882. *Post-irradiation Reactions in Neutron-irradiated Liquid Bromobenzene*

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The post-irradiation reaction in liquid bromobenzene, discovered earlier, has now been investigated at other temperatures, and also in heptane solution. After neutron irradiation, the organic ^{82}Br activity shows a rapid increase with time, followed by a plateau in which very little or no change occurs. In most cases, the reaction follows second-order kinetics with respect to a fraction of the inorganic ^{82}Br concentration.

Irreproducibility observed earlier in the kinetics was removed by employing a new separation method of the inorganic from the organic activity, using heptane and a saturated solution of potassium bromide in ethanol. By following the reaction very soon after the end of the irradiation, values of total organic retention of ^{82}Br in pure bromobenzene as low as 23·3% could be detected, the corresponding value for $Ph^{82}Br$ being 7·5%. These retentions increased to 66·7 and 29·6%, respectively, after keeping for 1 hr. at 50°. Extrapolation of the second-order plots to zero time gave values of retention close to zero.

No such reaction could be detected for the ^{80m}Br activity, the values of total retention obtained being in agreement with those reported in the literature, irrespective of the time of keeping prior to analysis.

In irradiated pure bromobenzene, the post-irradiation reaction at low temperatures did not appear to be temperature-dependent, and the larger fraction of the increase in organic ^{82}Br was due to an increase of the parent compound activity. When solutions of bromobenzene in heptane were irradiated, the same phenomena were observed, but the final retentions obtained were lower, this being almost exclusively due to a decrease in retention of parent compound. Moreover, the rate was now temperature-dependent, the reaction being faster at lower temperatures. The method of purification of the bromobenzene and the neutron flux used in irradiations did not appear to affect the course of the reactions and the values of the retention obtained. A possible mechanism of the reaction is discussed, and the removal of irreproducibility in bromobenzene experiments, widely reported in the literature, is pointed out.

WHEN organic bromides are irradiated with neutrons, they undergo the Szilard–Chalmers reaction,[1] in which a proportion of the radiobromine produced by radiative neutron capture is found in inorganic form and can be extracted with an aqueous reagent.

Many authors [2-6] working with bromobenzene have reported that the retention (fraction of organically bound radiobromine atoms) in this compound is variable. This irreproducibility has been ascribed to small amounts of impurities present in bromobenzene or produced radiolytically during irradiation. These impurities could react with extractable radiobromine to give organic bromine compounds. Willard [6] tried fifteen equally good methods of purification and the retention values varied greatly (54—90%); he sometimes observed major variations in retention with different samples obtained from the same bottle.

We discovered [7] that, in many liquid organic bromides, including bromobenzene, a post-irradiation reaction takes place when the irradiated sample is kept at 40°. This

[1] L. Szilard and T. A. Chalmers, *Nature*, 1934, **134**, 462.
[2] P. F. D. Shaw and C. H. Collie, *J.*, 1951, 434.
[3] P. C. Capron and E. Crevecoeur, *J. Chim. phys.*, 1952, **49**, 29.
[4] J. C. W. Chien and J. E. Willard, *J. Amer. Chem. Soc.*, 1954, **76**, 4735.
[5] M. Milman and P. F. D. Shaw, *J.*, 1956, 2101.
[6] J. E. Willard, " Proceedings of the Symposium on Chemical Effects of Nuclear Transformations," I.A.E.A., Vienna, 1961, vol. I, p. 215.
[7] N. A. Katsanos and A. G. Varvoglis, *J.*, 1964, 5935.

is shown by a pronounced increase in retention of ^{82}Br with time and, in most cases, follows second-order kinetics with respect to a fraction of the inorganic radiobromine concentration. If irradiation times are kept short ($\frac{1}{2}$—3 min.) and the delay between irradiation and treatment of the samples is always the same (15 min.), then reproducible retention values are obtained for bromobenzene, irrespective of the purification method and the neutron flux used in the irradiations. The rate of the post-irradiation reaction, however, and the final retention obtained, seemed to be influenced by both the above-mentioned factors, so that reproducible kinetics could not be obtained. Evidence has been given elsewhere [7] that the phenomena observed could not be due to exchange reactions similar to the reactions observed by Milman and Shaw.[5]

The objects of the present investigation were: (i) to see whether the irreproducibility in the kinetics of the above-mentioned phenomenon could be removed, this being probably due to the inefficiency of the conventional extracting reagents; and (ii) this having been accomplished, to study in more detail, and as soon as possible after the end of the irradiation, the reaction in bromobenzene. In this way, information could be obtained concerning the mechanisms of hot-atom reactions in liquids, based on the detailed kinetics of the phenomena. For this purpose, the studies were extended to other temperatures, in the range 50 to —28°, and also to solutions of bromobenzene in heptane. Effects due to both ^{82}Br and ^{80m}Br were studied.

EXPERIMENTAL

Materials.—Bromobenzene (" Puriss "; Fluka A.G.) was purified by means of preparative gas chromatography, using a $\frac{3}{8}$ in. × 20 ft. column. No impurity was detected when the purified product was analysed on another chromatographic column ($\frac{1}{4}$ in. × 30 ft.) having a sensitivity of 1 part in 10^5. Heptane (" for ultraviolet spectroscopy "; E. Merck A.G.) and absolute ethanol (" Pro analysi "; E. Merck A.G.) were used without further purification.

Neutron Irradiation.—All irradiations were performed in the swimming-pool reactor of Nuclear Research Centre " Democritus," operated at a power level of 100 kw. Specimens of bromobenzene (5—10 ml.), either pure or diluted with heptane, contained in a small, glass stoppered cylindrical Pyrex vessel, were placed behind a 3 in. thick lead block situated at a distance of 6 in. from the reflector of the reactor core. Under these conditions, the thermal-neutron flux was 5×10^9 neutrons cm.$^{-2}$ sec.$^{-1}$. Accompanying γ-doses, measured by means of the aerated Fricke dosimeter [$G(Fe^{3+}) = 15\cdot6$], were found to be *ca.* 1300 rad.min.$^{-1}$. The duration of each irradiation was 1—3 min., and the temperature of the surrounding water was 24° $\pm$ 1°.

Procedure, and Analysis of Samples.—Immediately after irradiation, the vessel was placed in a thermostat and kept at a constant temperature throughout the experiment, precautions being taken to prevent daylight from reaching the liquid. At definite time intervals, starting from *ca.* 1 min. after the end of irradiation, 0·5-ml. portions were withdrawn from the vessel and the separation of the inorganic from the organic radiobromine was carried out as follows. The irradiated bromobenzene was mixed with heptane (2 ml.) in a small separatory funnel. To this mixture, a saturated solution (5 ml.) of potassium bromide in absolute ethanol was added, and, after mixing, the resulting homogeneous solution was left for 15 min. Then doubly distilled water (5 ml.) was added to separate the ethanol from the mixture. The resulting mixture was shaken for 30 sec. and, after complete separation, 1 ml. of the heptane layer was pipetted into a small, stoppered Pyrex tube for counting. The sampling time was taken at the moment when the pipette, used to transfer the potassium bromide solution, was half-empty, *ca.* 7 sec. being required for the pipette to completely discharge its contents. When solutions of bromobenzene in heptane were irradiated, 2-ml. portions were mixed with 5 ml. of the ethanolic potassium bromide, the remainder of the treatment being as before. The mixtures of bromobenzene, heptane, and ethanol were a little cloudy, owing to the separation of some colloidal potassium bromide.

Almost simultaneously with the removal of the first portion, 200 λ of the irradiated bromobenzene were taken from the vessel and mixed with heptane (0·8 ml.) in a Pyrex counting tube. This was then used to determine the total activity. Three or four such samples were taken during each run to check whether any inorganic activity was lost on the walls of the vessel during the

experiment. In runs with bromobenzene–heptane mixtures, the total activity was obtained by taking 1-ml. samples from the irradiated solution and directly counting them.

Retentions as parent compound were found by subjecting a portion of the heptane layer to gas-chromatographic separation, the active parent compound being collected with cooling in 1 ml. of inactive bromobenzene contained in a small Pyrex collector tube (these tubes were constructed from similar Pyrex tubes with those used to count the total and the organic activity). No other active compounds were prepared or counted separately.

Counting Technique.—A scintillation counting system with a well-type NaI (Tl) crystal was used to determine the activities by γ-counting. 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 ^{80m}Br was in transient equilibrium. Second measurements were made 48 hr. later, and the activities due to ^{80m}Br and ^{82}Br were calculated from the two measurements. Parent compound activities were measured only after 48 hr. Retention values were calculated in the usual manner after suitable corrections had been made for decay.

RESULTS

The Separation Technique.—Evidence was obtained earlier [6,7] for the inefficiency of the conventional sodium sulphite–sodium bromide solution in the separation of the inorganic from the organic radiobromine activity in irradiated bromobenzene. If the solution is alkaline, a somewhat higher efficiency results. It was thought that the irreproducibility in the kinetics could possibly be removed by employing a more efficient method, namely, homogeneous exchange of the inorganic radiobromine with inactive bromide ions. This could be done by mixing the irradiated liquid with a saturated solution of potassium bromide in absolute ethanol, allowing sufficient time for exchange, and then separating the bromobenzene by adding water to the mixture. This method gave much better reproducibility, but the retention values were higher than those obtained with aqueous extraction. If, however, the bromobenzene is diluted with heptane (3—10 times its volume) before mixing with the ethanol solution, the proportion of inorganic activity removed is higher than with any other reagent, and the reproducibility is very good. Addition of some sodium sulphite to the ethanol did not have any effect. A sample of bromobenzene was irradiated for 3 min. and, after being kept for 24 hr. at 20°, the total retention was repeatedly (8 times) determined by each of the three above-mentioned methods. Extraction with an aqueous solution containing sodium sulphite, potassium bromide, and sodium hydroxide, each at a concentration of 0·2M, gave 57·8 $\pm$ 1·4%. Mixing with absolute ethanol saturated with potassium bromide gave 59·9 $\pm$ 0·5%, while separation, using heptane, as described in the Experimental section, gave 53·9 $\pm$ 0·2%. These are mean values of the eight determinations, and the numbers given with " $\pm$ " represent standard deviations (S.D.) of the individual values from the mean. Thus, the overall error in the determination of the total retentions of ^{82}Br by the three methods is 2·4, 0·8, and 0·4%, respectively. These include also errors due to counting statistics. Retention values as parent compound separated by means of gas chromatography are associated with a relative S.D. of 2·9%.

If the last of the three methods is used to follow the post-irradiation reaction, reproducible rate constants and R_∞ values are obtained at each temperature, irrespective of the duration of the irradiation and the purity of the irradiated material (cf. Tables 2 and 3). Bromobenzene, used as supplied, without any purification, gave the same results as that purified by means of gas chromatography. It seems that, by this method of separation, some radioactive species, which are not efficiently affected by the aqueous extraction, are quantitatively removed from the organic phase. These species are probably responsible for the irreproducibility in the kinetics, possibly because their concentrations are sensitive to variations in neutron flux, purity, etc., and/or because they are partially removed by the aqueous extraction. This is in accord with the lower retention values found by means of the heptane–ethanol method. The possibility that these lower retentions are due to alcoholysis of radioactive organic products, similar to the hydrolysis suggested by Chien and Willard,[4] must be ruled out, since it cannot be reconciled with the much higher retention found by using only potassium bromide in ethanol without heptane. Finally, it was checked by analysis that the composition of the bromobenzene–heptane mixture was not altered by the separation method.

The heptane–ethanol method was employed throughout the work described in this Paper.

Pure Bromobenzene.—A typical run, illustrating the variation of retention with time at

50·0°, is shown in Table 1. The data given for ^{82}Br retentions are consistent with a second-order process with respect to this species. In terms of retentions, this is described by:

$$\frac{1}{R_\infty - R_t} = \frac{1}{R_\infty - R_0} + kt, \qquad (1)$$

TABLE 1

The effect of post-irradiation heating at 50·0° upon the retention (% of total activity)
of pure bromobenzene

Time, measured from the end of the irradiation	^{82}Br Total retention	^{82}Br Bromobenzene	^{80m}Br Total retention
1·3 min.	23·3	7·5	50·1
2·2 ,,	27·0	9·9	49·9
3·5 ,,	30·9	12·5	46·4
5·0 ,,	35·0	14·5	48·7
5·9 ,,	38·1	15·6	51·4
7·4 ,,	40·9	17·1	49·2
8·7 ,,	44·6	18·8	50·8
10·6 ,,	48·4	20·2	54·9
12·8 ,,	51·5	22·0	49·6
17·5 ,,	54·4	23·8	56·6
24·8 ,,	59·0	25·6	54·2
60·5 ,,	66·7	29·6	62·2
3 hr.	66·2	31·5	65·3
22 ,,	69·3	32·0	—
46·5 hr.	69·5	32·9	—

where R_0 and R_t are retentions at times 0 and t, respectively, R_∞ is the highest retention obtained, and k is a second-order rate constant with dimensions (yield units)$^{-1}$ time^{-1}. A plot of $1/(R_\infty - R_t)$ against t would, therefore, yield a straight line with a positive slope of k and an
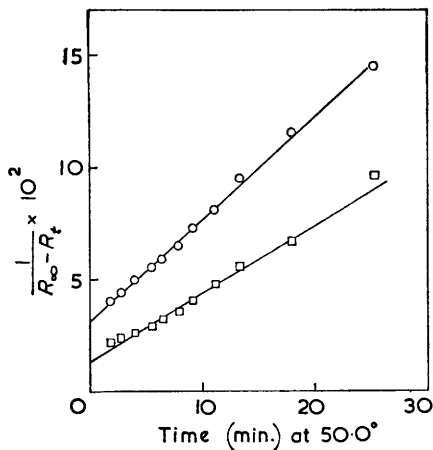

FIGURE 1. Second-order plots of data of Table 1

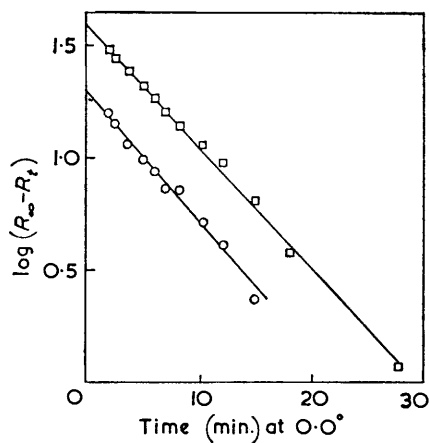□ Calculated from total retention of ^{82}Br
○ Calculated from retention as Ph^{82}Br

FIGURE 2. First-order plots of data at 0·0°

□ Calculated from total retention of ^{82}Br
○ Calculated from retention as Ph^{82}Br

intercept of $1/(R_\infty - R_0)$ from which R_0 can be calculated. Two such plots from the data of Table 1 are shown in Figure 1. Values very close to R_∞ were not included.

The values of total retention of ^{80m}Br seem to indicate that no such post-irradiation reaction takes place with this isotope. Although the last two values for ^{80m}Br in Table 1 show that something is happening, a definite conclusion cannot be drawn, since the experimental error of the retention values of this isotope, unlike that of ^{82}Br, is quite high (relative S.D. 6·7%). The mean value, however, calculated from all but the two last values of Table 1, is 51·0% and the

TABLE 2

Retention values (% of total activity) of pure bromobenzene and bromobenzene–heptane mixtures irradiated with neutrons [a] and then thermally treated at various temperatures.

Compound irradiated	Temp.	Total retention of ⁸⁰ᵐBr [b]	Total retention of ⁸²Br			Retention of ⁸²Br as PhBr			Other products containing ⁸²Br (R_∞)
			R_1 [c]	R_∞ [d]	R_0 [e]	R_1 [c]	R_∞ [d]	R_0 [e]	
PhBr	−20·4°	55·7 ± 1·2	27·1	54·9	16·0	9·5	24·3	5·5	30·6
PhBr	0·0	50·1 ± 0·9	23·5	53·6	14·1	9·1	24·8	4·4	28·8
PhBr	0·0	51·8 ± 0·8	26·5	52·4	15·2	9·9	22·4	5·0	30·0
PhBr [f]	20·0	50·8 ± 1·0	28·7	53·8	2·7	11·5	26·9	−1·4	26·9
PhBr [f]	20·0	—	28·0	53·9	4·8	—	—	—	—
PhBr [g]	20·0	—	27·9	53·9	3·5	—	26·9	—	27·0
PhBr [i]	20·0	—	36·4	52·9	−2·0	—	—	—	—
PhBr	50·0	51·0 ± 0·9	23·3	69·4	−3·6	7·5	32·5	0·1	36·9
PhBr + n-C₇H₁₆ [f]	−28·3	49·6 ± 0·6	22·5	38·2	−3·3	5·8	10·0	−4·4	28·2
PhBr + n-C₇H₁₆...	0·0	—	17·6	38·9	−1·1	5·0	11·1	1·0	27·8
PhBr + n-C₇H₁₆...	20·0	49·0 ± 1·5	18·6	40·6	2·4	4·8	10·2	3·2	30·4

[a] The duration of the neutron irradiations was 1 min., unless otherwise stated. [b] Mean values of measurements throughout each run. The errors given are standard errors (standard deviations of the mean). [c] First value of retention detected. [d] Highest retention obtained (mean of the last values of the run which differed from one another by less than 1%). [e] Zero-time retentions obtained by extrapolation. [f] 3-Min. irradiation. [g] Specimen irradiated for 3 min. as supplied, without any purification. [i] 6-Min. irradiation.

TABLE 3

Rate constants of the post-irradiation reaction in pure bromobenzene and bromo-benzene–heptane mixtures at various temperatures [a]

Compound irradiated	Temperature	Total ⁸²Br	Ph⁸²Br

First-order rate constants, $10k_1$, in min.⁻¹

Compound irradiated	Temperature	Total ⁸²Br	Ph⁸²Br
PhBr	−20·4°	1·10 ± 0·15 [e]	1·20 ± 0·12
	0·0	1·26 ± 0·02	1·38 ± 0·06
	0·0	1·20 ± 0·05	1·12 ± 0·10

Second-order rate constants, 10^3k_2, in (yield units)⁻¹ min.⁻¹

Compound irradiated	Temperature	Total ⁸²Br	Ph⁸²Br
PhBr [b]	20·0°	7·37 ± 0·38	9·10 ± 0·75
PhBr [b]	20·0	6·08 ± 0·20	—
PhBr [c]	20·0	6·90 ± 0·43	—
PhBr [d]	20·0	7·06 ± 0·35	—
PhBr	50·0	3·16 ± 0·11	4·56 ± 0·08
PhBr + n-C₇H₁₆ [b]	−28·3	18·8 ± 1·5	35·7 ± 2·8
PhBr + n-C₇H₁₆	0·0	12·72 ± 0·35	25·5 ± 2·1
PhBr + n-C₇H₁₆	20·0	9·08 ± 0·22	18·7 ± 2·0

[a] The duration of the neutron irradiations was 1 min., unless otherwise stated. [b] 3-Min. irradiation. [c] 6-Min. irradiation. [d] Specimen irradiated for 3 min. as supplied, without any purification. [e] All errors given in the Table are standard errors.

S.D. of the individual values from this mean is ±3·0. The deviations of the last two values from the mean exceed three times the S.D., and this can hardly be attributed to random errors. This phenomenon does not appear at lower temperatures, the retention of ⁸⁰ᵐBr being, within experimental error, constant throughout the same run.

Experiments were conducted at three other temperatures, namely, 20·0, 0·0, and −20·4°. Data obtained at the last two temperatures conform not to second-order, but to first-order, kinetics, as it is shown in Figure 2. Table 2 lists retention values of ⁸⁰ᵐBr and initial and final retentions of ⁸²Br, as well as extrapolated R_0 values at various temperatures. Zero time for extrapolation was taken as the moment corresponding to the middle of the irradiation time, which, in most cases, was 1 min. In Table 3, first- and second-order rate constants, calculated by standard least-squares procedures, are collected.

The total activity, corrected for decay, was found, within experimental error, to be conserved during each run. Small variations, however, did occur, particularly at 0°. All retentions were

calculated by using the activity of the first sample of the totals taken almost simultaneously with the first sample to be analysed.

In one experiment, bromobenzene was irradiated in a vessel packed with glass helices to increase the surface area. The total retention of ^{82}Br, determined after 24 hr. at 20°, was 52·7%. In another experiment, four samples were de-aerated, sealed *in vacuo*, and then irradiated for 3, 6, 9, and 12 min. The final retentions, obtained after 24 hr. at 20°, were 54·8, 54·7, 53·2, and 53·9%, respectively.

Bromobenzene–Heptane Mixtures.—Solutions of bromobenzene in heptane, of only one composition, were studied; 5 ml. of bromobenzene were mixed with 20 ml. of heptane (mole fraction of bromobenzene, 0·2591), and the mixture was irradiated and treated as described in the Experimental section. Phenomena similar to those described with pure bromobenzene were observed, except that lower initial and final retentions of ^{82}Br were found and that the reaction followed second-order kinetics at all temperatures studied. Again, no such reaction could be detected for ^{80m}Br, and the total retentions of this isotope did not differ significantly from those found previously in the pure system. Detailed results are found in Tables 2 and 3. It can be seen from Table 2 that the only component which suffered from the dilution with heptane was bromobenzene, whilst the amount of ^{82}Br contained in other organic species remained substantially the same as with the pure system.

The total activity in this system, unlike pure bromobenzene, was not conserved, a considerable fraction of apparently inorganic radiobromine being lost during each run by sticking on the walls of the containing vessel (*ca.* 18% in the first 20 min., 24% in 4 hr., and *ca.* 30% in 45 hr.). This activity could be removed at the end of the run by adding a trace of bromine to the irradiation vessel; however, corrections based on measurement of this activity could not be easily made, since the volume of the liquid remaining in the vessel diminished with time, and the loss of activity with time did not follow a very regular curve. Therefore, all retention values for the same run were found from the total activity of the first sample withdrawn from the vessel as soon as possible (*ca.* 1—1·5 min.) after irradiation and almost simultaneously with the first sample to be analysed. In this way, the loss of activity is not expected to have been large, and the reported retention values are higher only by an amount corresponding to this loss.

DISCUSSION

It has been increasingly recognised lately that, in chemical effects following nuclear reactions and radioactive transformations, factors other than the kinetic energy of the recoil atoms may be important in determining the final chemical state of these atoms. The results of the present investigation clearly show that the final distribution of ^{82}Br among the various species formed in bromobenzene is mainly governed by post-irradiation reactions. These reactions require considerable time for completion, and therefore can be followed by conventional techniques. The phenomena are most probably related to the newly discovered ^{82m}Br isotope [8] which decays by isomeric transition, with a half-life of 6·20 min., to ^{82}Br. The ratio of ^{82}Br produced from the isomeric state to the ^{82}Br produced directly is 9·0 ± 0·3, indicating that 90% of the ^{82}Br is produced *via* the ^{82m}Br isomer. The decay constant of ^{82m}Br, corresponding to the above half-life, is 0·112 min.$^{-1}$, and this agrees quite well with the first-order rate constants of Table 3.

The isomeric transition alone, however, cannot explain but a part of the phenomena reported here, namely, those taking place at or below 0°. At higher temperatures with pure bromobenzene, and at all temperatures with bromobenzene–heptane mixtures (−28·3 to 20°), the data cannot be fitted into a first-order equation, but are consistent with a second-order process. Moreover, the reaction in this case is temperature-dependent, being faster the lower the temperature. Experimental activation energies are calculated to be −4·7 and −2·3 kcal. mole^{-1} for the pure system and the bromobenzene–heptane mixture, respectively. The change of the kinetics with temperature and the negative activation energy certainly suggest that the mechanism of the reaction is probably complex and not a straightforward replacement process. This is also indicated by the fact that the reaction continues for a considerable time after all ^{82m}Br would have decayed to a negligible

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[8] J. F. Emery, personal communication.

amount, constant retention values being obtained usually 24 hr. after irradiation. Only when the reaction follows first-order kinetics, is it complete within a few half-lives of ^{82m}Br. In view of these facts, one is inclined to the view that, before organic stabilisation of the daughter ^{82}Br takes place, some other process occurs, possibly association of this with bromobenzene to form a donor–acceptor (charge-transfer) complex in which radiobromine plays the part of the acceptor. Such a complex between molecular bromine and bromo-benzene has been discovered spectrophotometrically by Keefer and Andrews,[9] who concluded that the bromine molecule is probably bound to the bromine atom of bromobenzene. ^{82}Br produced by isomeric transition is expected to be a much better acceptor than molecular inactive bromine, since it will be positively charged as a result of internal-conversion processes. The events which can produce an increase in retention with time could then be due either to an intramolecular exchange within the complex or to reactions of the complex with other species. This complex would thus play the role of a reaction intermediate, and it would be in chemical equilibrium with its components. This probably explains the negative activation energy, since the experimentally observed rate constant, k, would not only depend on λ, but would also be a function of the equilibrium constant, K, and the rate constant, k', for the subsequent reaction of the complex. Since K will normally decrease as the temperature rises, it is only necessary to assume that the increase in k' is of such a magnitude as to be outweighed by the decrease in K.

In bromobenzene diluted with heptane, the concentration of the complex would be lower, and this is consistent with the lower final retentions found.

The view that complex-formation occurs is also supported by two other facts. The first is the higher efficiency in separation of the inorganic from the organic activity which results when bromobenzene is diluted with heptane before mixing with the ethanolic potassium bromide. Complexed radiobromine would not exchange with bromide ions as easily as would free radiobromine. Dilution with heptane shifts the equilibrium towards the components, thus facilitating the exchange. The second is the loss of activity on the walls of the containing vessel in experiments with heptane solutions.

Initial retentions of the two bromine-82 isomers, both total and as parent compound measured experimentally, are low, much lower than those so far reported for the same compound in the literature, even than those determined in the presence of bromine. Extrapolated retention values due only to (n,γ) reactions are remarkably small and, in many cases, are not very far from zero (cf. Table 2). Negative values may be attributed to experimental errors affecting the slope of the linear plots. In view of these results, one is tempted to conclude that hot reactions in irradiated liquid bromobenzene occur to a small extent only.

The retention values of ^{80m}Br do not change with time, and are much higher than the initial retentions of ^{82}Br isotopes taken together. In fact, the retention values of ^{80m}Br are not very different from the final retentions, R_∞, of the ^{82}Br isotopes. This striking difference in the initial retention due to (n,γ) reactions of ^{79}Br and ^{81}Br is difficult to explain. The results with ^{80m}Br are reproducible, within experimental error, and the values obtained are more or less the same with pure as with diluted bromobenzene. The values of total retention found for this isotope do not differ greatly from some of the values reported earlier.[5]

Clearly, more experimental evidence is necessary in order to formulate a detailed explanation of the reactions reported in this Paper.

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[9] R. M. Keefer and L. J. Andrews, *J. Amer. Chem. Soc.,* 1950, **72**, 4677.