1146. *Thermal "Annealing" Phenomena in Some Neutron-irradiated Liquid Organic Bromides.*

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Post-irradiation thermal "annealing" phenomena in liquid organic bromides have been recognised and studied. Four compounds, *viz.* n-propyl bromide, bromobenzene, 4-bromo-*o*-xylene, and benzyl bromide were neutron-irradiated and then thermally annealed, at $40.0°c$, in the absence and in the presence of elemental bromine, added after irradiation. A pronounced increase in retention of ^{82}Br with time of heating was observed in all compounds, when no elemental bromine had been added. The maximum obtainable retention ranged from 69 to 99%, depending on the compound irradiated, the method of its purification and the conditions of the irradiation. Initial retentions, on the other hand, are not influenced by the latter two factors, reproducible results being obtained in all cases, provided that the delay between the end of irradiation and the beginning of the treatment of the samples was always the same.

The addition of elemental bromine to irradiated 4-bromo-*o*-xylene resulted in an increase of both the initial and the maximum obtainable retentions. In n-propyl bromide the opposite effect was observed; both initial and maximum retentions were lowered by the addition of bromine. In bromobenzene the reaction of annealing was completely suppressed by bromine. The increase of total retention in n-propyl bromide was found to be due almost exclusively to an increase in the amount of the parent compound when bromine was absent, and, in its presence, to formation of other products. In bromobenzene the increase of total retention was due to both parent and other products in the absence of bromine. The reaction was found to be second-order with respect to inorganic radiobromine. Some possible mechanisms of the reaction are discussed.

CHEMICAL effects following radiative neutron-capture in organic bromides have been the subject of numerous investigations during the past twelve years. All these investigations were mainly concerned with:

(*a*) the determination of organic retentions as well as of the distribution of active bromine atoms among the various organic species formed;

(*b*) the effect of added scavengers, especially elemental bromine; and

(*c*) isotope effects of the three main bromine isotopes, namely ^{80m}Br, ^{80}Br, and ^{82}Br.

Some work has recently been done on thermal and radiation annealing of certain organic halogen compounds.[1,2] These latter studies, as well as the numerous studies on thermal and radiation annealing of inorganic and other organic compounds, were carried out on crystalline materials.

The possibility of annealing phenomena occurring in liquids has never been examined. The object of this work was to investigate this possibility, with ^{82}Br as the recoiling atom.

[1] Veljkovic and Harbottle, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1517.
[2] Collins and Willard, *J. Chem. Phys.*, 1962, **37**, 1908.

Four organic bromides were studied: n-propyl bromide, bromobenzene, 4-bromo-*o*-xylene, and benzyl bromide. The four compounds were neutron-irradiated and then thermally annealed, at 40·0°, in the presence and in the absence of elemental bromine, added after irradiation. The total organic radiobromine retention and the retention in the form of the parent compound were studied as a function of heating time. A large increase in retention with time was observed in all compounds, this retention reaching in some cases values very close to 100%. This increase was mainly due to an increase in retention of parent compound. Effects due only to ^{82}Br were studied.

EXPERIMENTAL

Materials.—n-Propyl bromide ("Purum"; Fluka A.G.) was purified by three different methods. (*a*) By distillation in a Vigreux column (40 cm. × 1 cm. diam.). No impurity was detected when the distillate was subjected to gas chromatography. The sensitivity of our gas chromatograph, under the conditions stated, was of the order of 1 part in 10^5. (*b*) By the method described by Schuler and McCauley.[3] (*c*) By preparative gas chromatography, using a 30-ft. column (diethylene glycol succinate). Bromobenzene ("Puriss."; Fluka A.G.) was purified by methods (*a*) and (*c*) mentioned under n-propyl bromide. No impurity was detected when the product of (*a*) was analysed by gas chromatography. 4-Bromo-*o*-xylene was prepared[4] and then purified by fractional distillation under reduced pressure. Analysis as above showed only a trace of impurity, having a lower b. p. than the bromoxylene. Benzyl bromide ("Purum"; Fluka A.G.) was purified by fractional distillation under reduced pressure. Analysis as above proved inapplicable owing to the high b. p. of this compound, which suffers thermal decomposition in the chromatographic column. Chemically pure bromine (Merck) was used without further purification.

Neutron Irradiation.—All irradiations were performed in the swimming-pool reactor G.R.R.1 of Nuclear Research Centre "Democritus". Specimens of each bromide (10 ml.) contained in quartz or Pyrex glass ampoules, sealed at atmospheric pressure, were placed in a 1 in. thick lead container, situated near the reflector of the reactor core, the distance between the external wall of the container and the reflector being *ca.* 2 in. Under these conditions the proportion of fast neutrons in the flux is not expected to have been large and the total γ-dose received by each specimen ranged from 550 to 800 rad, depending on the time of irradiation. In only two experiments with bromobenzene [see Table 2, (*b*) and (*c*)] irradiation was performed behind a 3-in. lead block, placed at 2 in. from the reflector of the reactor core, and under these conditions each specimen received a total γ-dose of *ca.* 50 rad. Finally, one irradiation [see Table 1, (*b*)] was made in darkness. During irradiations, the temperature of the surrounding water was 24·5° ± 1·0°.

Annealing, Extraction, and Analysis of Samples.—The irradiated liquid was normally split into two specimens, one of which was annealed without addition of bromine, while the second was mixed with a preweighed amount of elemental bromine.

An aliquot portion (0·5 ml.) was then immediately withdrawn from both specimens to determine initial retentions, and then, 15 min. after irradiation, both specimens were placed in a thermostat at 40·0°, precautions being taken to prevent daylight from reaching the liquids. At definite time intervals, portions (0·5 ml.) were withdrawn from each specimen and extracted for 1 min. with the same volume of aqueous sodium thiosulphate (5 or 8%) and sodium bromide (5%). In experiments with bromobenzene and bromoxylene the extracting solution contained, in addition, sodium hydroxide (5%). Extractions were repeated three times, the volume of the extracting solution being always equal to the volume of the organic layer. In this way the remaining extractable activity was usually < 0·5%, but in a few cases 2%. After the extraction the organic layer was dried overnight (Sikkon), and the active parent compound separated by gas chromatography and collected with cooling in 1 ml. of inactive bromobenzene in a small Pyrex collector tube. This was then directly counted. No other active products were prepared or counted separately. Our chromatographic columns proved inadequate to separate bromoxylene, while in the case of benzyl bromide, separation was impossible, owing to thermal decomposition of this compound.

Counting Technique.—Before measurements, enough time was allowed (48 hr.) for other bromine isotopes to decay out. After this, the radioactive purity of ^{82}Br was checked by half-life determinations. No evidence of other isotopes of different half-lives was obtained. Radioactivity measurements of ^{82}Br were made by γ-counting in a well-type scintillation counter, with a sodium

[3] Schuler and McCauley, *J. Amer. Chem. Soc.*, 1957, **79**, 821.
[4] Wisansky and Ansbacher, *Org. Synth.*, Coll. Vol. III, 1955, 138.

iodide scintillation crystal. Samples for counting were prepared by diluting 100λ or 200λ from each layer in 2 ml. of distilled water for the aqueous phase or in 2 ml. of benzene for the dried organic phases, in small Pyrex tubes which were then counted. Pure parent compounds were counted in the collector tubes, which were constructed from the same Pyrex tubes. Total activity was calculated from the combined activities of the three extracts and that of the organic phase. Retentions were calculated after suitable corrections had been made for decay.

<div align="center">RESULTS</div>

The results of the studies with n-propyl bromide purified by three different methods are collected in Table 1. Specimen (*c*), with no bromine addition, was kept in the dark for 46·7 hr. After this the irradiated liquid was exposed to daylight. This, as is clearly seen, caused no appreciable effect in 26 hr.

The results for bromobenzene, purified by two different methods, are given in Table 2.
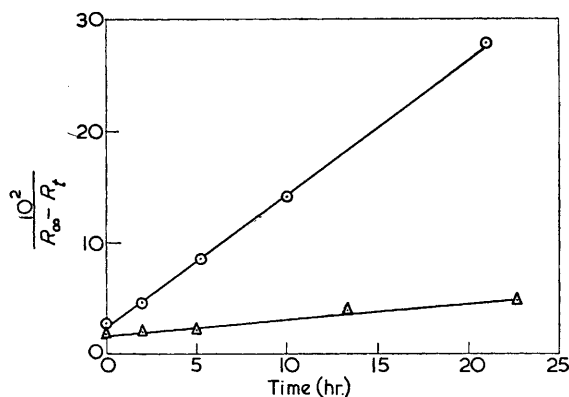
<div align="center">TABLE 1.</div>

The effect of post-irradiation heating at 40·0° on the retention (% of total activity of ^{82}Br) of n-propyl bromide, purified by three different methods.

| Heating time (hr.) | No bromine added after irradiation | | | | | | Bromine added after irradiation* | | | | |
| | Total retention | | | n-Propyl bromide | | | Total retention | | | n-Propyl bromide | |
	a	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*
0·0	53·9	41·1	50·5	25·5	—	22·3	42·6	39·5	42·2	22·9	—
2·0	69·8	43·8	86·4	41·9	24·6	—	44·6	—	—	21·5	—
5·0	—	49·3	84·2	—	—	—	—	42·7	44·4	—	—
5·2	79·9	—	—	52·2	—	—	49·2	—	—	22·1	—
10·0	84·6	—	—	—	—	—	53·0	—	—	27·4	—
13·3	—	71·3	—	—	43·4	—	—	—	—	—	—
13·5	—	—	86·8	—	—	40·2	—	—	—	—	—
21·0	88·1	—	—	61·6	—	—	57·5	—	—	28·1	—
22·7	—	74·3	84·8	—	—	—	—	54·6	45·9	—	18·4
26·5	91·6	—	—	61·6	—	—	—	—	—	—	—
32·7	91·7	—	—	61·2	—	—	—	—	—	—	—
37·2	—	94·5	—	—	—	—	—	—	—	—	—
46·0	—	—	—	—	—	—	84·8	—	—	27·2	—
46·7	—	—	84·5	—	—	—	—	74·9	51·8	—	21·3
49·8	—	95·5	—	—	—	—	—	—	—	—	—
70·5	—	—	—	—	—	—	88·6	—	—	21·4	—
71·5	—	—	—	—	—	—	—	91·0	—	—	—
72·5	—	—	85·9	—	—	—	—	—	59·1	—	—

Specimen *a* was purified by simple fractional distillation and irradiated for 20 sec. in a flux of $3·1 \times 10^{11}$ neutrons cm.$^{-2}$ sec.$^{-1}$. Specimen *b* was purified by the method of Schuler and McCauley[3] and irradiated for 30 sec. in $4·5 \times 10^{11}$ neutrons cm.$^{-2}$ sec.$^{-1}$. Specimen *c* was purified by gas chromatography and irradiated for 1 min. in $4·6 \times 10^{10}$ neutrons cm.$^{-2}$ sec.$^{-1}$.

* The mole fraction of bromine in specimen *a* was $4·34 \times 10^{-2}$; in specimens *b* and *c* it was $3·54 \times 10^{-2}$.

The second-order reaction of non-organically bound radiobromine in neutron-irradiated n-propyl bromide, in the absence of elemental bromine. ⊙ Values calculated from total retentions of Table 1(*a*). △ Values calculated from total retentions of Table 1(*b*).

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TABLE 2.

The effect of post-irradiation heating at 40·0° on the retention (% of total activity of [82]Br) of bromobenzene, purified by two different methods.

Heating time (hr.)	No bromine added after irradiation						6.04×10^{-2} Mole fraction of bromine added	
	Total retention			Bromobenzene			Total retention	Bromo-benzene
	a	b	c	a	b	c	a	a
0·0	60·4	60·5	59·1	53·6	40·2	26·4	60·6	43·9
0·5	—	70·8	64·5	—	46·7	28·0	—	—
1·0	63·7	—	—	53·6	—	—	58·7	43·9
1·5	—	73·0	63·5	—	—	29·0	—	—
3·0	—	—	65·2	—	—	27·6	—	—
4·0	68·2	74·2	—	57·3	51·6	—	58·9	41·1
6·0	68·3	—	—	60·5	—	—	58·1	41·5
7·0	—	—	63·4	—	—	28·0	—	—
10·0	70·8	—	—	62·0	—	—	57·4	34·0
21·2	75·6	—	—	64·2	—	—	57·0	38·0
22·5	—	—	67·0	—	—	—	—	—
26·0	—	75·7	—	—	—	—	—	—
31·5	79·9	—	—	66·7	—	—	57·3	39·1
45·7	81·5	—	—	63·3	—	—	58·4	—
47·0	—	—	65·1	—	—	27·2	—	—
69·7	82·2	—	—	62·8	—	—	59·6	—
71·0	—	79·0	—	—	—	—	—	—
95·0	—	—	70·9	—	—	—	—	—
96·0	—	80·3	—	—	—	—	—	—

Specimens *a* and *b* were purified by fractional distillation: *a* was irradiated for 30 sec. in a flux of 3.1×10^{11} neutrons cm.$^{-2}$ sec.$^{-1}$; *b* for 3 min. in 2.1×10^{10} neutrons cm.$^{-2}$ sec.$^{-1}$; *c* as for *b* but purified by gas chromatography.

With this compound a separate experiment was conducted to check any exchange reaction with elemental bromine. Bromobenzene (5 ml.), purified by distillation, was irradiated by a ^{60}Co source, being given a total γ-dose of 70 rad. This was then immediately mixed with elemental bromine (1·5 g.), previously irradiated for 3 min. in a flux of 2.1×10^{10} neutrons cm.$^{-2}$ sec.$^{-1}$. The mixture was kept at 40·0° for 46 hr., in the dark. The exchange occurring in this period was 0·5%, *i.e.*, only 0·5% of the total radiobromine was organically bound. The mixture was then kept in daylight, again at 40·0°, for another 24 hr., when the retention increased to 1·0%. The results with irradiated 4-bromo-*o*-xylene and benzyl bromide are listed in Tables 3 and 4, respectively. Only one method of purification was used for these two compounds.

TABLE 3

The effect of post-irradiation heating at 40·0° on the total retention (% of total activity of [82]Br) of 4-bromo-*o*-xylene, irradiated for 30 sec. in a neutron flux of 3.1×10^{11} neutrons cm.$^{-2}$ sec.$^{-1}$.

Heating time (hr.)	No bromine added after irradiation	4.62×10^{-2} Mole fraction of bromine added	Heating time (hr.)	No bromine added after irradiation	4.62×10^{-2} Mole fraction of bromine added
0	60·0	64·5	10	66·2	84·5
1·5	61·3	75·4	21·5	64·3	87·9
4	65·0	80·7	28·5	68·3	88·3
7	66·1	84·2	47·5	69·0	92·6
			71	69·2	86·6

The Kinetics of the Annealing Reaction.—An attempt was made to fit these results into a kinetic equation. We may first of all assume that the increase in retention with time is due to reactions of organic species (molecules or "radicals") with the recoil radiobromine "atoms."[*] The only concentrations known as functions of time are the concentration of inactive parent molecules and that of radiobromine atoms, in either organic or extractable combination. Since the first of these concentrations is not appreciably changed with time, the reaction, if it involves parent molecules,

[*] The concepts "radical" and "atom" are used here to mean some organic reacting species and bromine atoms, respectively, stabilised by some unknown process. This point is further discussed later.

TABLE 4.

The effect of post-irradiation heating at 40·0° on the total retention (% of total activity of ^{82}Br) of benzyl bromide, irradiated for 30 sec. in a neutron flux of $3·1 \times 10^{11}$ neutrons cm.$^{-2}$ sec.$^{-1}$.

Heating time (hr.)	No bromine added after irradiation
0	67·3
1	97·8
3·5	98·7
5·5	98·5
10	98·7
23	98·6

will be zero-order with respect to this concentration. It remains to check the order of the annealing reaction with respect to the concentration of non-organically bound radiobromine. The reaction is found to be second-order with respect to this species. Thus, if by R_∞ we denote the highest retention obtained and by R_t the retention at time t, a plot of $1/(R_\infty - R_t)$ against t would yield a straight line with a positive slope equal to the rate constant, k. Several such plots were constructed from the data of Tables 1, 2, and 3. The remarkably good linearity of these plots in most cases is a good indication that the annealing reaction does follow second-order kinetics. Values very close to R_∞ were not included in the plots. Two examples of these plots are given in the Figure; the rate constants calculated from several such plots, by standard least-square procedures, are given in Table 5.

TABLE 5.

Second-order rate constants [in (yield units)$^{-1}$ hr.$^{-1}$], at 40·0°, of the reaction of non-organically bound radiobromine in three neutron-irradiated liquid bromides.

Bromide	No bromine present $10^3 k$	$3·54—4·62 \times 10^{-2}$ mole fraction of bromine added $10^3 k$
n-Propyl bromide[a]	$12·05 \pm 0·17$[e]	$0·50 \pm 0·05$
n-Propyl bromide[b]	$1·41 \pm 0·19$	$0·91 \pm 0·20$
n-Propyl bromide[c]	—	$1·34 \pm 0·25$
Bromobenzene[d]	$4·83 \pm 0·30$	—
4-Bromo-o-xylene	$40·40 \pm 3·01$	$20·50 \pm 2·40$

[a, b, c, d] Calculated from the total retentions reported in Tables 1(a), 1(b), 1(c), and 2(a), respectively.
[e] All errors given in the Table are standard errors.

The data of Table 1(c), total retention with no bromine added, and Table 4 do not allow verification of a second-order process, since there are virtually only two values, corresponding to R_0 and R_∞. Finally, the data of Table 2(b) and (c), cannot be well fitted into a second-order kinetic equation. It is worth noting here that second-order kinetics were also found by Collins and Willard[2] in the thermal annealing reaction of solid hexabromoethane.

DISCUSSION

The results just presented point clearly to the fact that there is an initial retention (around 50% for n-propyl bromide and around 60% for all other bromides) and a retention caused by heating the samples.

TABLE 6.

Initial retentions of n-propyl bromide.

Method of purification	Without addition of Br_2		With addition of Br_2	
	% Total retention	% n-C_3H_7 ^{82}Br	% Total retention	% n-C_3H_7 ^{82}Br
Fractional distillation	53·9	25·5	42·6	22·9
Gas chromatography	50·5	22·3	42·2	—
Method of Schuler and McCauley[3]	41·1	24·6	39·5	—
Results of Chien and Willard[5]	—	—	42	—
Results of Herr *et al.*[6]	72	59·5	—	—

[5] Chien and Willard, *J. Amer. Chem. Soc.*, 1955, **77**, 3441.
[6] Herr, Stöcklin, and Schmidt, *Z. Naturforsch.*, 1959, **14**b, 693.

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The method of purification and the conditions of irradiation seem to have little effect on the initial retention of n-propyl bromide and bromobenzene. For n-propyl bromide this can be clearly seen from Table 6, where some results of other investigators are also included for comparison. Those of Chien and Willard must be compared with our results in the presence of elemental bromine, since the treatment of their samples after irradiation includes addition of elemental bromine before extraction. The results of Herr *et al.*, on the other hand, must be compared with our results without addition of bromine, since they did not add elemental bromine before extraction.

As Willard has pointed out,[7] gas chromatography should be considered the most effective method for purification of samples to be irradiated. The results obtained by this method agree well with those obtained by simple fractional distillation, but less well with those from Schuler and McCauley's method. Moreover, the results in the presence of bromine agree well with those of Chien and Willard, although they used a different method of purification. The retention value found by Herr *et al.* is considerably higher than ours, but this is probably because they treated their samples 8 days after irradiation, and this long delay of treatment, as our experiments show, may have a large effect on the retention. The increase in retention of ^{82}Br with increasing time of irradiation which Chien and Willard found in n-propyl bromide[5] could be due not only to the increase of the γ-dose but also to thermal-annealing phenomena similar to ours.

In bromobenzene the initial retention is also very little influenced by the conditions of irradiation or the method of purification. Simple fractional distillation and irradiation in $9\cdot3 \times 10^{12}$ neutrons cm.$^{-2}$ accompanied by a γ-dose of 800 rad gave a retention of $60\cdot4\%$. The same purification method and irradiation in $3\cdot78 \times 10^{12}$ neutrons cm.$^{-2}$ with an accompanying γ-dose of only 50 rad gave $60\cdot5\%$. Under the latter conditions, purification by gas chromatography gave $59\cdot1\%$. Willard,[7] using different purification methods, did not get reproducible results, his retention values ranging from 54—90%. He even found major variations in retention with different samples from the same bottle. This irreproducibility has also been obvious from the difference between the values reported in the literature by many other investigators.[8-13] This is in sharp contrast to our results where values of 60% were constantly obtained irrespective of the method of purification or the neutron flux used in the irradiations. It therefore seems probable that the main cause of irreproducibility in bromobenzene retention is the time elapsing between irradiation and treatment of the sample, as well as prolonged irradiations, in some cases[13] as long as 7 days. It is clearly shown by our results that 30 min. at $40\cdot0°$ suffices to increase the retention sometimes by 10%. The fact that, in the presence of bromine scavenger, Willard obtained reproducible results[7] also supports the above hypothesis, since we have found that addition of bromine stops the annealing reaction.

The data of Tables 1, 2, and 5 seem to indicate that the rate of the annealing phenomenon and the final retention are both influenced by the method of purification and/or the neutron fluxes employed, and also that the higher the integrated neutron flux the lower the rate of the phenomenon. When elemental bromine is present in n-propyl bromide the rate of the reaction is almost independent of the purification method and the neutron flux (see Table 5).

Some interesting features become clear. In n-propyl bromide without addition of bromine the increase in total retention was almost exclusively due to increase in retention of the parent compound. After the addition of bromine the increase was due to an increase in retention only of other products, that of the parent compound being constant. In bromobenzene without bromine the increase was due to both parent and other products. With bromine all reactions

[7] Willard, "Proceedings of the Symposium on Chemical Effects of Nuclear Transformations," Prague, 1960, Vol. I, p. 215.
  [8] Chien and Willard, *J. Amer. Chem. Soc.*, 1954, **76**, 4735.
  [9] Libby, *J. Amer. Chem. Soc.*, 1947, **69**, 2523.
  [10] Lu and Sugden, *J.*, 1939, 1273.
  [11] Shaw and Collie, *J.*, 1951, 434.
  [12] Capron and Crevecoeur, *J. Chim. phys.*, 1952, **49**, 29.
 [13] Milman and Shaw, *J.*, 1956, 2101.

ceased. It is noteworthy that in bromobenzene, though the total initial retention was reproducible, the retention as bromobenzene itself was not. Obviously the method of purification and the neutron flux changes the distribution of organically bound radiobromine, without altering the total organic retention.

It has been constantly assumed by many authors that the inorganic radiobromine in irradiated organic bromides exists only as free $^{82}Br_2$ and/or $H^{82}Br$. This hypothesis, however does not account for two experimental facts:

(*a*) the failure to remove a large fraction of the inorganic activity from irradiated bromobenzene by a single extraction with sodium sulphite–sodium bromide or sodium thiosulphate–sodium bromide systems, unless alkaline conditions prevail. This was also observed by Willard.[7] The phenomenon is less pronounced in n-propyl bromide.

(*b*) the effect on the reaction rate of elemental bromine added after irradiation in mole fractions of $(3\cdot5\text{—}4\cdot6) \times 10^{-2}$. It is calculated that, in our irradiations, about 10^{11} atoms of ^{82}Br are produced in the specimens, which amounts to about 10^{-13} mole of $^{82}Br_2$. Since forms such as $^{82}Br_2$ and $H^{82}Br$ are known to exchange rapidly with inactive Br_2, the specific activity of the non-organically bound radiobromine would go down by a factor of about 10^{10}. Such a tremendous "dilution" of radiobromine with inactive bromine would make the chance of its reaction with other species of the liquid, and therefore the chance of its return to organic combination, practically zero, because of competing reactions between these organic species and inactive bromine. On referring to Table 5, one sees that this is so only in the case of bromobenzene, where the reaction was stopped by the addition of bromine. In all other cases the specific rate of the reaction was decreased, but not much, *e.g.*, in the case of 4-bromo-*o*-xylene, the specific rate was decreased by a factor of two. Moreover the initial and maximum final retentions of this bromide are higher in the presence of bromine than in its absence.

For these reasons we cannot interpret the second-order kinetics, with respect to inorganic radiobromine, as simply meaning that molecules of $^{82}Br_2$ are involved. There remain two other explanations of the kinetics of the reaction. (*a*) The radiobromine atoms and the radicals produced by the original recoil are somehow stabilised, possibly by charge-transfer interaction, and then react to return the inorganic radiobromine to organic combination. The second-order kinetics in this case can be understood by assuming that the concentration of the stabilised "radicals" is equal to that of the stabilised radiobromine "atoms". (*b*) In n-propyl bromide the whole phenomenon might be due to products formed by radiolysis of the type:

$$CH_3 \cdot CH_2 \cdot CH_2 Br \rightleftharpoons CH_3 \cdot CH = CH_2 + HBr.$$
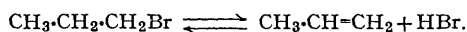
This is similar to a reaction found by Milman *et al.*[14] in $CH_2Br \cdot CH_2Br$. The second-order reaction could then be due to an exchange of inorganic radiobromine with HBr, which on recombination with $CH_3 \cdot CH = CH_2$ would yield $CH_3 \cdot CH_2 \cdot CH_2 \cdot {}^{82}Br$. This mechanism, however, cannot be regarded as very probable, since the concentration of olefins formed by radiolysis is expected to be negligible, in view of the very low γ-doses received by the samples. The second-order kinetics could be understood on the basis of this mechanism only if the concentration of olefins were comparable to that of inorganic radiobromine, a condition which is very unlikely to be fulfilled. Furthermore, such a mechanism is inconceivable for bromobenzene.

Relevant to all these is the fact that we found no exchange reactions between elemental bromine and bromobenzene in daylight and in the dark. This is in disagreement with the results of Milman and Shaw[13] who, in an analogous experiment, found 8% exchange in the dark and 98% exchange in daylight. This disagreement is probably due to the different conditions under which our experiments were conducted. Moreover, if similar exchange reactions were responsible for our annealing phenomena, they would be first-order with respect to radiobromine atoms.

[14] Milman, Shaw, and Simpson, *J.*, 1957, 1310.

Finally, daylight seems to have no effect on the annealing phenomena in the absence of elemental bromine. In the presence of bromine, the reaction is expected to be influenced by light, but we have not conducted any experiments to verify this.

Other investigations are well under way to further elucidate the mechanisms operative in the phenomena observed.

Conclusions

The basic conclusion of the present work is that a new phenomenon has been discovered when irradiated samples of organic bromides are thermally treated after irradiation, namely, an increase in retention with time, a reaction which in most cases follows second-order kinetics with respect to inorganic radiobromine concentration. Our feeling is that the frequent irreproducibility of results with many substances is due to such annealing reactions, since the time elapsing between irradiation and treatment of the sample has not usually been taken into account. Neglect of this phenomenon could gravely influence the interpretation of results in general.

The phenomenon is of considerable importance not only from the point of view of overcoming irreproducibility in many experiments, but also because such a phenomenon could throw some light on the basic phenomena and mechanisms of hot-atom chemistry.

The reason why we prefer the term "annealing" rather than "post-irradiation reactions" is that there might be an analogy between the mechanisms operative in these reactions and the annealing phenomena in solids, this latter field being still obscure.