270. *Chemical Methods of Concentrating Radioactive Halogens.*

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When organic halides are irradiated with neutrons a considerable amount of the radioactive halogen formed can be separated by extraction with suitable reagents (Szilard and Chalmers, *Nature*, 1934, **134**, 462). In the present paper a quantitative study of this phenomenon has been made, a variety of halides and a number of reagents to extract the radioactive product being used.

It has been found that although radio-iodine is separable mainly as the free element, chlorine and bromine are largely extracted as anions. The addition of a little aniline to the halide before irradiation has given a larger yield of extractable radio-bromine. A method based on this reaction for preparing highly active specimens of radio-bromine has been developed, and a concentration factor of 30,000 has been obtained.

Szilard and Chalmers (*Nature*, 1934, **134**, 462) first showed that by suitable chemical methods a radioactive isotope can be very highly concentrated and separated from non-radioactive isotopes. They irradiated ethyl iodide containing traces of iodine with neutrons and then extracted the iodide with water; the extract was found to contain a large radioactivity associated with only a small fraction of the total iodide irradiated. Later, Fermi, Amaldi *et al.* (*Proc. Roy. Soc.*, 1935, *A*, **149**, 522) applied similar methods to obtain concentrates of radioactive isotopes of the halogens, manganese, and arsenic. More recently, Paneth and Fay (J., 1936, 384) have used electrical methods of concentration, and Glückauf and Fay (J., 1936, 390) have shown that the halogen atoms expelled by recoil from captive γ-rays can frequently give rise to substitution products, *e.g.*, dibromobenzene from bromobenzene, etc.

Erbacher and Philipp (*Ber.*, 1936, **69**, 893; *Z. physikal. Chem.*, 1936, *A*, **176**, 169) have also studied the separation of radioactive halogens by aqueous extraction of irradiated alkyl halides and by adsorbing the halide ions on charcoal. These workers were primarily interested in obtaining the radio-halogens as free as possible from inactive halogen, and have devised methods which reduce the concentration of halogen in the aqueous solution to unweighable amounts whilst retaining a large amount of activity. They did not, however, compare the radioactivity of these extracts with the total radioactivity generated in the organic halide; hence it is difficult to compare their results with those obtained in this investigation.

The work described below was directed towards a quantitative study of the phenomena of chemical concentration of radio-elements. Special attention has been paid to radiobromine, since this element gives *inter alia* a radioactive isotope with a half-life of 33 hours which makes it particularly valuable as an indicator in kinetic studies.

Apparatus and Plan of Experiments.—The source of neutrons contained 200 mg. of radium sulphate mixed with powdered beryllium and sealed in a platinum cylinder. This fitted into a recess in a paraffin-wax cylinder around which an annular glass vessel held the liquid to be irradiated. This glass vessel fitted into a cavity in a large block of wax so as to utilise the neutrons which are scattered back by the wax.

The β-ray activity of the specimens was measured in annular glass vessels with very thin inner walls which fitted closely over a Geiger–Müller counter. Several such vessels were prepared of such a size that 25 c.c. of liquid gave a column of more than twice the length of the " window " which admitted β-rays to the counter. To allow for the inevitable variation from vessel to vessel of the thickness of the inner wall, the vessels were calibrated by measurements with a dilute solution of uranyl nitrate.

The impulses generated in the Geiger–Müller counter were passed to a simple one-valve amplifier; this was transformer coupled to a gas-filled relay which operated a telephone call counter. Later, a more elaborate amplifier followed by a thyratron " scale of eight " counter (Wynne-Williams, *Report Prog. Physics*, **1936**, **3**, 239) was used and the accuracy and speed of the experiments were much improved. This equipment was tested with a series of solutions of known uranium content and its response was found to be accurately proportional to the uranium content up to a speed of 600 impulses/min. At 1000 impulses/min. the correction for coincident counts was small.

Some of the earlier experiments were made with counters filled with air at 80 mm. pressure; later the mixture of 90 mm. of argon and 10 mm. of ethyl alcohol vapour recommended by Trost (*Z. Physik*, **1937**, **105**, 399) was used and found to be much more satisfactory. Although our counters were constructed with ebonite end-pieces, there was rarely a failure when constructing new counters and many of them have had a useful life of more than six months.

The general method adopted to study the extraction of the radioactive product was to irradiate an organic halide and then divide it into two or more portions. One was retained as standard, and the others then shaken with suitable reagents and separated. The activities of the samples of organic halides were then measured, and the loss on extraction determined. With this procedure no correction is needed for absorption of β-rays in the medium. In a few experiments it was necessary to measure an activity in an aqueous solution and compare it with an activity in an organic halide. The correction for the difference in self-absorption was then determined by appropriate subsidiary experiments.

In most cases the period of counting was chosen so that at least 1500 impulses were recorded; the error due to chance fluctuations was then less than 3%. The activities quoted in the tables below have been corrected for radioactive decay, for self-absorption (where necessary), and for variations in thickness of vessel walls.

A permanent standard of β-ray activity was constructed by mounting a few mg. of U_3O_8 on a strip of gummed paper inside a glass tube which fitted over the counter. This served as a convenient monitor for controlling the performance of the counter and indicated any change in its sensitivity. Measurements of this " uranium standard " were interpolated between other measurements and the results only accepted if its readings were sensibly constant. The activities of the specimens have been recorded in terms of this standard activity.

Influence of Free Halogen.—To test whether the presence of free halogen played an important part in the separation of the radio-element, parallel experiments were made in which the organic halide before irradiation with neutrons was submitted to the following pretreatments: (*a*) untreated, (*b*) shaken with aqueous sodium thiosulphate solution, (*c*) mixed with 1—3% of free halogen. After irradiation for 20 mins. (the halogen set free by γ radiation in this time interval is negligibly small), the specimen was divided into two parts and one was shaken with 5% sodium thiosulphate solution. The results of this series of experiments are recorded in Table I. The activities studied with this time of irradiation are those of bromine (half-life = 18 mins.) and iodine (half-life = 25 mins.).

With the bromobenzene and iodobenzene, the presence or absence of free halogen has little or no effect; with the aliphatic halides, the presence of traces of free halogen gives some increase in the amount of radioactive isotope which can be extracted.

TABLE I.

Effect of Free Halogen.

No.	Substance.	Pretreatment.	% Extraction.	No.	Substance.	Pretreatment.	% Extraction.
1	$C_2H_4Br_2$	(*a*)	49, 52. Mean 51	7	n-C_4H_9I	(*a*)	56
2	,,	(*b*)	56, 62, 63. Mean 60	8	,,	(*b*)	47, 48, 45. Mean 47
3	,,	(*c*)	68, 70. Mean 69	9	,,	(*c*)	55
4	C_6H_5Br	(*a*)	31	10	C_6H_5I	(*a*)	32, 31, 28. Mean 30
5	,,	(*b*)	26	11	,,	(*b*)	38, 40. Mean 39
6	,,	(*c*)	27, 33. Mean 30	12	,,	(*c*)	36

Influence of the Chemical Nature of the Reagent.—For these experiments, organic bromides were studied as sources of radio-halogen, and water, acids, alkalis, sodium thiosulphate solution, and metals as extracting reagents. All the observations were made after irradiation with neutrons for not more than 60 mins., so that the bromine activity measured is mainly due to the product with a half-life of 18 mins.

TABLE II.

Influence of Chemical Nature of Extracting Reagent.

No.	Substance.	Extracting reagent.	% Extraction.	Mean.
13	$C_2H_4Br_2$	Water	52, 42, 44, 43, 43	45
14	,,	5% HCl	45, 42, 46	43
15	,,	5% HNO_3	41	41
16	,,	5% H_2SO_4	40	40
17	,,	15% NaOH	51	51
18	,,	5% $Na_2S_2O_3$	49, 52	51
19	,,	Zn dust (2 g.)	53	53
20	,,	Zn, coarse powder (2 g.)	39	39
21	,,	Al foil (2 g.; 400 $cm.^2$)	25	25
22	,,	Cu powder (2 g.)	42, 48, 45	45
23	,,	Cu foil (2 g.; 55 $cm.^2$)	16, 19	18
24	,,	Ag foil (2 g.; 77 $cm.^2$)	28, 29	29
25	C_6H_5Br	Water	20, 20	20
26	,,	5% HCl	27, 27, 36	30
27	,,	15% NaOH	38, 40	39
28	,,	5% $Na_2S_2O_3$	31	31
29	,,	Zn dust (2 g.)	37	37
30	,,	Cu powder (2 g.)	29, 28	29

Metals were included as extracting agents since Mr. R. E. Siday (private communication) had found that copper foil acquired an intense activity when shaken with irradiated alkyl bromides. The large amount extracted by copper, silver, and aluminium foils is remarkable (Expts. 23, 24, and 21). The greater efficiency of finely divided copper and zinc (Expts. 19, 22, 29, 30) is probably due to the larger surface; these powders also contained oxides which may play some part in the separation.

With ethylene dibromide all the aqueous media give about 40% extraction of activity except sodium hydroxide and sodium thiosulphate solutions which extract a little more.

Effect of Organic Bases and Phenols.—The effect of adding small amounts of aniline and phenol to the halogen compound was investigated since it was hoped that these substances might react preferentially with the radio-bromine atoms liberated by γ-ray recoil. The results are set out in Table III.

In Expts. 28—60 the period of irradiation with neutrons was 20 mins. For Expts. 61—64 the specimens were irradiated for 2 hrs. to obtain a high enough intensity of the rather weak chlorine activity which has a half-life of 37·5 mins. Expts. 65 and 66 refer to the mixed long-period activities of bromine with half-lives of 4·5 hrs. and 33 hrs. The specimens were irradiated overnight and allowed to stand for at least an hour before measurement, so that most of the activity with a period of 18 mins. had decayed.

TABLE III.

Effect of Adding Organic Bases and Phenols.

No.	Substance irradiated.	Added substance.	Extracting reagent.	% Extracted.	Mean.
31	C_6H_5Br	None	5% HCl	27, 27, 36	30
32	,,	¼% Aniline	,,	45	45
33	,,	1% ,,	,,	62, 63	63
34	,,	2% ,,	,,	64, 67	66
35	,,	4% ,,	,,	75, 76	76
36	,,	6% ,,	,,	77, 74	76
37	,,	4% ,, (added after irradiation)	,,	31, 40	35
38	,,	None	15% NaOH	38, 40	39
39	,,	4% Phenol	,,	45, 54	49
40	,,	4% Dimethylaniline	5% HCl	72, 71	72
41	,,	3% *m*-Phenylenediamine	,,	68, 67	68
42	*n*-C_4H_9Br	None	,,	40, 39	40
43	,,	4% Aniline	,,	73, 74	74
44	,,	None	15% NaOH	38	38
45	,,	4% Aniline	,,	54, 60	57
46	$C_2H_4Br_2$	None	5% HCl	48, 47, 45, 42, 46	46
47	,,	4% Aniline	,,	80, 82, 81	81
48	,,	4% Phenylhydrazine	,,	74, 69	72
49	,,	4% Diethylamine	,,	68	68
50	,,	None	Water	52, 42, 44, 43, 43	45
51	,,	4% Aniline	,,	68, 73	71
52	,,	4% ,,	See footnote *	8	8
53	*n*-C_4H_9I	None	5% HCl	10, 11	11
54	,,	4% Aniline	,,	50, 46, 37	44
55	,,	None	5% $Na_2S_2O_3$	47, 48, 45	47
56	,,	4% Aniline	,,	44, 46	45
57	C_6H_5I	None	5% HCl	8, 12	10
58	,,	4% Aniline	,,	4, 6, 9, 11	8
59	,,	None	5% $Na_2S_2O_3$	32, 31, 28	30
60	,,	4% Aniline	,,	29, 32	31
61	C_6H_5Cl	None	5% $Na_2S_2O_3$	39, 33	36
62	,,	4% Aniline	5% HCl	69, 69	69
63	CCl_4	None	5% $Na_2S_2O_3$	59, 50	55
64	,,	4% Aniline	5% HCl	84, 92	88
65	C_2H_4Br	None	5% H_2SO_4	45, 49	47
66	,,	4% Aniline	,,	60, 63	62

* Extracted with 5% nitric acid, aqueous layer separated, made alkaline and the aniline + bromoaniline extracted with 20 c.c. of inactive ethylene dibromide. The activity of this solution was then compared with that of the untreated ethylene dibromide.

It will be seen from the table that aniline has a very marked effect in increasing the fraction of the activity which can be extracted by acids. The maximum effect is reached with about 4% aniline present *during* the irradiation (Expts. 31—36); if the aniline is added after irradiation with neutrons before extraction with acid, there is no appreciable increase in the extractable activity (Expt. 37). Other bases have a similar effect (Expts. 40, 41, 48), including the aliphatic base diethylamine (Expt. 49), and the three bromine compounds studied all give similar results. The longer-period activity of bromine shows the same effect (Expts. 65, 66). Phenol gives a small increase in the activity extractable by aqueous solutions.

In Expt. 52 the aniline extracted by hydrochloric acid was separated, and its activity measured. This accounted for only 8% of the total activity. The remaining activity in the aqueous solution was completely removed by precipitating a small amount of silver bromide in the solution and filtering it off; it must therefore have been present as HBr*. With the longer-period activity (4·5 hr. + 33 hr.) the activity of the bromine ion in the aqueous phase was also determined experimentally. The halogen was precipitated as the silver salt, which was dissolved in concentrated sodium thiosulphate solution and measured. The correction to this measurement for the difference in absorption coefficient of the β-rays between ethylene dibromide and the sodium thiosulphate solution used (85 g. of hydrated salt in 100 c.c. of water) was determined by dissolving known amounts of radioactive bromine in both solvents; the activity in the thiosulphate solution was 1·70 times that of the same amount of bromine dissolved in ethylene dibromide. The distribution of the radio-bromine when ethylene dibromide containing 4% of aniline is irradiated for 20 mins. and 16 hrs. is therefore as follows:

	18-Min. activity, %.	4·5-Hr. + 33-hr. activity, %.
Br* retained in $C_2H_4Br_2$	19	32
Br* substituted in $C_6H_5{\cdot}NH_2$	8	9
Br* removable as Br*	73 (by diff.)	59 (by diff.) 55 (by exp.)

DISCUSSION.

The primary cause of the separation of a radio-element by the Szilard and Chalmers method or its later developments is the recoil of the radioactive nucleus due to the emission of a capture γ-ray. If E_γ is the energy of the γ-ray in electron volts (eV), m the mass of the atom (H = 1), and E_a the energy of recoil in eV, then

$$E_a = 5{\cdot}33 \times 10^{-10} E_\gamma{}^2/m$$

The energies of the capture γ-rays for chlorine, bromine, and iodine have been measured by Kikuchi, Husimi, and Aoki (*Proc. Phys. Math. Soc., Japan*, 1936, **18**, 188) and are recorded in Table IV, together with the recoil energies and the energies of rupture of the carbon–halogen bond E_{C-X}.

TABLE IV.

Element.	E_γ(eV) × 10^{-6}.	E_a(eV).	E_{C-X}(eV).
Cl	6·2	585	3·3
Br	5·1	175	2·7
I	4·8	96	2·0

It will be seen that the recoil energy is always much larger than the energy of rupture of the bond, so that every halogen atom which captures a neutron will be torn from the parent molecule and can react as a free radical.

The reaction is comparable to a photochemical dissociation in the liquid phase and, as Franck and Rabinowitch (*Trans. Faraday Soc.*, 1934, **30**, 120) have pointed out, the shortness of the mean free path in a liquid effectively confines the fragments of the ruptured molecule in a cage of surrounding molecules for several vibrations. There appear to be two major possibilities: (*a*) The fragments reunite after the excess of energy has been dissipated by collisions with neighbouring molecules. (*b*) The free halogen atom may react with a neighbouring molecule. The type of reaction will depend upon the halogen element and the chemical character of its neighbours. It has already been found by Glückauf and Fay (*loc. cit.*) that the ejected halogen atoms can substitute in a variety of other molecules. Such substitutions and the recombination reaction (*a*) do not, however, account for the large amount of activity which can be extracted from the organic liquid by suitable aqueous media.

In the case of iodine the most facile reaction seems to be

$$I^* + I_2 \rightleftarrows I^*I + I \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where I* indicates the radioactive iodine atoms. The amount of I* produced is extremely small, so that traces of iodine in the solution ensure a large excess of I_2 in the neighbourhood of the liberated I* atom. This explanation of the influence of traces of iodine (Expts. 7—9) is essentially that given by Szilard and Chalmers (*loc. cit.*). Further, Expts. 53 and 55 show that only 11% of the activity generated in *n*-butyl iodide is in the form of the anion I*′, whilst 36% is present as molecular iodine which is retained in the organic solvent when the mixture is extracted with acid. In the presence of aniline, however, 44% is extractable by acid and is in the form of I*′, most probably as iodide ion. This may be explained by the reaction (2*a*).

$$R + X^* + NH_2Ph \longrightarrow Ph{\cdot}NHR^+ + X^{*-} \quad . \; . \; . \; . \quad (2a)$$

A similar reaction may occur when the RX* bond is not ruptured by the recoil but contains enough vibrational energy to bring about the reaction (2*b*) :

$$RX^* + NH_2Ph \longrightarrow PhNH_2R^+ + X^{*-} \quad . \quad . \quad . \quad . \quad (2b)$$

It is interesting to note that with iodobenzene aniline gives only about 8% of ionised radio-iodine (Expt. 58); this may be due to the weakness of diphenylamine as a base.

With chlorine and bromine compounds the main reactions seem to be either recombination or the formation of HX by the abstraction of a hydrogen atom. Similar reactions have been observed with other free radicals in the liquid phase (Grieve and Hey, J., 1934, 1799, 1966; Waters, J., 1937, 113). Further evidence for this view is furnished by the observations (*a*) that boiling the activated ethylene dibromide under a reflux condenser results in a loss of activity, (*b*) that all the activity in the aqueous extract is precipitated by silver nitrate, and (*c*) that a current of cold, dry air passed through irradiated ethylene dibromide removes a considerable amount of the activity.

The large increase in extractable activity in the presence of aniline is most probably due to reactions (2*a*) and (2*b*). It has indeed been found (Le Roux, Lu, and Sugden, *Nature*, 1939, **143**, 517) that this reaction can separate the isomeric ^{80}Br atoms of periods 4·5 hrs. and 18 mins. The isomer with a half-life of 4·5 hrs. emits a soft γ-ray with an energy of only 43,000 eV (Siday, *ibid.*, 1939, **143**, 681) and is converted into the isomer of half-life 18 mins. This soft γ-ray gives a recoil which can only activate but not disrupt the C–Br bond; yet in the presence of aniline a large amount of the product nucleus can be separated by reaction (2*b*).

Some further evidence that the reaction which produces radio-bromine ion is one which has little or no activation energy was obtained by irradiating *n*-butyl bromide (*a*) at room temperature and (*b*) at − 80°. The fraction of the activity which could be extracted by aqueous media was found to be quite independent of temperature. Incidentally, this showed that there is no appreciable exchange between the radio-bromine present as HBr* or Br*′ and the inactive bromine bond in the organic compound. Later work on the velocity of these exchange reactions has shown that they proceed much too slowly to play any significant part.

Some further experiments were made to elucidate the action of metal surfaces in separating radio-bromine, and these are summarised in Table V.

TABLE V.

Extraction of 18-*Min. Bromine Activity from Ethylene Dibromide by Metals.*

(1) Extracted by metal alone.
(2) Extracted by metal followed by a water extraction.
(3) Extracted from $C_2H_4Br_2$ previously saturated with dry HBr by metal alone.
(4) Extracted from $C_2H_4Br_2$ containing 4% aniline by metal alone.

Metal.	% Extraction.			
	(1).	(2).	(3).	(4).
Zn, coarse powder	39	56	—	41
Al foil (400 cm.^{2})	25	53	—	10
Cu foil (55 cm.^{2})	18	50	7	<1
Ag foil (77 cm.^{2})	29	48	0	27

(Water 45%; acids 41%; NaOH 51%; $Na_2S_2O_3$ 51%.)

The most likely explanation appears to be the formation of a firmly held film of HBr* on the surface of the metal. Since the amount of HBr* is infinitesimally small, a large fraction of it may be retained on the surface; when a large amount of inactive HBr is added little of the active HBr* is removed by the metal (col. 3).

When aniline is present the trace of radio-bromine is largely present as anion (col. 4). This is practically unadsorbed by copper but is still largely adsorbed by silver, possibly by the formation of silver bromide. The larger amounts removed by zinc and aluminium are probably due to the larger surface areas presented by the specimens.

Preparation of Radio-bromine Concentrates.—An effective method of preparing bromine compounds with a high intensity of radioactivity has been developed as a result of these experiments. A concentrate of this kind was required for use in kinetic studies of exchange reactions, and bromine compounds are particularly useful since the relatively high intensity of the 33-hr. period gives sufficient activity for the study of slow reactions. A typical experiment is described below which gave a concentration factor of 31,000.

2 L. of ethylene dibromide containing 5% by volume of aniline were irradiated with neutrons from the Ra–Be source for 19 hrs. 20 C.c. were set aside for comparison, and the bulk shaken with 500 c.c. of water. The aqueous extract, freed from organic matter by extraction with a little ether, was then precipitated with silver nitrate. The precipitate of silver bromide was filtered off, washed finally with alcohol, and dried rapidly. The dry bromide was transferred to a boat and reduced in a current of hydrogen at 600° in a tube furnace. The resultant hydrogen bromide was collected in a dilute solution of lithium hydroxide (Solution A). These operations were completed in 2—3 hours.

When reduction was complete, the solution of lithium bromide was diluted to 500 c.c., and the bromide content determined by titration of 25 c.c. by the Volhard method. The total Br present was 0·060 g. The radioactivity of the initial ethylene dibromide and the dilute aqueous solution was then compared by a series of alternate counts. After correction for the wall thickness of the vessel and for the different absorptions of the β-rays by ethylene dibromide and water, it was found that the activities at a standard time were: $C_2H_4Br_2$, 110 impulses/min.; aqueous solution of LiBr, 220 impulses/min.; ratio = 1 : 2.

Now ethylene dibromide (*d* 2·182) contains 1·86 g. of bromine per c.c., whereas the aqueous solution contains only $1{\cdot}2 \times 10^{-4}$ g. of bromine per c.c. Hence the concentration factor, or the ratio of the activity of the bromine per unit weight in the two solutions, is $(2 \times 1{\cdot}86)/1{\cdot}2 \times 10^{-4}$ or 31,000.

For kinetic studies the excess of lithium hydroxide in the solution A was neutralised exactly with hydrogen bromide and evaporated to dryness, thus giving a highly active specimen of lithium bromide which dissolved readily in acetone. If desired, hydrogen bromide, bromine, and many bromine compounds can be rapidly prepared from the lithium salt.

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