412. *Radiolytic Reactions in Neutron-irradiated Bromobenzene.*

By MIRIAM MILMAN and P. F. D. SHAW.

Factors affecting the distribution of the isotopes ^{80}Br, ^{80}Br*, and ^{82}Br among the compounds produced in neutron-irradiated bromobenzene have been investigated. A radiation-induced exchange between bromobenzene and bromine atoms produced by radiolysis is largely responsible for the greater retention of the longer-lived isotopes, the exchanged atoms occupying the same positions in the benzene ring as the original atoms. The chief cause of the variable results obtained previously is probably the presence of water in the bromobenzene, which under the influence of radiation reacts to give phenolic products which with elementary radio-bromine then give other organic compounds.

WHEN organic bromides are bombarded with slow neutrons, a proportion of the radiobromine produced can be extracted with an aqueous reagent, *e.g.*, sulphite or bromide solutions. This is because the recoil energies of the bromine atoms from the γ-rays emitted on neutron capture are greater than the chemical binding energies of C–Br bonds, so that dissociation occurs, leaving some radioactive bromine combined in new chemical species (cf. Szilard and Chalmers [1]).

Three possible radioactive isotopes of bromine may be produced by this means: ^{80}Br (half-life 18 min.), its isomer ^{80}Br* (4·5 hr.) which decays into ^{80}Br by emission of weak γ-rays and internal conversion electrons, and ^{82}Br (35 hr.). Libby and his co-authors,[2,3] working with *iso*- and *n*-propyl bromide, have reported that the retentions (fraction of radio-bromine left in organic combination) of these isotopes are the same; we have confirmed this for ethyl bromide and ethylene dibromide containing small quantities of elementary bromine (unpublished work). Capron and Crèvecoeur,[4] using bromobenzene, found a difference in the retentions of ^{80}Br and ^{80}Br*, that of the longer-lived isotope being the greater: they also found that the ratio of the isotopic retentions depended on the energy distribution of the bombarding neutrons, and concluded that the ^{80}Br and ^{80}Br* atoms produced had different recoil energies which arose from variations in the γ-ray cascades following neutron capture. Capron and Oshima [5] and Capron and Crèvecoeur [6] find similar effects in bromoform, and in *iso*- and *n*-propyl bromide; however, they admitted that the purity of the last two compounds was poor, and, as Libby and his co-workers [2,3] have pointed out, the presence of impurities which could react with inorganic bromine to return it to organic combination would favour greater retentions for the longer-lived isotopes. Chien and Willard [7] examined the organic retention of ^{80}Br and ^{80}Br* in the propyl bromides, bromoform, and bromobenzene, and found that the isotopic retentions were the same in the aliphatic bromides, but were unable to confirm this for bromobenzene owing to poor reproducibility of results, and they concluded that the retention differences

---

[1] Szilard and Chalmers, *Nature*, 1934, **134**, 462.
[2] Fox and Libby, *J. Chem. Phys.*, 1952, **20**, 487.
[3] Rowland and Libby, *ibid.*, 1953, **21**, 1495.
[4] Capron and Crèvecoeur, *J. Chim. phys.*, 1952, **49**, 29.
[5] Capron and Oshima, *J. Chem. Phys.*, 1952, **20**, 1403.
[6] Capron and Crèvecoeur, *ibid.*, 1953, **21**, 1843.
[7] Chien and Willard, *J. Amer. Chem. Soc.*, 1954, **76**, 4735.

observed by Capron *et al.* were due to impurities. Evidence for the radiolytic production of compounds causing an increased retention in bromobenzene has been given by Shaw and Collie,[8] who showed that the effect of such compounds could be reduced by the addition of bromine before irradiation.

The purpose of the present investigation was to examine in more detail the behaviour of bromobenzene on neutron irradiation, with a view to removal of the apparent discrepancy between the constancy of isotopic retentions in aliphatic bromides and the observed differences in bromobenzene.

The retentions observed in pure bromobenzene have been reported by Shaw and Collie [8] and by Chien and Willard [7] to be variable; this has been confirmed in the present work. In order to obtain comparable results, therefore, the retentions of all the isotopes were found from measurements on the same specimen of bromobenzene after it had been irradiated for seven days. The results obtained from two experiments are given in Table 1, (*a*) and (*b*); the calculation of the retentions of the ^{80}Br is complicated by changes in chemical composition undergone when ^{80}Br* decays into ^{80}Br (see, *e.g.*, DeVault and Libby [9]) and is given in the Appendix. The retentions show qualitatively that the order of increasing retention R is the same as that of increasing half-life, *i.e.*, $R(^{82}\text{Br}) > R(^{80}\text{Br}^*) > R(^{80}\text{Br})$. This strongly suggests that the observed differences might be due to slow reactions, possibly with impurities, in which extractable radio-bromine reacts to give organic bromine compounds.

TABLE 1. *Retentions* (%) *in bromobenzene.*

	^{82}Br	^{80}Br*	^{80}Br
(*a*) No Br present	73·1	65·5	58·2
(*b*) „ „	77·0	68·2	54·9
(*c*) 2·1 × 10^{-4} molar fraction Br present	66·0	47·2	41·1
(*d*) „ „ „	67·3	45·7	43·3

(The statistical errors due to counting were about ±1% in each case.)

The retentions obtained when small quantities of inactive bromine were added to bromobenzene before irradiation also showed the same sequence [Table 1, results (*c*) and (*d*)]. In this case, exchange between the extractable radioactive species (HBr and Br_2) ensured that all the inorganic radio-bromine was present as elementary bromine. Provided that the quantity of impurities capable of reacting with bromine was small compared with the amount of inactive bromine present, these results eliminated the possible explanation that the observed retention sequence was due solely to slow reactions with impurities.

Exchange in Bromobenzene.—A clue to the explanation of the observed effects was obtained from preliminary attempts, made in collaboration with I. B. Simpson, to analyse the organic products arising from the reactions following neutron capture. It was found that the fraction showing the greatest difference between the ^{82}Br and the ^{80}Br* isotope was bromobenzene, the retention in this fraction always being greater for the longer-lived ^{82}Br (see Table 3). The effect of bromine added before irradiation was to increase the percentage of active bromobenzene for both bromine isotopes. This suggested that, under the conditions of irradiation, exchange occurred between elementary bromine and bromobenzene, the exchange in the pure system being restricted because some of the extractable bromine was present as hydrogen bromide. To test this hypothesis, pile-produced ^{82}Br was dissolved in bromobenzene, and aliquot parts were left for 2 days in daylight, near a Ra–Be source, near a radium source, and in the dark. The retentions observed were respectively 98·0, 56·1, 43·5, and 8·0%; the distribution of the organic activity was approximately the same in each case, the active compounds produced being bromobenzene (88% of the total organic activity), dibromobenzenes (2%), and aliphatic compounds (6%). The activity induced in the specimen left near the Ra–Be source was small compared with that of the ^{82}Br used, and was neglected. The aliphatic compounds were those which reacted with refluxing alcoholic potassium hydroxide and were probably produced owing to the

---

[8] Shaw and Collie, *J.*, 1951, 434.

[9] DeVault and Libby, *Phys. Rev.*, 1940, **58**, 688.

presence of water in the bromobenzene (see Experimental). Under similar conditions, bromobenzene containing active hydrogen bromide gave a retention of 7·6%, of which about two-thirds was present as bromobenzene, the rest being dibromobenzenes.

The exchange was studied for bromine concentrations which were small compared with that of bromobenzene; it may therefore be assumed that no reverse reaction occurs, so that for a given bromine concentration, the number of radio-bromine atoms (N) exchanging is given by

$$-\mathrm{d}N/\mathrm{d}t = \alpha N \qquad \text{(i)}$$

or

$$\log N_t/N_0 = -\alpha t \qquad \text{(ii)}$$

where α is the fraction exchanging in unit time and N_t/N_0 [equal to $(1 - r)$] is the fraction of elementary radio-bromine molecules remaining after time t. The exponential form of the exchange for small bromine concentrations was verified, an induction period sometimes being observed.

A probable mechanism is the following:

$$\mathrm{Br_2} \overset{k_1}{\rightsquigarrow} 2\mathrm{Br} \qquad (1)$$

$$\mathrm{Br} + \mathrm{Br} \xrightarrow{k_2} \mathrm{Br_2} \qquad (2)$$

$$\mathrm{Br} + \mathrm{BrBr^*} \underset{k_3'}{\overset{k_3}{\rightleftharpoons}} \mathrm{Br_2} + \mathrm{Br^*} \qquad (3)$$

$$\mathrm{PhBr} + \mathrm{Br^*} \xrightarrow{k_4} \mathrm{PhBr^*} + \mathrm{Br} \qquad (4)$$

If the overall rate of (4) is small compared with that of (3), we may assume that reactions (3) are in equilibrium, so that

$$[\mathrm{Br^*}]/[\mathrm{BrBr^*}] = k_3[\mathrm{Br}]/k_3'c \qquad \text{(iii)}$$

where c is the concentration of inactive bromine. Applying stationary-state conditions to the bromine atoms, we have

$$k_1 c = k_2[\mathrm{Br}]^2 \qquad \text{(iv)}$$

Substituting (iii) and (iv), we have, for the rate of exchange:

$$k_4[\mathrm{PhBr}][\mathrm{Br^*}] = \frac{k_3k_4}{k_3'}\cdot\frac{[\mathrm{PhBr}][\mathrm{Br}][\mathrm{BrBr^*}]}{c} = \frac{k_3k_4}{k_3'}\left(\frac{k_1}{k_2}\right)^{\frac{1}{2}}\frac{[\mathrm{PhBr}][\mathrm{BrBr^*}]}{c^{\frac{1}{2}}}$$

For a constant geometry, k_1 is constant; [PhBr] is also effectively constant over the bromine concentration studied, and therefore the rate of formation of radio-bromobenzene [equal to —(rate of loss of radio-bromine)] is

$$\beta[\mathrm{BrBr^*}]/c^{\frac{1}{2}}, \text{ where } \beta = (k_3k_4/k_3')(k_1/k_2)^{\frac{1}{2}}[\mathrm{PhBr}]$$

Comparison with (i) gives $\alpha = \beta/c^{\frac{1}{2}}$.

To check this mechanism, specimens of bromobenzene containing different concentrations of labelled bromine were placed equidistant from 500 mc of radium, so that the γ-ray intensity corresponded to about 50 R per hr., and were extracted after 4 days. The values of α were calculated as above; the graph of α against $c^{-\frac{1}{2}}$ is given in the Figure, on which are also plotted results obtained similarly but by using the radiation and neutrons from a 500 mc Ra–Be source; the graphs are roughly linear over the concentration range (10^{-5} to 10^{-2} molar fraction) studied, although there is some evidence that at higher bromine concentrations the rate is decreasing more rapidly than expected from a $c^{-\frac{1}{2}}$ dependence.

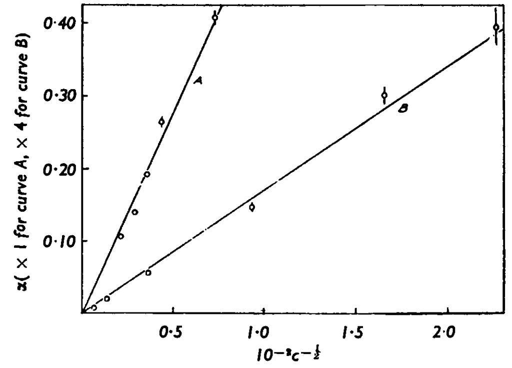
Mechanisms involving phenyl radicals or bromine atoms produced from the reaction

PhBr $\rightsquigarrow$ Ph + Br do not lead to $c^{-\frac{1}{2}}$ dependence, and consequently the contribution of this exchange to the reaction is small.

Mechanism of the Exchange.—Exchange with bromine atoms has been observed in compounds such as 2-bromopropene by Williams, Hamill, Schwarz, and Burrell,[10] who found that it involved proton transfer; for example:

$$CH_3{\cdot}CBr{:}CH_2 \xrightarrow{Br^*} CH_3{\cdot}\dot{C}Br{\cdot}CH_2Br^* \longrightarrow {\cdot}CH_2{\cdot}CHBr{\cdot}CH_2Br^* \xrightarrow{-Br} CH_2{:}CH{\cdot}CH_2Br^*$$

The equivalent mechanism in bromobenzene would involve substitution of the radio-bromine in the *ortho*- or *para*-position relative to the original bromine atom. To test whether any exchange occurred by this mechanism, solutions of labelled bromine in pure *o*-, *m*-, and *p*-dibromobenzene were left in ultraviolet light until complete exchange had occurred. To each isomer, carriers consisting of the other dibromobenzenes and 1 : 3 : 5-tribromobenzene were added; some of the *p*-dibromobenzene was recovered by freezing and the remaining carriers were fractionally distilled. The fractions containing dibromobenzenes were measured for activity and subsequently analysed by infrared spectrophotometry. The results (Table 2) show that for *p*- and *m*-dibromobenzene the exchange occurs without change of position of the entering atom. The errors given include those due to the analysis. A bad separation of the fractions obtained from the irradiated *o*-dibromobenzene rendered the result for this compound insignificant; however, if it was assumed that the activity of the *meta*-derivative was zero, the percentage of labelled *o*-dibromobenzene obtained was 92, which was consistent with the observed total retention. Exchange therefore occurs at the site of the existing bromine atoms in dibromobenzenes; it is probable that the exchange in bromobenzene is similar, since it is unlikely that the presence of another bromine atom would completely inhibit an exchange proceeding by proton-transfer.



Relation of the exchange rate α (*fraction exchanging per day*) *against* $c^{-\frac{1}{2}}$, *c being the molar fraction of inactive bromine present.*

A, for Ra–Be *source. B, for* Ra *source.*

TABLE 2. *Exchange in dibromobenzenes.*

		Activity (%) present as			
		(*a*) dibromobenzene			(*b*) tribromobenzene
Isomer irradiated	Br exchange (%)	*o*-	*m*-	*p*-	
para	91 ± 1	—	—	90 ± 1	0
meta	98 ± 1	−16 ± 20	127 ± 35	3 ± 1	0
ortho	99 ± 1	(See Experimental)	—	0	0

Products from Neutron Irradiation.—These products were analysed by adding dibromobenzenes and 1 : 3 : 5-tribromobenzene as carriers after extraction of the irradiated bromobenzene; the mixture was then refluxed with alcoholic potassium hydroxide; the potassium

---

[10] Williams, Hamill, Schwarz, and Burrell, *J. Amer. Chem. Soc.*, 1952, **74**, 5737.

bromide so obtained was acidified and treated with chlorine. The bromine liberated was taken up in inactive bromobenzene by successive extraction; it was hoped that this fraction (" aliphatic " in Table 3) would give a fair indication of the aliphatic radio-bromine compounds produced. However, it was found that the aqueous solution was still active after removal of bromine ions. This activity, which is discussed in the Experimental section, is called " aqueous " activity in Table 3.

The aromatic bromides were then obtained by distillation; in general, no attempt was made to separate the dibromobenzenes. Active compounds remaining after the distillation of the latter were measured together with the tribromobenzene as residues, which were found to contain less than 2% of the total activity.

TABLE 3. *Analysis of irradiation products* (% *of total activity*).

	No Br present				Br present (c in molar fractions)							
	(a)		(b)		(c) $c = 4·0 \times 10^{-4}$		(d) $c = 9·7 \times 10^{-5}$		(e) $c = 2·18 \times 10^{-4}$		(f) $c = 4·68 \times 10^{-4}$	
Fraction	^{80}Br*	^{82}Br	^{80}Br*	^{82}Br	^{80}Br*	^{82}Br	^{80}Br*	^{82}Br	^{80}Br*	^{82}Br	^{80}Br*	^{82}Br
Total retention	52·5	75·4	45·1	80·2	50·5	66·3	47·0	69·9	40·4	62·2	40·0	63·1
Bromobenzene	15·4	30·5	18·3	40·0	17·3	32·6	22·4	45·6	19·3	37·2	15·4	33·0
Dibromobenzenes ...	4·1	8·9	4·2	12·1	6·2	11·8	6·2	9·6	6·4	7·6	5·8	10·4
" Aliphatic "	17·1	25·4	16·1	20·8	14·7	15·7	8·0	7·9	7·1	4·5	4·9	6·6
" Aqueous " activity	—	—	—	—	13·9	11·7	2·7	3·3	3·7	3·6	—	—

In experiments (a), (b), and (c) the irradiated bromobenzene was not completely dry (see Experimental); in the other experiments it was dried over sodium. The statistical errors of counting were less than ±4% in all fractions except for the " aliphatic " and aqueous activities for which the errors are about ±5% (^{80}Br*) and ±10% (^{82}Br).

Owing to the short half-life of ^{80}Br, no analysis could be made of the distribution of its activity.

It was possible to obtain results for the analysis in bromine-free bromobenzene only when the latter contained traces of water. Sodium-dried bromobenzene always acquired a faint yellow colour owing to liberation of elementary bromine.

Effects of water. During the measurement of the amount of inorganic ^{80}Br produced by decay of organic ^{80}Br* compounds, it was found, contrary to expectation, that successive extracts of extracted irradiated bromobenzene always contained a significant amount of ^{80}Br* activity. Also, if bromobenzene was extracted after its removal from the neutron source, and if the elementary bromine liberated from the extract by chlorine was taken up in bromobenzene, the retention so obtained [equal to (1 — bromine activity from extract/total activity)] was always greater than the retention measured normally (organic activity/total activity). This indicated that active water-soluble compounds other than hydrogen bromide or elementary bromine were produced during the irradiations. The efficiency of extraction of these compounds by an aqueous reagent was greater for more basic reagents, suggesting that water-solubility was conferred by a phenolic or acidic group.

Water present might be expected to give phenolic compounds (cf. Stein and Weiss [11]) produced by OH radicals obtained from the radiolytic dissociation of water. These could then react with active bromine to form further brominated phenols.

To test this, pile-produced ^{82}Br was dissolved in bromobenzene saturated with water and left on the Ra–Be source for 12 hr., at the end of which the bromobenzene had become turbid owing to formation of aqueous hydrogen bromide. Inactive 1 : 3 : 5-tribromophenol was added to the irradiated solution and recovered by extraction with alkali followed by acidification. It was found that approximately 40% of the total activity was present in this fraction. A parallel experiment was also performed, the solution of active bromine in bromobenzene being left in darkness for 12 hr. to verify that no tribromophenol was formed without the influence of radiation, and that no exchange effects conferred activity to the carriers.

[11] Stein and Weiss, *J.*, 1949, 3245.

DISCUSSION

The aliphatic radio-bromine must be largely produced by slow reactions since in pure bromobenzene considerable differences in isotopic retentions are observed in this fraction; also, in the presence of bromine, the aliphatic retentions are reduced and (within experimental error) become equal for $^{80}Br^*$ and ^{82}Br. Wet bromobenzene containing bromine became paler during irradiation and also showed larger aliphatic and water-soluble fractions than those obtained from sodium-dried specimens. The increased retentions of these fractions in such circumstances are consistent with the known formation of tribromophenol, which might react further to give tribromophenol bromide (tetrabromo*cyclo*hexa-2 : 5-dienone). This could react with alkali to give polymers (Railford and LeRosen [12]) with the elimination of potassium bromide. If water-soluble, the polymerised material might account for the observed involatility of the aqueous fraction (see Experimental).

It is also possible that some of the active compounds originally present might be truly aliphatic, being produced by disruption of benzene rings by the recoil particles (Stein and Weiss [13]), followed by reaction of the fragments with the neighbouring active bromine atom. After the hydrolysis the activity from such compounds would be found largely in the aliphatic fraction, but bromo-acids or ketones might be produced from $-CBr_3$ or $>CBr_2$ groups and remain in the aqueous fraction.

The formation of active aliphatic products in incompletely dry bromobenzene containing no bromine could be explained similarly, the observed activities being greater because no inactive bromine was present to undergo preferential reaction with phenols, etc., produced. However, the possibility of production of unsaturated aliphatic compounds by the recoil particles [13] and their subsequent saturation by active bromine is not excluded.[8]

The sum of the individual fractions should ideally be equal to the measured retentions; that this is not so is probably because the hydrolyses of the aliphatic compounds present were not complete, and it was difficult to avoid losses in these fractions. More confidence can be placed in the values obtained for the mono- and di-bromobenzene fractions, since in these allowance for losses could be made exactly.

When bromine is present in the irradiated bromobenzene the variation of the activity in the bromobenzene fractions can be satisfactorily explained on the basis of the observed exchange. Since the rate of production of the active extractable bromine from the recoil process is equal to the total rate of loss from this fraction, at equilibrium we have $r = I(\lambda + \beta/\sqrt{c})$, where r is the rate of formation and I is the number of radio-bromine molecules of decay constant λ present at equilibrium. If i is the corresponding quantity which would have been observed had no exchange occurred, then r would have been equal to $i\lambda$, that is,

$$r = i\lambda = I(\lambda + \beta/\sqrt{c}), \text{ or } i - I = I\beta/\lambda\sqrt{c}$$

On division by the total number of radioactive atoms produced this becomes $e - E = \beta E/\lambda\sqrt{c}$, where e and E are the efficiencies of the overall extraction process, *i.e.*, $E = (1 - r)$.

$(e - E)$ is the fraction of the radioactive bromine atoms exchanged; this quantity, subtracted from the observed bromobenzene activities given in Table 3, should therefore give the fraction of active bromobenzene produced during the recoil process. To be consistent with the observations of Libby, Willard, and others, this quantity should be the same for both isotopes, and in view of the small concentrations of inactive bromine present it should also be the same for all specimens; that this is approximately true can be seen in Table 4; under the conditions of irradiation the value of β calculated from exchange data was $2{\cdot}08 \times 10^{-4}$ (molar fraction)$^{\frac{1}{2}}$/hr.

A similar calculation for the specimens which did not contain bromine during irradiation is not possible since the effective concentration of elementary bromine is not known.

---

[12] Railford and LeRosen, *J. Amer. Chem. Soc.*, 1946, **68**, 397.

[13] Stein and Weiss, *J.*, 1949, 3254.

In view of the complexity of the other processes shown to occur, for example, the formation of dibromo- and phenolic derivatives, the differing isotopic retentions in other fractions could be treated similarly to those in bromobenzene; the overall retentions for the three bromine isotopes might then become the same, as found in aliphatic bromides.

TABLE 4.

Molar fraction of bromine	$Ph^{80}Br^*$ (%)	$(e - E)$	$Ph^{80}Br^*$ (%) for no exchange	$Ph^{82}Br$ (%)	$(e - E)$	$Ph^{82}Br$ (%) for no exchange
$9{\cdot}70 \times 10^{-5}$	22·4 ± 0·6	7·1 ± 0·2	15·3 ± 0·6	45·6 ± 1·3	32·0 ± 1·0	13·6 ± 1·6
$4{\cdot}00 \times 10^{-4}$	17·3 ± 0·5	3·3 ± 0·1	14·0 ± 0·5	32·6 ± 1·0	17·7 ± 0·5	14·9 ± 1·3
$4{\cdot}68 \times 10^{-4}$	15·4 ± 0·5	3·7 ± 0·1	11·7 ± 0·5	33·0 ± 1·1	18·0 ± 0·5	15·0 ± 1·2
$2{\cdot}18 \times 10^{-4}$	19·3 ± 0·6	5·3 ± 0·2	14·0 ± 0·6	37·2 ± 1·1	26·8 ± 0·9	10·4 ± 1·4

The sharp reduction in retention on increasing the bromine concentration observed by Chien and Willard [7] is to be expected because of the $c^{-\frac{1}{2}}$ dependence of the exchange; this might also account for the differences in the ^{80}Br and ^{82}Br retention ratios found by Capron *et al.*[4, 5, 6] when they altered the position of their bromobenzene relative to the neutron source and hence the γ-ray flux.

EXPERIMENTAL

Neutron Irradiation.—Specimens to be irradiated were placed round a 500-mc Ra–Be source held centrally in a large paraffin trough containing water, and the whole was covered with a block of paraffin wax. Irradiations were performed in darkness. Before irradiation, specimens were stored in daylight to reduce so far as possible any induction period preceding the exchange induced by radiation from the source.

Materials.—Bromobenzene was obtained from British Drug Houses Ltd. and was purified by keeping it with bromine in daylight until no further loss of colour occurred. It was then shaken with dilute sodium sulphite solution and washed with water. After storage over calcium chloride it was distilled through a 15-in. column packed with glass helices. Before use it was dried either by boiling it to expel a little bromobenzene vapour which contained most of the water, or by storing it over sodium and performing subsequent operations in a dry-box containing phosphoric oxide. "AnalaR" bromine was obtained from the same source and was used without further purification. Pile-produced ^{82}Br was available as ammonium bromide; bromine was obtained from this by mixing it intimately with a large excess of manganese dioxide and treating it with sulphuric acid, the evolved bromine being condensed. Hydrogen bromide was made by treating the ammonium bromide with phosphoric acid; a small quantity of bromine evolved was removed by bubbling the evolved gas through bromobenzene.

Extraction and Measurement of Samples.—The irradiated liquid was normally split into two specimens, one of which was extracted with a dilute solution of sodium sulphite containing, when necessary, sodium bromide as a carrier. After the extraction the liquid was dried ($CaCl_2$) and a little bromine was added, to ensure that the activity from $H^{80}Br$ which might be produced from the decay of $^{80}Br^*$ remained in solution by exchange with the added bromine. If this precaution was neglected there was considerable danger of losing activity on the walls of the containing vessel. The second sample was retained for measurement of the total activity produced; when bromine was not present during the irradiation it was added to prevent accumulation of the inorganic activity on the walls of the containing flask or counter. The flask used for the irradiation was allowed to drain and was extracted separately with sulphite–bromide solution. This was then acidified and treated with chlorine, the liberated bromine being taken up into inactive bromobenzene by successive extraction. The activity from this, after correction for dilution, was added to the total activity obtained.

An M-6 counter, supplied by Twentieth Century Electronics Ltd., was used to determine the activities. Measurements were made at least 3 hr. after the last chemical or physical operation in order to ensure that the ^{80}Br produced directly by neutron capture had decayed and that the ^{80}Br from $^{80}Br^*$ was in transient equilibrium. The counts from the decay of $^{80}Br^*$ were small, the particles counted being chiefly those from the ^{80}Br disintegrations. Second measurements were made 15 hr. later and the activities due to the $^{80}Br^*$ and ^{82}Br were calculated from the two measurements.

Exchange.—The exponential nature of the exchange was checked by irradiating a solution of ^{82}Br in bromobenzene with a 1000-w tungsten lamp at 15°. Portions (1 ml.) were removed at constant time intervals and extracted with sulphite; carbon tetrachloride (10 ml.) was then added and the solution was separated and dried ($CaCl_2$) before measurement. Before following the exponential law, the exchange showed an induction period, the duration of which was different for different specimens of bromobenzene; by following the above purification procedure the delay was about 0·05—0·10 of the half-period for exchange. The dependence of the exchange on the total bromine concentration was determined by making up a series of solutions of inactive bromine in bromobenzene. These were then kept in light to destroy the inhibitor responsible for the induction period, and aliquot parts of labelled bromine were added in darkness. The solutions were arranged symmetrically round 500 mc of radium at a distance of 9 cm. and were extracted after 3—4 days' irradiation.

The exchange between bromine and dibromobenzene was studied by dissolving labelled bromine in the *ortho-* and the *meta-*isomer and in a solution of *p*-dibromobenzene in carbon tetrachloride; the solutions were irradiated for 20 hr. with ultraviolet light. After extraction equal (weighed) quantities of the remaining dibromobenzenes and a little **1** : **3** : 5-tribromobenzene were added. Some *p*-dibromobenzene was obtained by freezing the mixture; after recrystallisation from alcohol a weighed quantity was dissolved in 10 ml. of carbon tetrachloride and its activity was determined; the total activity due to the *para*-isomer in the original mixture was calculated from the known recovery and dilution. The remaining mixture was fractionally distilled; weighed amounts of consecutive fractions were diluted and their activities were determined. The infrared absorption spectra of these fractions were taken, and analyses were obtained by comparison with the spectra of pure specimens of *o*-, *m*-, and *p*-dibromobenzene. The accuracy of the analyses as judged from the results for different absorption bands was ±5%.

Products from Neutron Irradiation.—100 ml. of bromobenzene were irradiated with reproducible geometry between the specimen and source. On removal from the source 25 ml. were retained for measurement of the total activity, the remainder being extracted; to 50 ml. of this, weighed amounts of *o*-, *m*-, and *p*-di- and **1** : **3** : 5-tri-bromobenzene were added and the mixture was refluxed with 50 ml. of 2N-alcoholic potassium hydroxide for 2 hr. The alcohol was distilled off and the flask and residue were washed with sodium bromide solution; a trace of bromine was added to the aromatic fraction, the purpose of which was to saturate olefinic bromo-compounds in which the bromine might be relatively inactive. The bromine was then extracted with sulphite solution and the refluxing was resumed after addition of a further 50 ml. of 2N-alcoholic potassium hydroxide. The process was then repeated and the aqueous extracts were evaporated to a small volume, acidified, and treated with chlorine, the liberated bromine being taken up into inactive bromobenzene by successive extraction (aliphatic fraction). The activity of the aqueous residues was corrected for that of ^{40}K, and also for the differing self-absorption in water and in bromobenzene to enable comparison with other fractions (measured in bromobenzene). No activity from the aqueous residues could be distilled in steam whether the solution was acid or alkaline. High-boiling compounds (*e.g.*, dibutyl phthalate) were added to the residue and distilled off; a negligible activity was found in the distillate. A large portion of the activity was not water-soluble, and remained in a flocculent precipitate, the nature of which was not determined.

The remaining mixture of the aromatic bromine compounds was distilled and the mono- and di-bromobenzenes were measured after dilution with inactive bromobenzene. The **1** : **3** : 5-tribromobenzene was not distilled but left as a residue in the flask.

Formation of Bromophenol.—Pile-produced ^{82}Br was added to bromobenzene which had been previously saturated with water. The solution was split into two aliquot parts, one of which was left in darkness, the other being left on the Ra–Be source for 3 days. The activity of the bromobenzene induced by the neutron source was negligible compared with that of the ^{82}Br added. The bromobenzene was extracted with an alkaline sodium sulphite solution containing a weighed amount of tribromophenol. The latter was recovered by acidification and was recrystallised; it was made up to a standard volume and its activity determined.

APPENDIX

Measurement of the ^{80}Br retentions is complicated by the formation of inorganic ^{80}Br from the decay of organic ^{80}Br* and *vice versa.* In order to determine the retentions it is therefore necessary to know the fraction of organic ^{80}Br* decaying to inorganic ^{80}Br (f_1) and the fraction of inorganic ^{80}Br* decaying to give organic ^{80}Br (f_2). f_1 can be determined by extracting bromobenzene, and re-extracting it 4 hr. later, when any ^{80}Br produced directly by the (n, γ) reaction will have decayed to a negligible activity. f_2 was determined by leaving unextracted bromobenzene for 4 hr., to allow the decay of directly produced ^{80}Br, and then extracting the solution. Neglecting the activity due to ^{82}Br, for which allowance is easily made from measurements taken 15 hr. later, we have for the activity remaining in the bromobenzene

$$\{(1 - f_1)N_0 + f_2N_i\}\lambda_1\lambda_1/(\lambda_2 - \lambda_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

where N_0 and N_i are the number of organic and inorganic ^{80}Br* atoms at the time of extraction and λ_1 and λ_2 are the decay constants of ^{80}Br* and ^{80}Br respectively.

At the time of measurement, t min. after extraction, the activity in the bromobenzene is

$$\{[f_2N_i + (1 - f_1)N_0]e^{-\lambda_2 t} + N_0(e^{-\lambda_1 t} - e^{-\lambda_2 t})\}\lambda_1\lambda_2/(\lambda_2 - \lambda_1) \quad . \quad . \quad . \quad (b)$$

The last term of this represents the new ^{80}Br activity produced by the decay of ^{80}Br*.

The extracted bromobenzene was measured 4 hr. later (to re-establish transient equilibrium) and N_0 and $(N_0 + N_i)$ were determined. As f_1 is known, this enables f_2 to be calculated from (b).

Calculation of the retention. If ν_0 is the number of organic ^{80}Br atoms, produced directly by neutron capture, present at the time of removal from the source, and $(N_0' + N_i')$ are the corresponding numbers of organic and inorganic ^{80}Br* atoms, at the time of extraction t_1 min. later, the activity of the extracted fraction is

$$A_1 = \{\nu_0 + [f_2N_i' + (1 - f_1)N_0']\lambda_1/\lambda_2\}\lambda_2 e^{-\lambda_2 t_1} + [f_2N_i' + (1 - f_1)N_0'](e^{-\lambda_1 t_1} - e^{-\lambda_2 t_1})\lambda_1\lambda_1/(\lambda_2 - \lambda_1)$$

At the time of measurement (t_2 min. after the removal from the source) the activity is

$$A_2 = A_1 \exp[-\lambda_2(t_2 - t_1)] + N_0'\{\exp[-\lambda_1(t_2 - t_1)] - \exp[-\lambda_2(t_2 - t_1)]\}\lambda_1\lambda_2/(\lambda_2 - \lambda_1)$$

N_0' and N_i' are determined from the measurements of the extracted (N_0') and unextracted ($N_0' + N_i'$) bromobenzene made 4 hr. later. f_1 and f_2 being known, ν_0 may be calculated.

The calculation of the ^{80}Br in the unextracted fraction is straightforward. If ν_i is the number of inorganic ^{80}Br atoms produced directly by neutron capture, the total activity from ^{80}Br at the time of removal from the source is

$$A_3 = (\nu_0 + \nu_i)\lambda_2 + (N_0' + N_i')\lambda_1$$

At the time of measurement (t_3 min. later)

$$A_4 = A_3 e^{-\lambda_2 t_3} + (N_0' + N_i')(e^{-\lambda_1 t_3} - e^{-\lambda_2 t_3})\lambda_1\lambda_2/(\lambda_2 - \lambda_1)$$

Hence $(\nu_0 + \nu_i)$ and the retention, $\nu_0/(\nu_0 + \nu_i)$, can be calculated.

The authors thank Lord Cherwell, F.R.S., for laboratory facilities, and Dr. F. B. Strauss of the Dyson Perrins Laboratory who kindly took the infrared spectra.

CLARENDON LABORATORY, PARKS ROAD, OXFORD. [*Received, November* 16*th*, 1955.]