·025
		2·375 ± 0·022	0·322 ± 0·006	0·124 ± 0·009	2·821 ± 0·025
No I present	KI	2·190 ± 0·021	0·398 ± 0·006	0·163 ± 0·009	2·751 ± 0·025

The first and the second refluxing recorded in Table II were for 30 and 60 minutes respectively; clearly the conversion of the aliphatic radio-iodine was never complete, but unfortunately further refluxing would not have given results which were statistically significant.

The aliphatic radio-iodine obtained in the presence of iodine may be produced by the direct combination of a de-energised radio-iodine atom with a " ruptured " benzene ring in the recoil process. The small variation of the activities extracted with and without free iodine present (about 9% of the total activity extracted from iodine–iodobenzene solutions), compared with the corresponding quantity (50%) for bromobenzene may be explained by the reluctance of iodine to add to double bonds, with the possible exception of " styrene-type " bonds which might be formed by the combination of " split " benzene rings and phenyl radicals in the vicinity of recoiling atoms. Such an explanation would account for the absence of a similar effect in ethyl iodide (Shaw and Collie, *J.*, 1949, 1217).

The efficiency of extraction in the presence of iodine (100 mg./l.) was 40·8 ± 1·2%. This value, though higher than that reported by Lu and Sugden (*loc. cit.*), appeared anomalously low compared with those for other organic monohalides [see Table III (*a*)], particularly when these are corrected for exchange when necessary [by multiplying by $\tau_{\text{radioactive}}/\tau_{\text{effective}}$ (see Shaw and Collie, *loc. cit.*)] in order to assess the efficiency of the direct production of extractable radiohalogen by the recoil process [Table III (*b*)].

TABLE III.

Substance (+100 mg. of free halogen/l.).	(*a*) Efficiency, %.	(*b*) Efficiency, % (corrected for exchange).	(*c*) Efficiency, % (for substance +50 mg. of halogen +100 mg. of NO/l.).*
C_6H_5I	41 ± 1	41 ± 1	49 ± 2
C_6H_5Br	56 ± 1	56 ± 2	55 ± 2
C_2H_5I	64 ± 2	65 ± 2	63 ± 2
C_2H_5Br	55 ± 2	60 ± 2	—

* See, however, Experimental section.

It is difficult to conceive that the difference between the efficiencies in bromo- and iodobenzene can be connected in any way with a difference in the nuclear properties of the two halogens, *e.g.*, in the energies of the quanta emitted on neutron capture, since one might then expect to find a similar difference in the efficiencies of ethyl iodide and bromide. This suggests that the low extraction efficiency in iodobenzene, relative to that for bromobenzene, might be caused by some chemical property of iodine which is not shared by bromine.

In bromobenzene one of the most probable " hot " reactions of energetic bromine atoms will be:

$$\text{PhBr} + \text{Br}^* \text{ (recoiling)} \longrightarrow \text{Ph-} + \text{Br} + \text{Br}^*$$

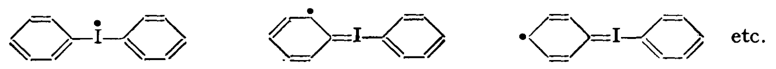
(cf. Libby, *J. Amer. Chem. Soc.*, 1947, **69**, 2523). If immediate combination of any of these radicals is not always possible owing to their high energies, it might be expected that the highly reactive phenyl radical will react with a neighbouring bromobenzene molecule as follows:

$$\text{Ph-} + \text{PhBr} \longrightarrow \begin{cases} \text{Ph·C}_6\text{H}_4\text{Br} + \text{H} \\ \text{Ph}_2 + \text{Br} \end{cases}$$

(cf. Hey, *J.*, 1934, 1966; Wieland, *Annalen*, 1934, **514**, 145).

It can be seen that the occurrence of reactions of this type will tend to increase the extraction efficiency, since combination of the radio-bromine atom (assumed to be de-energised by further collisions) with the hydrogen or bromine atoms produced will result in the formation of extractable radio-bromine compounds.

In the case of iodobenzene there appears to be an alternative fate for any free phenyl radicals produced, namely, addition to an iodobenzene molecule to form an iodonium radical. It might be expected that this would be resonant-stabilised in a way analagous to that for the diphenylmethyl radical, *i.e.*:



This might be possible for phenyl radicals in iodobenzene and not in bromobenzene because iodine can exist in a tervalent state of moderate stability as, for example, in phenyl iodochloride.

If this occurred, then two factors would tend to diminish the extraction efficiency in iodobenzene: first, the number of hydrogen and iodine atoms which might otherwise have been produced by the mechanism described above will be reduced and, secondly, there would be a chance of producing diphenyliodonium iodide molecules:

$$\text{Ph}_2\text{I}^- + \text{I}^* \longrightarrow \text{Ph}_2\text{I}^+\}\text{I}^-$$

The latter would carry the heat of recombination and might decompose into two molecules of iodobenzene, since this substance is known to have a low thermal stability (Hartman and Meyer, *Ber.*, 1894, **27**, 502) and to decompose rapidly at about 120°.

An attempt to confirm the general validity of this argument was made by irradiating, with neutrons, iodobenzene–iodine solutions which had been previously saturated with nitric oxide. If the iodonium radicals were stabilized, the above decomposition might occur relatively slowly, being limited by the frequency of collisions between the radicals and the radio-iodine atom; in this case, combination of some of the radicals with nitric oxide molecules could occur before such collisions; the above decomposition would therefore be reduced, and the extraction efficiency correspondingly increased. Such an effect was detected [see Table III (*b*)]; under similar conditions no increase in efficiency was obtained with bromobenzene, indicating that in this case the radicals capable of playing a rôle in the recoil process were short-lived. The ethyl iodide–nitric oxide irradiation was performed to show that the result obtained with iodobenzene was not caused by reaction between iodine atoms and nitric oxide, etc.

Evidence for the formation of the Ph–I–Ph structure under similar conditions has been obtained from the photolysis of iodobenzene by ultra-violet light. This was done while a slow stream of nitric oxide was passed through the liquid; after some time the nitric oxide was removed with hydrogen peroxide, the excess of which was destroyed with sulphur dioxide. On addition of potassium iodide, a yellow precipitate was obtained. Recrystallisation gave colourless diphenyliodonium iodide. The suggested reactions are:

$$\mathrm{PhI} + h\nu \longrightarrow \mathrm{Ph}^{-} + \mathrm{I}^{-}$$

$$\mathrm{Ph}^{-} + \mathrm{PhI}^{-} \longrightarrow \mathrm{Ph_2I}^{-} \xrightarrow{\mathrm{NO}} \mathrm{Ph_2I{\cdot}NO} \xrightarrow{\mathrm{H_2O_2}} \mathrm{Ph_2I^{+}\}NO_3^{-}}$$

$$\mathrm{Ph_2I^{+}\}NO_3^{-}} \xrightarrow{\mathrm{KI}} \mathrm{Ph_2I^{+}\}I^{-}}$$

Further evidence for the formation of the Ph_2I structure has been obtained from a specimen of iodobenzene irradiated with fast neutrons in the Harwell pile. The product contained diphenyliodonium iodide as fine crystals. Unfortunately this cannot be taken as evidence for the formation of diphenyliodonium radicals by the neutron-induced recoils, since the high γ-ray flux, with its associated secondary electrons, would also lead to a similar disruption of iodobenzene molecules.

EXPERIMENTAL.

Irradiations, extractions, and measurement of the iodobenzene were performed as described for ethyl iodide (Shaw and Collie, *J.*, 1949, 1217).

The transformation of the aliphatic iodine present in the irradiated material into silver iodide was carried out as described for bromobenzene (preceding paper), except that all operations were done in diffuse light to reduce photo-decomposition, and the distillations at reduced pressure to prevent production of iodine by pyrolysis in the last stages.

Neutron-irradiation of Organic Halides containing Nitric Oxide.—About 120 c.c. of the pure halide were saturated with nitric oxide (from nitric acid and copper; dried over calcium chloried; no stringent precautions were taken to exclude air). The halide (10 c.c.) was then shaken with a known amount of standard hydrogen peroxide solution and separated. The aqueous layer was titrated with standard potassium permanganate solution; the decrease in the hydrogen peroxide content was assumed to be caused by oxidation of nitric oxide to nitric acid. The amount of the nitrogen oxides present in the halides was always calculated as though nitric oxide only was present. The nitric oxide-saturated halide (100 c.c.) was then irradiated after the addition of 5 mg. of the appropriate free halogen.

After irradiation, the specimen was divided into two aliquots of which one was measured directly, and the other extracted with hydrogen peroxide and then with sodium sulphite solution before measurement. The extracted radio-halogen and an extract from the walls of the irradiation vessel were also measured to ensure that " settling " of the extractable species on the walls of the vessel had not occurred. During this treatment iodobenzene became yellow, but there was no detectable loss of nitric oxide during irradiation for 4 hours.

Production of Diphenyliodonium Iodide from the Photolysis of Iodobenzene.—Iodobenzene (40 c.c.) in a quartz vessel (diameter, 2·5 cm.) was held 1·5 cm. from a 100-w. quartz mercury-discharge tube. The whole was surrounded by a piece of metal which had been " smoked " with magnesium oxide in order to scatter some of the ultra-violet light back into the irradiation vessel. A slow stream of nitric oxide, prepared as above, was passed into the iodobenzene through a quartz delivery tube. Analysis of the solution showed that the equilibrium concentration of " nitric oxide " was approx. 0·25 g./l. (at 40°). After 3 hours the iodobenzene was shaken with hydrogen peroxide, which was then separated; the yellow peroxide layer was shaken with carbon tetrachloride to remove last traces of iodobenzene. Sulphur dioxide was passed into the peroxide layer until reduction was complete, and a few crystals of potassium iodide were added. A yellow precipitate was formed; the aqueous suspension was heated until the precipitate dissolved, and was then boiled, the yellow colour of the solution disappearing; on cooling a paler precipitate was recovered.

The whole process was repeated until enough precipitate had been obtained for analysis. The precipitate was filtered from the cooled suspension, and recrystallised twice from water and finally from alcohol (in order to ensure absence of iodide ions).

A specimen of diphenyliodonium iodide (cf. Lucas, Kennedy, and Wilmot, *J. Amer. Chem. Soc.*, 1936, **58**, 157) was purified by recrystallisation as described above. Its m. p. depended on the rate of heating, almost certainly because of decomposition (accompanied by a brown coloration) which began at about 120°. Under standard conditions the m. p. of the authentic material was 159—162°, and for the precipitate 160—162°, and the mixed m. p. was 162°. For analysis, diphenyliodonium iodide (9·74 ± 0·04 mg.; from the irradition experiment) was boiled in 5% nitric acid with a slight excess of silver nitrate, giving 5·60 ± 0·04 mg. of silver iodide (Calc. for $Ph_2I{\cdot}I$: 5·61 ± 0·02 mg.).

Under these conditions, it was found that approx. 15 mg. of diphenyliodonium iodide could be prepared for the liberation of about 50 mg. of iodine by photolysis.

On two occasions a suspension of colourless crystals, m. p. ~82° (decomp. at ~87°), was observed in the irradiated iodobenzene. They were soluble in hydrogen peroxide, and after reduction with sulphur dioxide the resulting solution gave a white precipitate on addition of potassium iodide. The quantity available did not suffice for identification as diphenyliodonium iodide, but on this assumption the original crystals were probably the I-nitroso-derivative.

Diphenyliodonium Iodide from Pile-irradiated Iodobenzene.—The irradiated iodobenzene (5 c.c. containing free iodine) contained 9 mg. of fine crystals, insoluble in cold carbon tetrachloride, water, or alcohol, but soluble in hot water or alcohol. After recrystallisation from alcohol they melted at 157°; 1·40 ± 0·04 mg. of the substance gave 0·63 ± 0·04 mg. of silver iodide (Calc. for $Ph_2I{\cdot}I$: 0·60 ± 0·02 mg.).

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THE CLARENDON LABORATORY, OXFORD.

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