249. *The Szilard–Chalmers Reaction in Ethyl Bromide.*

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The nature of the reactions following neutron capture by the bromine atom in ethyl bromide has been investigated by analysing the products at different free bromine concentrations. The products from the processes associated with the slowing down of the energetic atoms consist largely of compounds which could only be produced from highly fragmented ethyl bromide molecules. By contrast, the product from the ensuing diffusion-dependent reactions consists only of ethyl bromide.

WHEN organic halides are irradiated with neutrons, part of the radio-halogen produced can be extracted with an aqueous reagent, and part remains in organic combination. This effect, first observed by Szilard and Chalmers,[1] occurs because, after neutron capture, the radiation emitted by a halogen atom may impart to it a recoil energy of the order of tens of electron volts. The parent molecule therefore dissociates, and, in the ensuing chemical reactions, the radioactive atom may form inorganic or new organic species (see, for example, Glückauf and Fay [2]). The most recent reviews of the work of several investigators who have attempted to determine the nature of these reactions are by Willard.[3, 4]

One of the first attempts to account for the distribution of the active halogen atoms among the new chemical species was Libby's " billiard-ball hypothesis." [5] In this it was assumed that recoiling atoms lose their energy by elastic collisions with neighbouring atoms, which were regarded as free; this seemed plausible since the chemical binding energies of atoms in molecules are small compared with the recoil energy. In these circumstances, the only single collisions capable of reducing the high energy of the recoiling atoms to the thermal region are " head-on " collisions with other (halogen) atoms having approximately the same mass, whereupon the recoil energy is transferred to an inactive atom which is projected from the site of the collision; the de-energised radio-halogen atom is thus left in a liquid " cage " with the radical to which the inactive atom was originally joined. The ensuing combination must therefore result in the formation of a molecule of the parent compound, and the theory successfully accounted for the large percentage of the activity present in the parent compound (cf. refs. 2 and 6).

Glückauf and Fay [2] and Fox and Libby [6] also found that among the new organic compounds produced those formed by substitution of bromine in the original compound predominated. To account for this, Libby and his co-workers [6, 7] postulated that, when the energy of the recoiling atom was reduced by collision to a few electron volts, whole molecules could be activated by inelastic collisions which caused rupture of C–H bonds and combination of the organic radical with the de-energised radio-halogen atom.

An account of the criticisms of this theory has been given by Willard.[3] For present purposes, one of the most important of these is the implausibility of the assumption that the collisions can be treated as elastic when the recoiling atom has a high energy. This can be simply illustrated for a molecule such as ethyl bromide by considering a collision in the direction of a C–Br bond such that the bromine atom is caused to move towards the carbon. Since the whole molecule is confined by the walls of the liquid [8] the C–C bond must be considerably activated and might dissociate. Evidence for such activation has

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[1] Szilard and Chalmers, *Nature*, 1934, **134**, 462.

[2] Glückauf and Fay, *J.*, 1939, 1273.

[3] Willard, *Ann. Rev. Nuclear Sci.*, 1953, **3**, 193.

[4] *Idem, ibid.*, 1955, **6**, 141.

[5] Libby, *J. Amer. Chem. Soc.*, 1947, **69**, 2523.

[6] Fox and Libby, *J. Chem. Phys.*, 1952, **20**, 487.

[7] Friedman and Libby, *ibid.*, 1949, **17**, 647.

[8] Cf. Franck and Rabinovitch, *Trans. Faraday Soc.*, 1934, **30**, 120.

been given by Collie and Shaw[9] who found that methylene dibromide was produced in neutron-irradiated ethyl bromide.

Willard and his colleagues[10, 11] have suggested as an alternative theory that the reactions of halogen atoms following neutron capture occur in two stages. In the first the recoiling (highly energetic) atom loses energy by inelastic collisions producing a large local concentration of molecular fragments (free radicals and inorganic atoms); the active atom might then combine with one of these when it has lost sufficient energy, thus producing organic or inorganic molecules. After losing its energy, the active atom, together with some of the free radicals produced, diffuses into the surrounding liquid. After many collisions with solvent molecules these radicals might combine among themselves, or with the active atom, until the system becomes so dispersed by diffusion that the probability of such reactions is negligible. In this and the following papers, reactions occurring in the first stage are termed " high-energy reactions " (after Willard[3]), and those in the second stage diffusion-dependent or " diffusive " reactions.

This theory succeeds in accounting for the disproportionately large drop in retention (defined as the fraction of the total activity produced which is present in organic combination) found when small quantities of elementary halogen are present in the halide during irradiation. This effect was discovered by Lu and Sugden,[12] and has been investigated by others, particularly Willard and his colleagues,[10, 11] who also found that as the halogen concentration is further increased, the retention becomes relatively insensitive to change in it. The initial sharp decrease in retention was ascribed to the removal, by reaction with the added halogen, of organic radicals which might otherwise react with the active atom in the diffusion-dependent stage. When the halogen concentration is sufficiently great, the formation of organic halides by such processes can be made negligible, and the radioactive organic compounds present are then those produced predominantly by combination of the active atom with a radical in the initial (high energy) stage.

Proof that bromine atoms are involved in the processes following neutron capture in ethyl bromide has been given by Goldhaber and Willard[10] and Roy, Williams, and Hamill[13] who added small quantities ($\sim 10^{-3}$ molar fraction) of 1 : 2-dibromoethylene to the liquid before irradiation; the retention was increased from 32 to 60%. Since 1 : 2-dibromoethylene exchanges readily with bromine atoms,[14] this shows that 28% of the radiobromine produced ultimately enters inorganic combination by thermal processes; the remaining 40% of the inorganic active bromine is attributed to molecules produced in the high-energy stage.

No attempt has been made to determine the nature of the reactions occurring in either the diffusion-dependent or high-energy stages. In the latter, the radicals available for combination with the active atom might consist of extremely unstable molecular fragments, di-radicals, etc., since considerable energy has been dissipated among relatively few molecules. The compounds produced by combination of the active atom with one of these should therefore indicate how far solvent molecules are disrupted by the recoiling atom; for example, methylene dibromide formed from radicals (made by breaking the C–C bonds in ethyl bromide) might be produced predominantly in the high-energy stage. During the slower diffusive stage, however, highly unstable fragments might disproportionate or react with solvent molecules to form more stable radicals, so that the compounds formed by combination with the active atoms would differ chemically from those from the first stage.

We now give an account of an investigation of the nature of the products formed in the two groups of reactions following neutron capture by bromine in ethyl bromide.

[9] Collie and Shaw, *J. Chim. phys.*, 1951, **48**, 198.
[10] Goldhaber and Willard, *J. Amer. Chem. Soc.*, 1952, **74**, 318.
[11] Levey and Willard, *ibid.*, p. 6161.
[12] Lu and Sugden, *J.*, 1938, 1273.
[13] Roy, Williams, and Hamill, *J. Amer. Chem. Soc.*, 1954, **76**, 3274.
[14] Williams, Hamill, Schwartz, and Burell, *ibid.*, 1952, **74**, 5737.

Retentions in Pure Ethyl Bromide.—Earlier figures for the retentions in this substance [15, 16, 17] are considerably greater than that (32%) obtained by Goldhaber and Willard [10] in specimens carefully purified by different methods. The last authors ascribed the earlier high values to the effects of impurities capable of returning the inorganic radiobromine to organic combination.

In the present work the ethyl bromide was purified by two methods, one of which was identical with one used by Goldhaber and Willard; if the period of irradiation was greater than about four days the ethyl bromide became yellow owing to elementary bromine, and the observed retentions agreed with those found by the last authors. It is possible (cf. ref. 18) that the bromine might have been formed by the action of gamma-rays on the ethyl bromide in the presence of oxygen, which was not excluded in our work. However, for shorter irradiations the retentions found were variable and significantly greater (35—39%). Attempts were made to see whether this could be caused by the effects of impurities such as those postulated by Goldhaber and Willard, by observing the retention found by extraction 12 hrs. after removal of the ethyl bromide from the neutron source. During this period the specimens were kept either in darkness or near a 500 mc radium source to simulate the γ-ray flux from the Ra–Be neutron source. No transfer of the activity from the inorganic to the organic fraction was observed, and it is therefore improbable that the greater retentions could be produced by reaction with impurities.

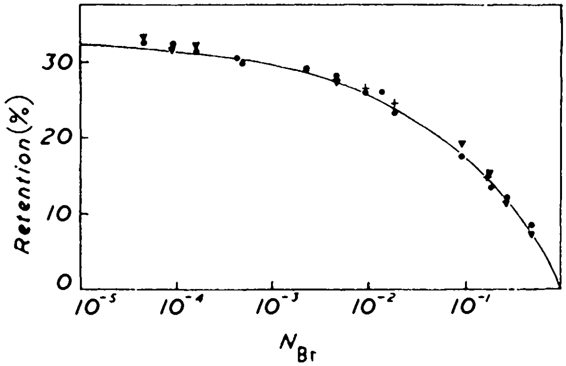

FIG. 1. *Retention o, ethyl bromide as a function of the molar fraction of bromine.*
+ ^{80}Br; ● $^{80}Br^*$; ▼ ^{82}Br.

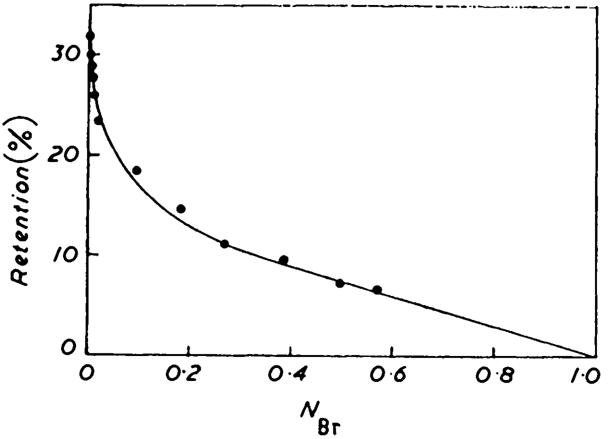

FIG. 2. *Retention of ethyl bromide as a function of the molar fraction of bromine. The points shown are the weighted mean of the values, given in Fig. 1, taken at the same molar fraction of bromine.*

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[15] Libby, *J. Amer. Chem. Soc.*, 1940, **62**, 1930.

[16] Hamill, Williams, Schwartz, and Voiland, University of Notre Dame Radiation Chemistry Report, March 1st, 1951; quoted in ref. 10.

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

[18] Chien and Willard, *J. Amer. Chem. Soc.*, 1955, **77**, 3441.

Possible explanations of this effect are given in the Discussion. For present purposes the discrepancy between our results and those of Goldhaber and Willard is not unduly disturbing since, by the addition of small quantities of inactive bromine (10^{-5} molar fraction), the retentions were stabilised and agreed with those quoted for similar conditions by them.[10]

Retentions with Bromine Present.—By extrapolating the less sensitive part of the plot of retention against bromine concentration it is possible to obtain a value for the retention due to high-energy processes at zero bromine concentration. Its value in ethyl bromide has been reported as 25% [10] and 20%.[13] In view of this discrepancy, the retentions of ethyl bromide as a function of bromine concentration were re-determined, the concentration of bromine being varied over a greater range than that used previously. The results are shown in Figs. 1 and 2; the purpose of the semi-logarithmic plot is to show more clearly the retentions obtained at low concentrations. Fig. 2 shows that the initial fall of the curve at low bromine concentration gives way to an almost linear portion which can be extrapolated to retentions of 0 and 15% at 1 and 0 molar fraction of bromine respectively.

The retentions found for the three isotopes of bromine produced (^{80}Br, ^{80}Br*, and ^{82}Br; half-lives 18 min., and 4·5 and 35 hr. respectively) are the same within experimental error (Fig. 1), in agreement with previous observations [6, 7, 19] with other aliphatic bromides.

Analysis of the Products from Neutron-irradiation.—The active products from ethyl bromide were analysed at two concentrations of elementary bromine; the results are given in the Table, in which the percentage activities of the fractions are the weighted mean of the results obtained for ^{80}Br* and ^{82}Br, which were identical within the statistical error of counting.

	N_{Br}		(c) Ratio :	Activity at $N_{Br} = 0$ due to	
	(a) $8\cdot9 \times 10^{-5}$	(b) 0·27	$\frac{\%\text{ activity in }(a)}{\%\text{ activity in }(b)}$	(d) High-energy processes	(e) Diffusive processes
Retention	31·47 ± 0·49	12·75 ± 0·29	—	—	—
Ethyl bromide	22·60 ± 0·38	6·03 ± 0·18	3·75 ± 0·13	8·25 ± 0·25 (5·79) *	14·35 ± 0·45 (16·81) *
Methylene dibromide...	2·21 ± 0·06	1·27 ± 0·04	1·74 ± 0·07	1·74 ± 0·05	0·47 ± 0·08
Ethylidene dibromide	1·87 ± 0·09	0·91 ± 0·10	2·06 ± 0·25	1·24 ± 0·14	0·63 ± 0·17
Ethylene dibromide ...	1·04 ± 0·05	0·70 ± 0·11	1·49 ± 0·25	0·96 ± 0·15	0·08 ± 0·16
Bromoform	0·56 ± 0·03	0·51 ± 0·03	1·10 ± 0·09	0·70 ± 0·04	−0·14 ± 0·05
Tribromoethane	0·86 ± 0·07	1·04 ± 0·05	0·83 ± 0·08	1·42 ± 0·07	−0·56 ± 0·10
Tetrabromoethane (residue)	0·32 ± 0·04	0·24 ± 0·03	1·33 ± 0·18	0·32 ± 0·04	0·00 ± 0·06

* Corrected values : See Discussion.

The errors given in this Table, and those in the following papers, are the standard deviations derived from the counting statistics.

Experiments were performed to confirm that no exchange occurred between the fractions during their separation by fractional distillation, in agreement with Rowland and Libby's observation,[20] but it was found that with normal separation procedure an error was introduced owing to incomplete separation of the neighbouring fractions. This was probably about 2—3% of the activity of these fractions; *e.g.*, for the experiment in column (*a*) in the Table the error in the bromoform fraction due to poor separation could be as much as 3% of (1·04 + 0·86), the percentage activities of the neighbouring ethylene dibromide and tribromoethane fraction. The errors quoted, which are those due to the statistics of counting, should therefore be increased by this amount.

The results differ from those obtained by Collie and Shaw [17] with less rigorously purified material. Their results were undoubtedly influenced by impurities, as suggested by Willard.[3] Preliminary experiments, not described here, have shown that the presence

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[19] Chien and Willard, *J. Amer. Chem. Soc.*, 1954, **76**, 4735.

[20] Rowland and Libby, *J. Chem. Phys.*, 1953, **21**, 1495.

of sulphur dioxide (a possible impurity from sulphite extraction) in ethyl bromide causes results similar to those found earlier.

DISCUSSION

The retentions in pure ethyl bromide found in the present work are greater than those found by Goldhaber and Willard.[10] This could be explained if the high γ-ray flux (from a 3c Sb–Be source) used in their experiments produced bromine more rapidly than that from the 500 mc Ra–Be source used by us. Alternatively, the greater retentions might be due to reactions in which inorganic bromine is returned to organic combination; since no evidence for these could be found in a γ-ray flux comparable with that associated with the neutron irradiation, these reactions could only be initiated by neutrons. Owing to the greater energy of the neutrons from the Ra–Be (than the Sb–Be) source, a small stationary concentration of organic radicals may be produced by protons from (*n,p*) scattering. If this were so, higher retentions might be caused by reactions of the type:

$$R + BrBr^* \longrightarrow RBr^* + Br$$

Very small concentrations of inactive bromine would suffice to reduce the concentration of such radicals to negligible proportions.

It is also possible that the purity obtained by us was less than that obtained by Goldhaber and Willard, but the reasonable consistency of the retentions (35—39%) obtained in differently purified specimens makes this explanation improbable.

The linear form of Fig. 2 at high bromine concentrations is consistent with the interpretation that in this region the retentions are predominantly produced by high-energy processes, since the probability of a recoiling atom's forming an organic bromide at this stage should be proportional to the concentration of organic radicals in the vicinity of the recoil "track." Since such radicals can only be produced from ethyl bromide molecules, it would be expected that R_E, the retention due to high-energy processes, would be proportional to $(1 - N_{Br})$ (where N_{Br} is the molar fraction of bromine present). The value (15%) of R_E obtained by extrapolation to zero bromine concentration is lower than that obtained by Goldhaber and Willard [10] or by Roy *et al.*; [13] however, this was expected since the measurements by these authors covered only a small range of bromine concentration, a fact which might also explain the discrepancy between their values for R_E.

On this interpretation, the ratio of R_E at $N_{Br} = 0$ to that found at $N_{Br} = 0{\cdot}27$ is 1·37 $[1/(1 - 0{\cdot}27)]$. For the results given in the Table, the corresponding ratio for those products whose formation is by high-energy processes should also be the same, and compounds which are produced in the diffusion-dependent processes should show a ratio greater than this. Column (*c*) shows these ratios for the individual fractions; the greatest ratio is that found for ethyl bromide, indicating that a large proportion of this fraction is produced by diffusion-dependent reactions. If it is assumed that, at $N_{Br} = 0{\cdot}27$, only high-energy processes are responsible for the production of the active organic bromides, it is possible to estimate the yields of individual fractions from such processes occurring at $N_{Br} = 0$; the values obtained are given in column (*d*), and were found by multiplying the figures in (*b*) by 1·37.

The activities obtained by subtracting the figures in column (*d*) from those in (*a*) should now give an estimate of the diffusion-dependent yields of the individual fractions [column (*e*)]. Since the total yield expected from such processes is 17% (= 32 − 15), it can be seen that the predominant product is ethyl bromide.

The negative values in column (*e*) probably mean that the yields of these fractions are not reliable. They could arise if active compounds, for which no carriers were added, were present in the irradiated ethyl bromide, since these might appear with the carrier fractions in variable amount. Support for this can be obtained from the fact that the sums of the individual fractions in (*a*) and (*b*) are less than the total observed retentions, indicating that loss of activity, for which no correction was made, occurred during the fractional distillation.

The ethyl bromide fractions are unlikely to be subject to the same error, since we had sufficient to allow more generous rejection of the first and last fractions during the distillation.

The arguments above are based on the assumption that the total organic yield at $N_{Br} = 0{\cdot}27$ is from high-energy reactions; if this were so, the retention would be only 10·95%, whereas that found was 12·75%. The difference (1·80%) is probably due to the occurrence of diffusion-dependent reactions, and this therefore indicates that the true yield of ethyl bromide from high-energy processes should be approximately (6·03 − 1·80) = 4·23%. Using this modified value, and performing the above operations, we find that the yields of ethyl bromide at $N_{Br} = 0$ from the two sets of reactions are 5·79 and 16·81%, the latter being almost exactly equal to the graphical estimate for the total activity produced by diffusive reactions.

The experiments therefore support the hypothesis [10, 11] that the reactions occur in two stages. By use of the extrapolation technique of Goldhaber and Willard [10] and Roy *et al.*[13] it has been possible to show that probably the entire yield from diffusion-dependent reactions consists of ethyl bromide, the other active products bring produced by high-energy reactions. This is consistent with the view that the products from the initial stage should be more complex than those from the final stage. The degree to which molecular fragmentation occurs may be surmised from the formation of substances, such as methylene bromide or bromoform, which indicates that C–C bonds are broken, and that possibly fragments as small as :CHBr are produced; for example, such a radical could add bromine to form bromoform or combine with a similar radical to give dibromoethylene, subsequent saturation of which could give tetrabromoethane. However, in view of the difficulty in reproducing the activities in such fractions the interpretation of such processes must remain highly speculative, needing a more substantial experimental basis than that here provided.

The formation of ethyl bromide in the diffusion-dependent reactions could be by any of the following :

$$C_2H_5\cdot + Br^* \longrightarrow C_2H_5{\cdot}Br^* \quad \dots\dots\dots \quad (A)$$

$$C_2H_5\cdot + BrBr^* \longrightarrow C_2H_5{\cdot}Br^* + Br \quad \dots\dots\dots \quad (B)$$

$$\text{or } C_2H_5{\cdot}Br + Br^* \longrightarrow C_2H_5{\cdot}Br^* + Br \quad \dots\dots\dots \quad (C)$$

Reaction (*C*) may be neglected, because its activation energy is prohibitively high [21] (25 kcal./mole) for the thermal atom involved, and it has been shown [10, 13] that active bromine atoms, diffusing from the site of their formation, normally form inorganic compounds. The relative importance of reactions (*A*) and (*B*) is discussed in more detail later,[22] but it is noteworthy that both involve ethyl radicals. From the relative activities of the fractions produced in the high-energy processes it appears that unless reaction (*C*) is important in this case, approximately one half of the radicals involved are ethyl radicals, the others being " complex." Since none of the latter exists for sufficient time to play an observable part in the thermal processes, which involve only simple ethyl radicals, it is probable that they form ethyl radicals by removal of bromine atoms from solvent molecules.

EXPERIMENTAL

Purification of Ethyl Bromide.—(i) Ethyl bromide (British Drug Houses Ltd.) was distilled and then stored in daylight with elementary bromine to remove olefins. It was then shaken with dilute sodium sulphite solution, separated, and dried ($CaCl_2$); the liquid was then distilled in a column (40 cm. × 1·5 cm. diam.) packed with glass helices, the middle 50% being retained.

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[21] Liberatore and Wiig, *J. Amer. Chem. Soc.*, 1940, **8**, 349.
[22] Milman and Shaw, *J.*, 1957, 1317.

(ii) As in ref. 11, after preliminary distillation, the ethyl bromide was shaken with concentrated sulphuric acid, then washed several times with dilute sodium carbonate solution, and finally with distilled water. After being dried ($MgSO_4$) it was fractionally distilled as above.

Technique.—Neutron irradiations were performed in darkness by placing standard 50 ml. flasks containing ethyl bromide round a 500 mc Ra–Be source held centrally in a trough of water made from paraffin wax. It was found that the retentions of samples containing $N_{Br} = 10^{-5}$ were unaffected by the distance from the source and no rigorous precautions were taken to ensure constant geometry.

Extractions were made by shaking a portion of irradiated ethyl bromide with dilute sodium sulphite solution containing sodium bromide as carrier. After separation, the liquid was dried ($CaCl_2$) and a little elementary bromine was added. The unextracted portion was poured into a fresh flask and a little bromine added to ensure that any inorganic ^{80}Br produced by decay of $^{80}Br^*$ did not settle on the walls of the containing flask or the counter. The irradiation-flask was washed out with sodium bromide solution which was then treated with chlorine; the bromine produced, together with excess of chlorine, was successively extracted with carbon tetrachloride. The activity of this was measured to ensure that none of the active inorganic species had been absorbed on the walls during irradiation, since otherwise a spurious value for the activity of the unextracted fraction would result.

All measurements were made on liquid samples with an M.6 counter (Twentieth Century Electronics Ltd.). In experiments on ^{80}Br (half-life 18 min.), the period of irradiation was only 10—15 min., and the activities of the different fractions were measured as soon as possible. The activity was again measured 4 hr. later to determine to what extent activity from $^{80}Br^*$ had contributed to the first measurement; this was negligible unless the period between removal from the source and the first measurement was very long. For experiments with $^{80}Br^*$ and ^{82}Br the period of irradiation was greater than 15 hr. At least 4 hr. were allowed to elapse between extraction and measurement to ensure that ^{80}Br, directly produced by neutron capture, had decayed to negligible proportions, and to allow the establishment of transient equilibrium between $^{80}Br^*$ and ^{80}Br. A further measurement was made 15 hr. after the first, thus enabling the determination of the activities due to $^{80}Br^*$ and ^{82}Br. Any activity obtained from the walls of the irradiation flask was corrected for dilution, and also for the greater density of carbon tetrachloride than of ethyl bromide by using an empirically determined " self-absorption " curve.

The yellow colour produced on neutron irradiation was shown to be due to bromine by its disappearance on shaking with sulphite, and by the liberation of iodine from starch–iodide paper; freshly prepared ethyl bromide did not react with the latter. For specimens held near the Ra–Be source, 10^{-5} molar fraction of bromine, determined by colorimetric matching with standards, was produced by five days' irradiation.

The absence of reactions capable of producing organic bromides from the extractable radiobromine was checked by irradiating a specimen for 15 hr. This was divided into three aliquot parts; one was extracted immediately after removal from the source, and the others were left for 12 hr. in darkness, one near 500 mc of radium and the other in a place free from radiation. They were then extracted; in both cases the rate of loss of radiobromine from the inorganic fraction (fraction lost per hour) was $0 \pm 0{\cdot}0012$, the retention for $^{80}Br^*$ being 35·1%.

Retentions with Bromine Present.—The extractions were performed with sodium sulphite solutions of appropriate concentration. For the extraction of the more concentrated solutions of bromine, the sulphite solution was cooled with a slurry of ice, to prevent evaporation of the ethyl bromide by the heat of reaction between the bromine and sulphite. Counts were made as already described, and were corrected for the differing densities and also for the volume of bromine used. For example, if a certain solution contained A ml. of ethyl bromide and B ml. of bromine, then C ml. of the unextracted solution contained $CA/(A + B)$ ml. of ethyl bromide; in order to compare its activity with that of C ml. of extracted ethyl bromide, the activity of the former therefore had to be multiplied by the factor $(A + B)/A$.

Analysis of the Products from Neutron-irradiation.—100 ml. samples of ethyl bromide containing bromine were irradiated for five days; 12 ml. were retained for measurement of the total activity, the rest being extracted. To 50 ml. of the latter were added 10 ml. portions of methylene, ethylidene, and ethylene bromide and bromoform, and 5 ml. of 1 : 1 : 2-tri- and 1 : 1 : 2 : 2-tetra-bromoethane (all from British Drug Houses Ltd., distilled). The mixture was re-extracted to remove any bromine which might have been present in the carriers.

After being dried ($CaCl_2$), the mixture was separated into its consitutents by fractional distillation in a column packed with glass helices and purposely made small (20 cm. × 1·5 cm.) to ensure small hold-up. Ethyl bromide and methylene and ethylidene dibromide were collected at atmospheric pressure, the remaining carriers being separated under reduced pressure. As a check on the purity of each fraction, the boiling and condensing temperatures were taken, the fraction being re-distilled if these temperatures differed by more than about 0·2°; this criterion was not applied to the tetrabromoethane fraction which was recovered as the residue in the distilling flask. The volumes of the various fractions recovered pure (about 2—3 ml.) were measured, and made up to 11 ml. with carbon tetrachloride. The activities of each fraction were corrected for losses occurring during the fractionation and for the density of the resulting carbon tetrachloride solution.

The use of bromoform as a carrier was suggested by its production on neutron-irradiation of methyl bromide [23] and by the formation of iodoform (1%) in irradiated methyl iodide.[24]

In order to check that no exchange occurred between the fractions during the distillation, ethylene dibromide labelled with ^{82}Br was mixed with the remaining carriers, and separated as above. After applying the above corrections it was found that 96% of the active material was recovered as ethylene dibromide, the remaining activity being distributed between the ethylidene dibromide (1·6%) and bromoform (2·8%) fractions. By adding more (inactive) ethylene dibromide to the latter fractions it was shown that their activity was caused by the presence of ethylene dibromide, and was not produced by exchange.

The authors are indebted to Prof. Lord Cherwell, F.R.S., for laboratory facilities.

THE CLARENDON LABORATORY, OXFORD. [*Received, July 7th,* 1956.]

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[23] Hazelwood, personal communication.
[24] Shaw, unpublished results.