

95. Comparison of Weak Neutron Fluxes by Use of Organic Bromides.

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A quantitative study has been made of some of the factors influencing the reproducibility of extractions (using an aqueous extracting agent) of radio-bromine from neutron-irradiated ethyl bromide, bromobenzene, and ethylene dibromide with a view to furnishing a sensitive method of comparing weak neutron fluxes. The chief cause of non-reproducibility of extractions of these substances is the presence of olefinic impurities produced by the recoiling radio-bromine atoms. Evidence for the stability of the methylene molecule has been obtained. By irradiating specimens containing a trace of elementary bromine, and by making corrections when necessary for exchange between the extractable radioactive species and the bulk of the (inactive) liquid, extractions can be made reproducible to better than $\pm 1\%$.

Aniline present during the neutron-irradiation of ethylene dibromide reduces the amount of radio-bromine extractable with potassium bromide, owing to the formation of bromoaniline, but at the same time reduces the exchange occurring in the pure liquid, and if present in sufficient quantity, increases the amount of extractable radio-bromine by playing a direct part in the γ -recoil process (cf. Lu and Sugden, *J.*, 1938, 1273).

THE work described in this paper is an extension of a method of comparing weak neutron fluxes reported previously (Shaw and Collie, *J.*, 1949, 1217). The latter made use of the Szilard-Chalmers effect (*Nature*, 1934, 134, 462) in ethyl iodide, by means of which about half of the radio-iodine produced by the reaction $^{127}\text{I} (n, \gamma) ^{128}\text{I}$ can be extracted with an aqueous reagent and concentrated so that the reduction in activity caused by self-absorption effects is small. The method suffers from a defect that in certain physical applications (*e.g.*, see Halban, Kowarski, and Magat, *Compt. rend.*, 1939, 208, 572) the time elapsing between the removal of the neutron source and the measurement of the extracted radio-halogen is necessarily large compared with 25 minutes (the half life of ^{128}I), and consequently there is a serious loss of measurable activity. This difficulty can be reduced by using organic bromides as the detectors, since some of the bromine isotopes [^{80}Br (excited state) and ^{82}Br] produced by neutron capture have longer half-lives (4.4 and 34 hours respectively).

The compounds investigated were ethyl bromide, bromobenzene, and ethylene dibromide. It was found that in the presence of small quantities of elementary bromine the reproducibility of extraction of radio-bromine from the neutron-irradiated halides could be made better than 1%. In the absence of bromine none of these compounds purified by conventional methods could be made to give reproducible extractions; the extent of this irreproducibility is indicated in Table I which gives the efficiency of extraction (the activity extracted/total activity produced $\times 100 = 100 -$ the "retention") for these substances under different conditions.

TABLE I.

Compound.	Efficiency of extraction. Pure compound.	(All compounds irradiated to saturation at 15°.)
		Compound + 0.01 g. of Br_2 /100 c.c.
Ethyl bromide	35 \pm 10 *†	54 \pm 3 †
Ethylene dibromide	45 \pm 10 *†	62 \pm 2
Bromobenzene	27 \pm 10 *	55 \pm 2

* Not reproducible.

† "Exchange" occurs.

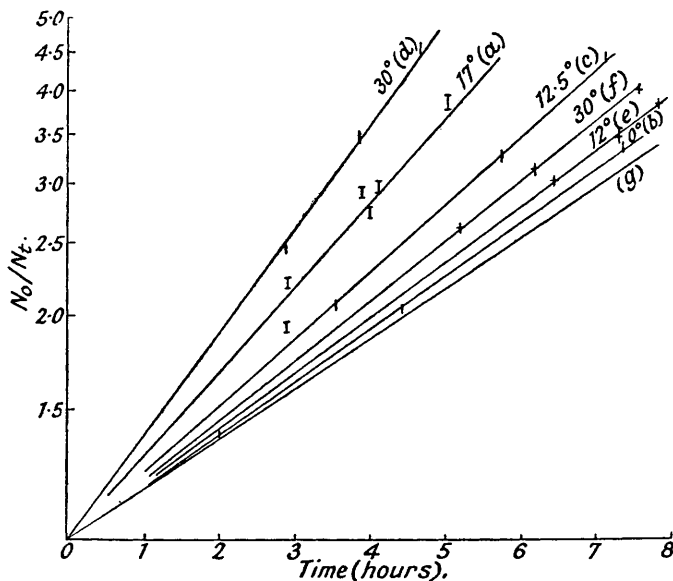
The object of this paper is to give an account of the stabilising action of traces of elementary bromine in extractions of the above organic bromides and to discuss the optimum conditions for their use as neutron detectors.

In this paper, the term "exchange" is used extremely loosely to describe the slow disappearance of the extractable radioactive species by any means other than decay; as will be seen later, although sometimes this may refer to a true chemical exchange between the extractable radio-bromine and the bulk of the (inactive) organic bromide, under certain conditions the extractable radio-bromine probably disappears by some other mechanism.

Ethyl Bromide.—In the absence of elementary bromine, a considerable, variable fraction (up to 40%) of the extractable radio-bromine adhered to the walls of the irradiation flask.

The adsorbed material was easily removed by washing with potassium bromide solution and was incorporated with the main aqueous extract. Thus while loss caused by variable adsorption was not in itself a cause of variation it was thought possible that it might indirectly be the cause of the variable results obtained under these conditions. If the rate of exchange between the extractable radio-bromine and the bulk of the ethyl bromide was different when the former was adsorbed or in the liquid, the overall exchange rate would be variable and would lead to variation in the activity extracted. The exchange was followed by splitting irradiated specimens of ethyl bromide into two aliquots, extracting one immediately and leaving the other for a variable time before extraction. The exchange curve obtained is shown in Fig. 1, curve (a); the variation in the exchange rates was not sufficient to account for the variation in the activity extracted initially, which varied from 9400 to 15800 counts/10 minutes. No marked correlation was observed between the amount of extractable radio-bromine adhering to the walls and the

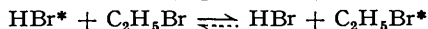
FIG. 1.



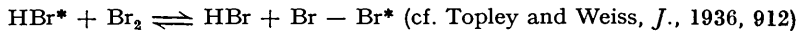
N_t = Activity extractable after time t .

), Purified C_2H_5Br ; +, $C_2H_5Br + Br$; I (curve a), see text; g, Natural radioactive decay.

magnitude of the activity extracted initially. A more probable explanation of the variation in the rate of exchange is that the exchange proceeds by the mechanism:



and that the concentration of hydrogen radio-bromide present is dependent on the exchange:



i.e., is dependent on the concentration of elementary radio-bromine present. Reasons for supposing that the latter quantity (and hence the exchange) is not constant are given later.

In all experiments the isotope whose disintegration was measured was the excited state of ^{80}Br (4.4 hours, half-life), and hence measurements were unaffected by the possibility of extra activity accruing in the extractable fraction owing to the formation of 18-minute ^{80}Br produced by the radioactive decay of the excited state (cf. Segré, Halford, and Seaborg, *Physical Rev.*, 1939, 55, 321).

If a large quantity of ethyl bromide was purified (as described later), portions of this gave extractions consistent (to within $\pm 2\%$) with those from other irradiated portions of the same batch, provided that an aliquot used for an irradiation and extraction was not re-mixed with it. On repetition of the purification process reproducible results were again obtained with specimens from the purified batch, although the activities obtained under identical irradiation (etc.) conditions were different from those of the first batch. By using quantities from such purified batches it was possible to construct exchange curves by the method described for ethyl iodide (Shaw and Collie, *loc. cit.*); the results obtained are shown in Fig. 1, curves (b), (c), and (d).

If it is assumed that the back-reaction of the exchange is negligible owing to the fact that effectively all the bromine atoms in the ethyl bromide are inactive, the rate of disappearance of the extractable species may be written $dN/dt = -(\lambda + k)N$, where N is the number of extractable radio-bromine atoms, and λ and k are the radioactive decay and exchange constants respectively. By integration, this becomes $\ln(N_0/N_t) = (\lambda + k)t$, where N_0 and N_t are the number of extractable radio-bromine atoms present at times $t = 0$ and t respectively; by subtracting λ from the slopes of the curves shown, the values of k (the fraction exchanging per hour) may be obtained. By equating $k = \alpha \exp(-E/RT)$ where α is a constant and E is the heat of activation for the exchange, one obtains $\alpha = 2.4 \pm 0.4 \times 10^{15}$ and $E = 21.5 \pm 3.0$ kcal. per g.-mol. These values are only approximate, owing to the difficulty in obtaining reproducible extractions from batch to batch of ethyl bromide. The value of α is consistent with the view that the exchange occurring is between hydrogen radio-bromide and (inactive) ethyl bromide. The heats of activation between *n*-butyl and *n*-propyl bromides and hydrogen radio-bromide have been measured by Leroux and Sugden (*J.*, 1939, 1279) and Elliot and Sugden (*J.*, 1939, 1836) in ionising solvents and found to be 18.87 and 18.13 kcal./g.-mol. respectively; the nearness of these figures to the activation energy found might also add corroborative evidence for the mechanism of the exchange, although it is difficult to conceive of an ionic mechanism for the exchange in pure ethyl bromide, owing to the low dielectric constant of this substance.

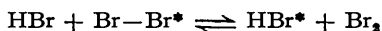
In the presence of small quantities (0.01 g./l.) of elementary bromine the exchange is greatly reduced; the exchange curves obtained are shown in Fig. 1, curves (e) and (f). The values of α and E (in the same units as above) for this "exchange" are 7.6×10^3 and 9 ± 3 respectively. The low value of α suggests that the reaction occurring may be with some impurity; however, after irradiation to saturation of bromine-ethyl bromide solutions, the activities (which are proportional to the effective half-life τ' , defined as $\ln [2/(\lambda + k)]$) obtained were independent, within $\pm 1.5\%$, of the methods used for purification of the ethyl bromide and bromine. The whole anomaly is analogous to that in ethyl iodide, and so far no explanation of it can be advanced.

The reproducibility of extractions of ethyl bromide containing a trace of bromine is illustrated in Table II(a); the activities shown are corrected for the radioactive decay occurring between extraction (at the time of removal from the neutron source) and measurement, and to "saturation-irradiation" by using the expression:

$$\text{Activity at saturation} = \text{Activity extracted} / (1 - 2^{-T/\tau'})$$

where T is the time of irradiation and τ' the effective half-life (defined above). As can be seen from Table II(a) the activity extracted was independent of the concentration of bromine in the irradiated mixture within the limits indicated; a similar independence has already been shown for ethyl iodide.

The rôle of added iodine in ethyl iodide has been shown to be solely to inhibit the exchange occurring; in ethyl bromide, the bromine appears to do more than this, since if the amount of extractable radio-bromine which would have been obtained had no exchange occurred is calculated by multiplying the activities at saturation by $\tau_{\text{radioactive}}/\tau_{\text{effective}}$, the resulting activity is not the same for ethyl bromide irradiated with and without bromine. It was thought that the variations in the activities extracted from pure ethyl bromide might be ascribed to small ethylenic impurities either present initially owing to incomplete "saturation" of the compound by the purification process or produced by the γ -recoil process. In either case any elementary radio-bromine produced might be expected to add to the double bonds and be lost from the extractable fraction; such an effect would probably be less marked in the case of ethyl iodide, owing to the reluctance of iodine to add to double bonds. The stabilising influence of bromine in ethyl bromide irradiations could then be explained by assuming that the olefinic impurities would be saturated preferentially by the (inactive) bromine present, thus preserving radio-bromine present for extraction. On this basis the variation in the activities extracted from pure ethyl bromide could be ascribed to variable ethylene (etc.) or hydrogen bromide content; in the latter case the amount of elementary radio-bromine present would also be variable owing to exchange of the type:



which occurs readily even in non-ionising solvents (Topley and Weiss, *loc. cit.*).

The feasibility of this type of explanation was tested by measuring the activity extractable from an aliquot of a purified batch of ethyl bromide [Table II(b)], and then repeating the experiment after a little ethylene had been passed into it; the activity obtained is shown in

Table II(c), and was significantly less than that shown in (b). Attempts were made to confirm the validity of this explanation by adding various carriers to extracted specimens of ethyl bromide and separating them by fractional distillation, a technique used first by Glueckauf and Fay (*J.*, 1936, 390). The activities obtained, expressed as percentages of the total radio-bromine produced are given in Table III; the activities from (a) (bromine present during irradiation) are the mean of two experiments. The errors given are statistical only, and in general should be increased by about 3% to cover errors inherent in the method used (see later).

TABLE II.

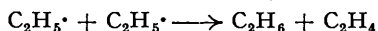
(a) Br (mg./l.)	Activity extracted (per 5 mins.)	(b) Activity (per 5 mins.) from purified batch of ethyl bromide.	(c) Activity (per 5 mins.) from ethyl bromide used in (b) + trace of ethylene.
22	21,600 ± 200	14,900 ± 150	10,300 ± 120
40	21,600 ± 200	14,700 ± 150	10,500 ± 120
45	21,500 ± 200		
55	21,800 ± 200		
122	21,900 ± 200		

TABLE III.

Fraction.	0.01 g. of Br per 100 c.c. of C ₂ H ₅ Br.		No Br present.	
	(a).	(b).	(c).	(d).
(1) CH ₃ Br	4.02 ± 0.26	4.21 ± 0.23	4.60 ± 0.32	4.65 ± 0.35
(2) CH ₂ Br ₂	4.05 ± 0.20	10.30 ± 0.49	6.12 ± 0.24	9.40 ± 0.42
(3) C ₂ H ₅ Br	23.52 ± 1.62	31.41 ± 2.05	34.62 ± 1.94	29.22 ± 1.93
(4) CH ₃ ·CHBr ₂	3.42 ± 0.24	8.09 ± 0.41	6.95 ± 0.37	7.85 ± 0.36
(5) CH ₃ Br·CH ₂ Br	4.53 ± 0.30	13.72 ± 0.61	7.04 ± 0.36	8.31 ± 0.41
(6) CH ₂ Br·CHBr ₂	1.92 ± 0.32	} 6.81 ± 0.35	3.62 ± 0.20	2.29 ± 0.27
(7) CHBr ₂ ·CHBr ₂	1.07 ± 0.12		2.80 ± 0.18	1.93 ± 0.13
Sum of (1) to (7)	42.53 ± 1.76	74.54 ± 2.28	65.75 ± 2.05	63.65 ± 2.11
Sum of (1) to (7) (determined directly)	44.98 ± 2.85	76.10 ± 3.92	68.45 ± 3.74	66.51 ± 4.02
Percentage extracted ...	54.65 ± 2.92	24.95 ± 2.19	31.41 ± 2.20	36.25 ± 2.72

If one assumes (after Libby, *J. Amer. Chem. Soc.*, 1940, **62**, 1930) that the main process responsible for the "slowing-down" of the energetic atoms is collision with other bromine atoms, then about eight collisions are necessary to reduce the translational energy from about 175 ev. to about 1 ev., it being further assumed that on average half the energy is lost per collision. This corresponds roughly to a path length of 20 Å. (calculated by using van der Waals radii taken from Pauling, "Nature of the Chemical Bond," 2nd edition, 1945), and, if all the molecules "touched" by the recoiling atom and other bromine atoms (energised by collision) are considered as potentially capable of playing a direct part in the recoil process, the total number of such molecules will be about 30 per recoil. Since the concentration of bromine molecules in run (a) (Table III) was 1 per 20,000 ethyl bromide molecules, it appears that the probability of the added bromine playing a direct (or immediate) part in the recoil process was only about 1 per 660 recoils. At higher concentrations of bromine (1—6%) the added bromine may play a significant part in the recoil processes, and evidence for this has been obtained by Lu and Sugden (*loc. cit.*) and Friedman and Libby (*J. Chem. Physics*, 1949, **17**, 647).

It seems probable, therefore, that the activity of the fractions in (b), (c), and (d) in excess of those in (a) cannot be explained by direct participation of the bromine present in the recoil processes, but must be caused by slower secondary processes occurring after the recoil. It can be seen that the variation in activity of fractions 5, 6, and 7 can all be explained by assuming that radio-bromine adds to olefinic compounds (acetylene, vinyl bromide, and 1:2-dibromoethylene, respectively), presumably produced in the recoil process. For example, ethylene may be produced by the disproportionation of two ethyl radicals:



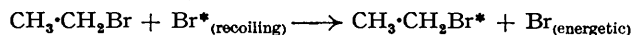
(Bawn and Whitby, Faraday Soc. Discussion, "The Labile Molecule," 1947, p. 228). The formation of vinyl bromide may occur by a similar process; the production of dibromoethylene is more difficult to explain but this may be brought about by recombination of highly fragmented ethyl bromide molecules. An alternative explanation is that fraction 7 may contain active heavier molecules (having more than two carbon atoms) for which no carriers were added.

The formation of ethylidene dibromide in variable amount is assumed to be caused by addition of hydrogen radio-bromide to vinyl bromide, although this explanation is open to the objection that hydrogen bromide adds to double bonds extremely slowly under optimum conditions.

The most interesting feature of Table III is the variation in activity of the methylene dibromide fraction. As already indicated, one must seek a relatively slow mechanism for the formation of the methylene radio-bromide produced in the absence of elementary bromine in order to account for the "protective" action of the latter. A feasible explanation to account for this is that methylene is produced by the recoil process and may then exist until a collision with a bromine molecule occurs. There is considerable evidence, recently reviewed by Laidler and Casey (*J. Chem. Physics*, 1949, 17, 1087) that methylene exists in a singlet state (all electrons paired) which is more stable than the triplet (biradical) state by at least 27 kcal./g.-mol. (Bawn and Dunning, *Trans. Faraday Soc.*, 1939, 35, 185). Other evidence for this is based on the theoretical work of Lennard-Jones (*ibid.*, 1934, 30, 70), and the spectrum of methylene (Herzberg, *Rev. Mod. Physics*, 1942, 14, 195) which has been discussed by Laidler and Casey (*loc. cit.*; *J. Chem. Physics*, 1949, 17, 213).

These facts imply that methylene should behave as an unstable molecule rather than a free radical of transient life, and that it therefore may exist in solutions of irradiated ethyl bromide until collision with bromine (or some other suitable molecule) transforms it into a more stable compound. Pearson, Purcell, and Saigh (*J.*, 1938, 409) have stated that methylene is less reactive than the methyl radical under certain conditions; this seems to be corroborated by the result shown in Table III in which it can be seen that the active methyl bromide fractions were approximately independent of the presence of bromine.

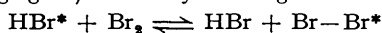
The ethyl bromide fractions will owe their large activity partly to exchange of the extractable species with ethyl bromide and partly to the reaction:



By using the above exchange curves it is possible to show that in runs (b), (c), and (d), the ethyl bromide activities would have been 20—25% of the total if no exchange had occurred. This indicates that 20—25% of the active bromine atoms produced react as above; as first emphasised by Libby (*J. Amer. Chem. Soc.*, 1947, 69, 2527), this reaction is more probable than many others in the recoil process, since a recoiling bromine atom can lose the greatest energy in a collision with an atom of the same mass, *i.e.*, a recoiling bromine atom of appreciable energy can undergo this reaction whereas collision with other (lighter) atoms present is less likely to result in the bromine atom's losing sufficient energy to enable it to combine immediately with the radicals produced.

The appreciable activities of fractions 2 and 4—7 in the presence of elementary bromine [run (a)] might be explained by assuming that, in the vicinity of a recoiling atom, the local concentrations of methylene, ethylene, etc., and radio-bromine are greater than those throughout the bulk of the liquid, owing to the "caging" effect of the surrounding ethyl bromide molecules (cf. Franck and Rabinovitch, *Trans. Faraday Soc.*, 1934, 30, 120; Libby, 1947, *loc. cit.*).

As summary of the above discussion it can be stated that the results obtained with ethyl bromide are explicable if it is considered that the changes taking place occur in three stages: (i) Ejection of the recoiling radio-bromine atom which produces unstable or unsaturated molecules and may combine directly with the free radicals, etc., produced. This stage is considered to be unaffected by small concentrations of impurities present in the irradiated liquid. (ii) Diffusion of the newly-formed molecules, etc., into the bulk of the liquid. These may react further with ethyl bromide or with impurities present in small quantity, or with HBr^* or $\text{Br}-\text{Br}^*$ to form non-extractable compounds. The stabilising action of free bromine is to saturate compounds containing olefinic double bonds which may be produced, thus leaving the extractable radio-bromine compounds free for subsequent extraction. In run (a), the number of radio active ($\text{Br}-\text{Br}^*$) bromine molecules was $\sim 10^7$ and, since that of the inactive bromine present was $\sim 10^{19}$, loss of radio-bromine molecules by this mechanism may be neglected. (iii) "Exchange" between the extractable species and ethyl bromide. This is reduced by the presence of free bromine, possibly because of a lower concentration of hydrogen radio-bromide (assumed to be the exchanging agent) caused by exchange of the type:



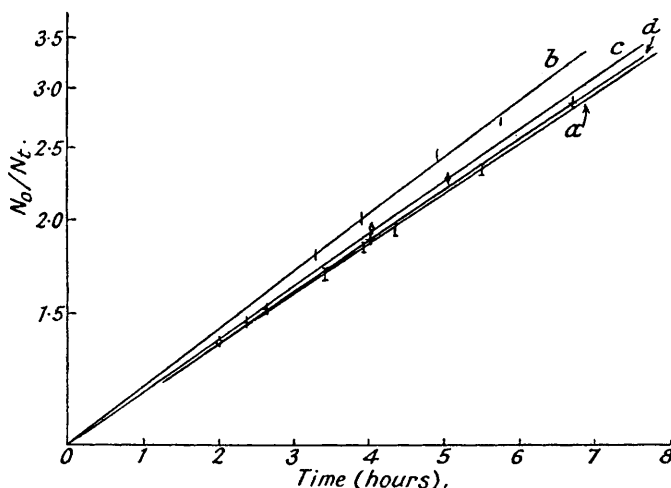
The reaction leading to the loss of extractable radio-bromine in the presence of free bromine had not yet been elucidated.

Ethylene Dibromide.—In the presence of bromine, extractions of this substance were reproducible (see Table IV) and no exchange could be detected at 15° [see Fig. 2(a)]. By correcting

the activities in Table IV (obtained from 3-hours irradiations) to saturation-irradiation using the formula given above but with k (the exchange constant) equal to 0, one obtains the value $48,800 \pm 550$. The corresponding value obtained experimentally from a specimen irradiated to saturation was $48,050 \pm 450$, in fair agreement with the calculated value. This indicates that no extra exchange was caused by γ -rays from the 500-mc. Ra-Be source used, though for greater γ -ray fluxes this probably does not hold (Williams, *J. Phys. Coll. Chem.*, 1948, 52, 603).

In the absence of bromine, extractions of this substance were variable; this inconstancy is probably to be explained in terms similar to those given for ethyl bromide. It was found that aliquots of purified batches of ethylene dibromide gave results which were reproducible within the batch, but that re-purification gave results which might differ considerably from those of the first batch. Exchange occurred at 15° [Fig. 2(b)], and traces of ethylene present in the ethylene dibromide reduced the extractable activity; for example, extractions of an aliquot of an

FIG. 2.



a, Natural radioactive decay. *b*, *c*, *d*, see text.

|, Purified $\text{CH}_2\text{Br}\cdot\text{CH}_2\text{Br}$; I, $\text{CH}_2\text{Br}\cdot\text{CH}_2\text{Br} + \text{Br}$; \circ , $\text{CH}_2\text{Br}\cdot\text{CH}_2\text{Br} + \text{NH}_2\text{Ph}$ (0.5%);
+, $\text{CH}_2\text{Br}\cdot\text{CH}_2\text{Br} + \text{NH}_2\text{Ph}$ (4.0%).

irradiated batch gave an activity of $12,200 \pm 150$ for a 3-hours irradiation, but after passage of a little ethylene into another aliquot the activity extracted under the same conditions was 7900 ± 100 .

TABLE IV.

(All activities refer to ethylene dibromide irradiated for 3.00 hours.)

(a) Concn. of Br (mg./l.).	Counts per 15 mins.	(b) Concn. of aniline (g./l.).	Counts per 15 mins.
50	$18,400 \pm 200$	5	$12,200 \pm 150$
100	$18,500 \pm 150$	10	$15,750 \pm 150$
100	$18,300 \pm 150$	10	$15,500 \pm 150$
100	$18,550 \pm 150$	20	$16,900 \pm 200$
100	$18,600 \pm 150$	20	$16,900 \pm 200$
100	$18,300 \pm 150$	40	$17,800 \pm 200$
		40	$18,000 \pm 200$
		40	$18,250 \pm 200$
		40	$17,850 \pm 200$

Use of ethylene dibromide containing added bromine was not altogether reliable since difficulty sometimes was encountered in keeping such solutions. For example, after successful use of a specimen of ethylene dibromide for irradiations, etc., the colour of the added bromine sometimes started to disappear, causing a white turbidity and formation of hydrogen bromide. When this occurred results were erratic; further addition of bromine produced more substitution, and re-stabilization of the ethylene dibromide to bromine could only be effected by careful redistillation.

In view of this, a brief examination was made of extractions of this substance containing aniline (cf. Lu and Sugden, *loc. cit.*). The aniline used was always freshly distilled in a darkened

room, since preliminary experiments showed that use of photo-decomposed aniline reduced the extractable activity considerably and made the results variable. The variation of the activities extracted (with potassium bromide solution) with aniline concentration is shown in Table IV(b).

Attempts were made to determine the radio-bromine present as bromoaniline, etc., by following the normal potassium bromide extraction by one with hydrochloric acid. These were not successful owing to the ease with which the activity disappeared on to the walls of the glass vessels and counters used. However, it appeared that about $16 \pm 3\%$ of the total radio-bromine was present as bromoaniline, and that this fraction was roughly independent of the aniline concentration for concentrations of 0.5–4.0. It was shown [Fig. 2(c) and (d)] that the rate of exchange between the extractable species and ethylene dibromide was reduced in the presence of aniline; curves (c) and (d) are for 10 and 40 g. of aniline per litre of ethylene dibromide. If the exchange normally proceeds by the reaction:



the inhibition of the exchange may be explained by the formation of aniline hydrobromide. This would reduce the concentration of free hydrogen radio-bromide; aniline hydrobromide is assumed to exchange much more slowly or not at all. The activity extractable was also independent of traces of ethylene present; thus, an aliquot of the specimen (mentioned above) containing ethylene together with 40 g. of aniline per litre gave an activity of $18,200 \pm 200$ counts per 15 minutes.

This suggests that the rôle of the added aniline is to remove all elementary radio-bromine produced, by the formation of bromoanilines and hydrogen bromide. This is consistent with the low values of the activities extracted when the concentration of aniline is small [see Table IV(b)]. For example, in the presence of small quantities of bromine the saturation activity is 48,800 counts/15 minutes, as shown above. This activity gives a measure of the total extractable radio-bromine produced directly from the recoil process, since there is no exchange under these conditions and the concentration of bromine is so low that direct participation by the bromine present is improbable. By correcting the activities obtained for a concentration of 10 g. of aniline per litre to saturation, by using $\tau_{\text{effective}}$ from curve (c) of Fig. 2, one obtains $39,950 \pm 650$; if this value is now multiplied by $\tau_{\text{radioactive}}/\tau_{\text{effective}}$ the resulting activity (41,850) is that which would have been obtained if no exchange had occurred. This is less than the value obtained in the presence of bromine—a result in qualitative agreement with the above explanation of the formation of bromoaniline.

As the aniline concentration is increased, the extractable activity also increases. By correction of the activities obtained with 40 g. of aniline per litre by the above method, the activity at saturation-irradiation for no exchange is found to be 48,050. The extra activity obtained must be caused by direct participation of aniline in the recoil process, as suggested by Lu and Sugden (*loc. cit.*).

It may be noted that values of the "efficiency of extraction" or "retention" have no significance when "exchange" occurs unless the time and temperature of irradiation are also specified. The importance of temperature is obvious since the activity extractable depends on the exchange which is (in general) itself temperature-dependent. The time of irradiation must also be taken into account since the rate of growth of the extractable radio-bromine is governed by its rate of disappearance ($\lambda + k$), whereas that of the total activity is governed by λ only.

Bromobenzene—Extractions of purified specimens of bromobenzene were not reproducible except from purified batches; in the presence of bromine, extractions were reproducible and independent of the bromine concentration within the limits indicated in Table V. No exchange could be detected in either case after heating irradiated specimens (with or without bromine present) at 100° for 2 hours.

TABLE V.

Concn. of Br (mg./l.)	100	100	200	200
Activity per 15 mins. at saturation	$15,200 \pm 200$	$15,250 \pm 200$	$14,950 \pm 200$	$15,300 \pm 200$

In the light of the above results, the low efficiency of extraction in the absence of bromine might be caused by the formation of compounds containing "aliphatic" double bonds, by the addition either of molecules or of free-radicals to activated bonds in benzene rings (cf. Miller and Dobson, *J. Chem. Physics*, 1950, **18**, 865), or by the splitting of benzene rings by the recoiling atoms (cf. Stein and Weiss, *J.*, 1949, 3254). Any elementary bromine produced could then add subsequently to such unsaturated molecules; according to this explanation, the variability of

the results could be ascribed either to the incomplete saturation of such molecules by the purification process or to small amounts of hydrogen bromide present as impurity (cf. ethyl bromide).

In the presence of elementary bromine, saturation of such molecules would occur preferentially by addition of inactive bromine molecules, thus preserving the active molecules for extraction. Confirmation of the general validity of these ideas was obtained by extracting irradiated specimens of bromobenzene and then refluxing the liquid with reagents which might be expected to react with aliphatically bound bromine, but which would leave unaffected any attached to the aromatic ring. The results obtained are shown in Table VI.

TABLE VI.

[Activities correspond to counts ($\times 10^{-2}$) per 15 mins., corrected to time of removal from source and to saturation-irradiation.]

Original state of C_6H_5Br .	Activity extracted.	Treatment.	Activity from 1st refluxing.	Activity from 2nd refluxing.	Total activity.
(a) No Br present.....	713 \pm 8	A	282 \pm 7	25 \pm 1	1020 \pm 11
(b) " ".....	608 \pm 8	B	365 \pm 5	45 \pm 1	1018 \pm 10
(c) " ".....	604 \pm 8	C	356 \pm 5	59 \pm 3	1019 \pm 10
(d) 0.20 g. of Br per l. ...	869 \pm 8	B	174 \pm 2	38 \pm 1	1081 \pm 8
(e) " " ".....	864 \pm 8	C	161 \pm 5	45 \pm 1	1070 \pm 10

A, alcoholic potassium hydroxide; B, alcoholic silver acetate; C, alcohol-zinc reduction.
Total time of treatment = 7 hours; duration of 1st refluxing = 2—2½ hrs.

It is probable that the "fixing" of the aliphatic bromine was never complete, but further reaction would have been useless since the activities obtained would have been too low to be statistically significant. In the absence of bromine it can be seen that the sum of the activity extracted and the activity obtained from the treatment was approximately constant, in agreement with the above suggestion. In the presence of bromine the same quantity was larger by about 5%; this could be caused by direct participation of the added bromine in the recoil process, although such participation seems unlikely for the reasons advanced above; an alternative explanation might be that, in the absence of bromine, compounds containing groups such as $-CH_2CHBr^*$, etc., react only with difficulty, but that in the presence of bromine (when the double bond may be saturated) the bromine is more easily attacked by the reagents used.

In the presence of bromine, the aliphatic radio-bromine may be produced by (a) the disruption of benzene rings (as outlined above) by an energetic radio-bromine atom, followed by addition to the residual aliphatic radical, or (b) by addition of radio-bromine to an unsaturated molecule (produced by the same recoil) while these are "caged" together by the surrounding bromobenzene molecules (cf. Franck and Rabinovitch, *loc. cit.*).

Use of Organic Halides as Neutron Detectors.—Chemical aspects. All the halides studied gave results which were reproducible to $\pm 1\%$ if due attention was paid to the corrections necessitated by exchange, etc. For most purposes, perhaps, the use of ethyl iodide containing a small quantity of iodine is most convenient since reproducibility is a function only of exchange and no other complicating effects (addition of iodine to double bonds, etc.) appear to be present. Of the bromides, bromobenzene-bromine solutions are the most suitable, since the bromine remains in solution for long periods and no exchange occurs. However, if large quantities of the detecting liquid are required, the greater availability of ethylene dibromide favours its use; in this case, ethylene dibromide-bromine mixtures are the most convenient, but due care must be taken to ensure their stability. Mixtures of aniline with ethylene dibromide are less suitable, since exchange corrections must be made and also the activity extracted is dependent on the concentration and purity of the aniline.

The general method has been applied successfully in this laboratory by other authors (*e.g.*, see Parsons and Collie, *Proc. Physical Soc.*, 1950, **63**, A, 839), but it has been found that extraction of large quantities (5 litres) of organic halides gave erratic results caused by incomplete mixing of the halide with the sulphite extracting agent when these were shaken manually. On reducing the quantity shaken to 2.5 litres and repeating the process, results were again reproducible and the time of processing was only increased by about five minutes.

Physical aspects. For all these halides, it is necessary that the energy of the neutron fluxes to be compared is the same, since the proton- and halogen-scattering and capture cross-sections are functions of the neutron energy.

Use of ethyl iodide is convenient since the correction for saturation and decay is easily calculable, whereas with bromides this is extremely difficult owing to the number of isotopes

produced and the complexity of the decay scheme of ^{80}Br . In practice, when it is desired to compare weak neutron fluxes by using bromides, it is better to adhere to a rigorous time schedule, keeping constant the time of irradiation (unless this is done to saturation), the period between the removal of the detector from the neutron source and processing, and the time of measurement. The second of these is particularly important since the 18-minute ^{80}Br (ground state) may also be produced in an extractable form by the decay of the excited state in organic combination; for this reason the temperature of the irradiation should also be held constant (see Segré *et al. loc. cit.*).

EXPERIMENTAL.

The organic bromides were purified by redistillation, treated with elementary bromine, extracted with sodium sulphite solution, and dried (CaCl_2). Treatment with bromine was adopted to saturate possible olefinic impurities since these were shown to reduce the amount of extractable radio-bromine. After irradiation and extraction of a bromide, the treatment with bromine, etc., was (in general) repeated, but not the distillation. This method was adopted since often the conditions under which this method of comparing the neutron fluxes is used render a lengthy redistillation impractical. Commercial specimens of ethylene dibromide often contained olefinic impurities, the added bromine disappearing rapidly.

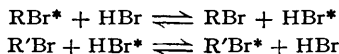
Neutron irradiation, and extraction and precipitation of the radio-bromine produced, were performed as described previously for ethyl iodide (Shaw and Collie, *loc. cit.*). Measurements were always made on the excited ^{80}Br isotope; this decays (half-life, 4.4 hours) with weak γ -emission into the ground state, which then decays (half-life, 18 minutes) with β and weak γ -emission. The actual radiation detected by the counter was the β -radiation of the unexcited ^{80}Br isotope in transient equilibrium with the longer-lived isomer. Each specimen was measured twice; the first count was made not less than 4 hours after extraction, in order to allow any unexcited ^{80}Br produced directly by the (n, γ) process to decay and also to establish radioactive equilibrium between the excited and the ground state. The second measurement was made about 20 hours later, in order to correct the activity for ^{82}Br (half-life, 34 hours) produced.

In general, measurements were not corrected for "self-absorption" since it was always arranged that the superficial density of the silver bromide counted corresponded to that at the maximum of the self-absorption curve (Collie, Shaw, and Gale, *Proc. Physical Soc.*, 1950, **63**, A, 282).

Exchange rates were measured as described for ethyl iodide (Shaw and Collie, *loc. cit.*).

Extraction efficiencies were measured by counting portions of the extracted and unextracted halide after neutron irradiation; it was found that sometimes an appreciable fraction of the extractable radio-bromine adhered to the walls of the vessel used for the irradiation; the walls of the vessel were therefore extracted separately with dilute potassium bromide solution and the radio-bromide was measured after precipitation as silver bromide.

Analyses of the Products from Irradiated Ethyl Bromide.—These were performed by adding small quantities (about 10 g.) of suitable substances as carrier and then separating them by distillation. 100 C.c. of ethyl bromide, irradiated to saturation with respect to ^{80}Br , were divided into two equal portions; these were extracted separately with aqueous potassium bromide or sodium sulphite, if free bromine was absent or present respectively. One portion was measured directly, and the other was washed with water to ensure complete removal of radio-bromide ions; the latter was then treated with bromine to saturate compounds such as vinyl radio-bromide, etc., which might be produced by the recoiling atoms. The bromine was then removed by shaking the mixture with sodium sulphite solution, and weighed quantities of methylene, ethylene, and ethylidene dibromides, and 1:1:2-tri- and 1:1:2:2-tetra-bromoethane were then added. The mixture was re-shaken with sulphite to ensure the removal of bromine which might have been present in the carriers, and dried over calcium chloride [Table III(b) and (c)] or anhydrous sodium sulphate [run (d)]. After filtration, the liquid was cooled to about -10° and a weighed quantity of methyl bromide was added. All the carriers added were previously purified by redistillation and, in the case of methyl bromide, by sulphite extraction and drying over calcium chloride. The above order was adopted to minimise possible errors caused by adsorption of small quantities of some of the radio-active species present on the calcium chloride, etc., and also to ensure that no elementary bromine or hydrogen bromide was present, since in the presence of the latter exchange between the organic bromides present might have occurred during the subsequent distillation by mechanisms of the type



where R and R' are alkyl or bromoalkyl.

The mixture was then distilled through a vacuum-jacketed fractionating column (20-cm. long, packed with Fenske spirals) which had been previously cooled to about -10° . The first fraction (methyl bromide) was collected in carbon dioxide-acetone; fractions were only collected when the temperature of a thermometer placed in the column was steady. It was advisable to cool the liquid after the ethylidene dibromide had been distilled and to continue the fractionation under reduced pressure, since otherwise "cracking" occurred and a satisfactory separation became impossible.

The various fractions (except ethyl bromide) were then weighed and diluted to 40 c.c. with alcohol and measured as described previously (Shaw and Collie, *loc. cit.*). The weights of the various substances added initially being known, corrections for the activity lost by the fractionation can be effected. Both the fractionated and the unextracted ethyl bromide were measured without previous dilution with alcohol. Since there were three different types of measurements (namely, measurements of carrier with alcohol, of

ethyl bromide, and of silver bromide obtained from the original extraction), it was necessary to convert two types of measurement into the third for comparative purposes. The equivalence between the silver bromide and the ethyl bromide counts could be established from a knowledge of the extraction efficiency of ethyl bromide containing a trace of free bromine. The conversion factor required to transform counts from the carrier (in alcohol) into those obtained from pure ethyl bromide (where "self-absorption" and β -scattering, etc., would be different) was determined experimentally by measuring a highly active specimen of ethyl bromide and a portion of it diluted with alcohol, so that the final density was equal to that of the alcoholic carrier solutions used. The errors given in Table III take into account the additional statistical errors arising from these conversions.

Conversion of "Aliphatic" Bromine Obtained from Irradiated Bromobenzene into Silver Bromide.—In each method used, the irradiated specimen of bromobenzene was extracted, washed free from radio-bromide ions, and dried (CaCl_2). The first method was to reflux bromobenzene with a solution of potassium hydroxide in alcohol which had been previously dried over soda-lime. After 2 hours the bromobenzene and alcohol were distilled off and the residue was acidified with nitric acid; the bromide produced was then precipitated by addition of silver nitrate, and the activity of the resulting silver bromide was measured. It was found that this process led to the formation of much more potassium bromide than expected, presumably because of reaction between the potassium hydroxide and the bromobenzene when the latter was distilled. By weighing the silver bromide produced it was possible to correct for the extra activity obtained from radio-bromine present initially in aromatic combination. The process was then repeated with the same bromobenzene and fresh alcoholic potassium hydroxide.

The second method was to reflux the irradiated bromobenzene (prepared as above) with a solution of freshly precipitated silver acetate (0.02 g.) in alcohol; after 2 hours' refluxing the alcohol and bromobenzene were distilled off and the residue was dissolved by washing it with nitric acid and then concentrated aqueous ammonia. The aqueous solutions were then mixed and acidified when necessary, and 10 mg. of potassium bromide were added; a little silver nitrate was added to ensure that this was in excess, and the silver bromide was filtered off and measured. The process was then repeated with fresh silver acetate.

The third method was to reflux bromobenzene prepared as above with zinc dust and alcohol (dried as before) for 2 hours; the zinc bromide produced was recovered by distilling off the organic liquid and dissolving the residual zinc in nitric acid containing 10 mg. of potassium bromide as carrier. The bromide was precipitated with silver nitrate and the whole process repeated.

Aniline-Ethylene Dibromide Irradiations.—These were performed as for ethyl iodide irradiations (*loc. cit.*); the aniline used was distilled in a darkened room before use. Extractions were made with water containing about 10 mg. of potassium bromide. After use, the ethylene dibromide was purified by extraction several times with hydrochloric acid and drying. The substance was then redistilled, "saturated" with bromine (as described above), and extracted with sodium sulphite solution.

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