55. *Electrolytic Dissociation Processes. Part III. The Exchange of Radio-bromine between Inorganic and Organic Bromides.*

By Fred Fairbrother.

The exchange of radio-bromine between a number of pairs of inorganic and organic bromides has been studied. With radioactive aluminium bromide the exchange generally reaches completion very quickly at room temperature, the notable exception being bromobenzene, with which the exchange is slow. Other inorganic bromides, *e.g.*, stannic bromide and antimony tribromide show less power of exchange and only exchange readily with the more easily ionisable organic bromides, *e.g.*, *tert.*-butyl bromide. The ease of exchange is correlated with the energy of formation of a metal complex ion and the ionisation potential of the organic radical.

In a previous communication (J., 1937, 503) it was shown that the hydrogen chloride liberated in Friedel–Crafts reactions using aluminium chloride is in radioactive equilibrium with the latter, and also that an exchange of chlorine atoms takes place between the aluminium chloride and the organic chloride even in the absence of a third component. Experiments have now been carried out with a number of pairs of inorganic and organic bromides, which show that in many cases the exchange of bromine atoms is complete and rapid. The number of such possible combinations involving the variation of both the inorganic and the organic bromides is clearly very large. The present results, however, form a general survey of the problem and indicate the general nature of the exchange.

Radioactive aluminium bromide readily exchanges all its bromine atoms with those of most organic bromides when simply dissolved in the latter, or when both reactants are dissolved in carbon disulphide; this exchange occurs with great rapidity at room temperature. The only exception found was bromobenzene, with which the exchange with aluminium bromide is very slow.

Stannic bromide is less able to exchange its bromine atoms. It exchanges slowly, but

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with measurable speed, with *tert.*-butyl bromide and benzyl bromide, but shows no exchange under similar conditions with ethyl bromide. It forms a very convenient reagent for the introduction of radio-bromine into *tert.*-butyl bromide, which undergoes rapid decomposition in the presence of aluminium bromide.

Other inorganic bromides, such as antimonious, auric, zinc, cupric, mercuric, and indium bromides, were also found to possess more or less power of exchange with certain classes of organic bromides, but no exchange was observed with potassium, calcium, or phosphorous bromide.

Brejneva, Roginsky, and Schilinsky (*Acta Physicochim. U.R.S.S.*, 1936, **5**, 549), in an investigation on the possibilities of the introduction of radioactive halogens into organic molecules, report the radioactive exchange between aluminium bromide and a number of organic bromides. They used a different technique from that used in the present work, with which on the whole their results are in agreement. They state, however, that benzyl bromide will exchange its bromine with aluminium bromide, whereas if these two substances be brought together, even in the presence of considerable carbon disulphide as diluent, there is an immediate condensation to a red solid and a vigorous evolution of hydrogen bromide.

EXPERIMENTAL.

The radio-bromine was prepared by irradiating about 5 kg. of ethylene dibromide with a 200-mc. radium–beryllium source of neutrons placed in the centre, the containing vessel being surrounded by an average of about 15 cm. radial thickness of paraffin wax. The irradiation was

FIG. 1.
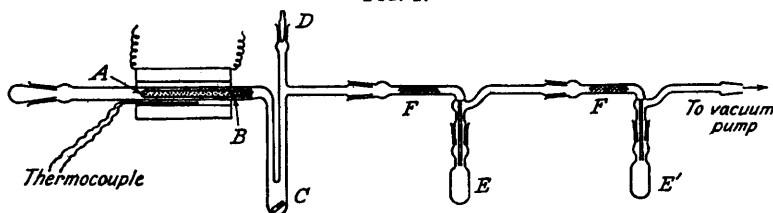
carried out overnight or over several days, after which the radio-bromine was extracted by shaking with an aqueous solution of 1 g. of potassium bromide. The bromide was next precipitated as silver bromide, which was quickly washed and dried; an exception to this was made in the case of active mercuric bromide, which was prepared directly from the potassium bromide by the addition of a solution of mercuric acetate and cooling in ice, the mercuric bromide being only slightly soluble at $0°$. In all other cases the active silver bromide was used as an intermediate product.

Aluminium bromide. This was prepared, and its exchange experiments carried out, in the apparatus shown in Fig. 1, which was made of Pyrex glass throughout, the ground joints being made vacuum-tight with picein wax. The active silver bromide was intimately mixed with about three times its weight of cleaned aluminium filings, placed in a hard-glass tube A, and kept in position by a loose plug of glass wool. This tube was then placed in the outer tube B, and the apparatus closed and evacuated to a few μ mm. of mercury. B was then gently heated externally by a small electric furnace; at about $450°$ the reaction $2Al + 6AgBr^* = Al_2Br^*_6 + 6Ag$ occurred rapidly but smoothly, and the $Al_2Br^*_6$ volatilised on to the cool part of the tube. From thence, by manipulation of a small gas burner, it was volatilised into the cooled exchange vessel C. The final product was quite white. The use of aluminium filings was found to be necessary as the reaction with aluminium powder was too violent and ejected the reaction mixture into the exchange vessel. The entire apparatus as shown in Fig. 1 was dismantled and cleaned before each experiment.

On completion of the preparation of the active aluminium bromide, A and B were cooled, and dry air admitted into the apparatus. The stopper D was then removed for a few moments, and the liquid bromide, alone or in carbon disulphide solution, added through a long capillary thistle funnel. A small pellet of iron enclosed in a glass tube and operated by a magnet, served to stir the contents of C.

At the end of the time allowed for the exchange, one of two methods was used for the partition of the aluminium bromide from its reaction partner : (*a*) the organic bromide was quickly

volatilised in a vacuum at room temperature and condensed in the receiver E, which was cooled in liquid air or in carbon dioxide–acetone. A 7-cm. plug of glass wool F prevented any transfer of solution into the receiver by spray or bumping. This method of partition was used especially for the more volatile and the easily hydrolysed bromides, and is designated below as " vac." When the aluminium bromide was used to prepare a radioactive organic bromide for experiments with a second inorganic bromide, the latter was placed in E, which then became the reaction vessel, and the partition was brought about by volatilisation into a second receiver E'. The alternative method of partition, (*b*), consisted in removing the contents of C by suction through a capillary tube and transferring them below the surface of dilute nitric acid (about 1·5M) in which the aluminium bromide was immediately decomposed; the organic component was then extracted by ether. A control experiment showed that no exchange of Br^- with the organic bromide occurred during the time required for these operations. This method of partition is designated as " aq."

Stannic bromide. This was prepared and used in an apparatus similar to the above, but with a somewhat narrower tube B, which was filled with fairly coarse tin powder (prepared by vigorously stirring molten tin whilst it cooled) and heated to about 150°. The AgBr* was gently warmed with a mixture of potassium dichromate and sulphuric acid in a small flask, and the liberated bromine led over the tin in a stream of dry nitrogen. The initial stage of the reaction

FIG. 2.
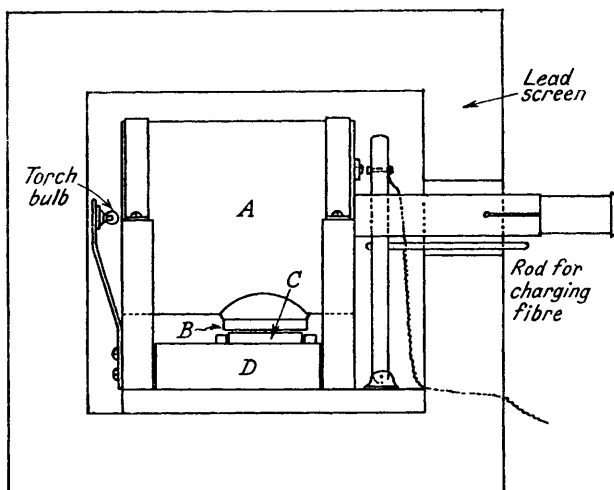
between fresh tin and bromine is slow and care was required to secure the reaction of all the bromine; a charge of tin powder which had already been treated with bromine, and freed from moisture by a preliminary drying in the nitrogen stream, reacted more readily. The samples of SnBr*$_4$ were quite white and free from excess bromine. For convenience in handling, the active SnBr*$_4$ was in some cases diluted by the addition of about 1 g. of pure inactive SnBr$_4$.

With the exception of HgBr*$_2$, all the other inorganic bromides were used in the inactive state, exchanges being carried out with organic bromides in which the radio-bromine had been introduced by aluminium bromide or stannic bromide. In the case of antimony tribromide a 10% Rochelle salt solution was used for the aqueous partition, to prevent precipitation of antimonious oxide.

In all cases, on completion of the partition, the bromine in the two compounds was converted by appropriate methods into silver bromide, from the activity of which the specific activities of the bromines concerned in the exchange were calculated. The activity of the silver bromide specimens was measured as follows. A Lauritsen quartz-fibre electroscope (*Rev. Sci. Instr.*, 1937, **8**, 438) was mounted in a copper ionisation chamber (A, Fig. 2) of about 1-litre capacity, lagged with felt to prevent sudden temperature changes, and provided on the under side with a thin aluminium foil window B, of about 3 mg./sq. cm. A weighed amount (0·5—1·0 g.) of the radioactive silver bromide was placed in a 5-cm. Petri dish C, which fitted in a shallow cavity in a horizontal wooden slide D, by which it could be placed in accurate registration immediately underneath the aluminium window.

The electroscope was mounted inside a 5-cm. thick lead screen, which reduced the natural background drift to about half that of the unscreened electroscope. This background was frequently measured and remained very constant, about 0·16 division per min., for most of the experiments. The activities of the samples measured, except where no exchange had occurred, were always much greater than the background, usually by more than 10—100 times. The correction for the self-absorption of the radiation by the silver bromide was estimated by observing the reduction in activity on interposing a series of aluminium foils between the silver bromide and the electroscope, and extrapolating to zero absorber. This correction amounted to about 10% per g. of silver bromide in the dish and any uncertainty was minimised by taking approximately equal quantities of AgBr* for each measurement. Apart from measurements involving the selective extraction of the 18-min. period of ^{80}Br, little correction was required for the decay of the activity of the specimens during measurement, as the latter was usually carried out after the 18-min. period had disappeared, and required a time which was short compared with the half-life of the 4·5-hr. period. The estimated overall precision of the measurements was about ± 5—10% of the total activity of each specimen; a recorded exchange of only a few units % in the following table is regarded as outside the experimental error.

The results of the exchange experiments are summarised in the table, in which the reactants are given as MBr and RBr respectively, the radioactive component being marked with an asterisk, thus—$Al_2Br^*_6$. The times of contact of the reactants are given in minutes and r, the "ratio of activities," indicates the ratio of the specific activity of the initially inactive bromine to that of the initially radioactive bromine, at the time of partition : a ratio approaching unity indicates therefore a complete exchange. Unless otherwise indicated, all exchanges were carried out at room temperature (about 15°) and the reactants were mixed together without solvent, in the case of insoluble solutes, being shaken together.

MBr.	RBr.	Time, mins.	Partition.	r.
$Al_2Br^*_6$	C_2H_5Br	5	vac.	0·90
$Al_2Br^*_6$	$CH_2Br\cdot CH_2Br$	20	vac.	0·97
$Al_2Br^*_6$	n-C_4H_9Br	10	vac.	0·97
$Al_2Br^*_6$	$tert.$-C_4H_9Br	5	vac.	1·0
$Al_2Br^*_6$	$CH_3\cdot COBr$	20	vac.	0·80
$Al_2Br^*_6$	$CH_2{:}CHBr$	<2	vac.	0·97 [1]
$Al_2Br^*_6$	$CH_2{:}CH\cdot CH_2Br$	<2	aq.	0·84 [2]
$Al_2Br^*_6$	CBr_4	20	aq.	0·89 [3]
$Al_2Br^*_6$	PBr_3	30	vac.	0·98
$Al_2Br^*_6$	C_6H_5Br	90	vac.	0·03 [4]
$Al_2Br^*_6$	C_6H_5Br	90	vac.	0·82 [5]
$Al_2Br^*_6$	$C_6H_5\cdot CH_2Br$	—	—	— [6]
$Al_2Br^*_6$	$C_2H_5Br + C_6H_5\cdot NO_2$	10	vac.	0·025
$Al_2Br^*_6$	$C_2H_5Br + C_6H_5\cdot NO_2$	40	vac.	0·075
$SnBr^*_4$	C_2H_5Br	120	vac.	<0·01
$SnBr^*_4$	n-C_4H_9Br	60	vac.	0·12
$SnBr^*_4$	$tert.$-C_4H_9Br	15	vac.	0·10
$SnBr^*_4$	$tert.$-C_4H_9Br	150	vac.	0·92
$SnBr^*_4$	$CH_3\cdot COBr$	25	vac.	0·62
$SnBr^*_4$	$CH_2{:}CH\cdot CH_2Br$	30	vac.	0·02
$SnBr^*_4$	$C_6H_5\cdot CH_2Br$	150	vac.	1·05
Au_2Br_6	$C_2H_5Br^*$	30	vac.	++ [7]
Au_2Br_6	$tert.$-$C_4H_9Br^*$	30	vac.	0·74 [8]
$SbBr_3$	$tert.$-$C_4H_9Br^*$	30	ac.	1·0
$SbBr_3$	$C_2H_5Br^*$	100	vac.	—
$SbBr_3$	$CH_2Br\cdot CH_2Br^*$	120	aq.	—
$SbBr_3$	$CH_2Br\cdot CH_2Br^*$	120	aq.	0·20 [9]
$HgBr_2$	$C_2H_5Br^*$	5	vac.	—
$HgBr_2$	$tert.$-C_4H_9Br	100	vac.	+
$HgBr^*_2$	$C_6H_5\cdot CH_2Br$	30	vac.	+
$ZnBr_2$	$tert.$-$C_4H_9Br^*$	90	vac.	+
$CuBr_2$	$tert.$-$C_4H_9Br^*$	90	vac.	+
$AsBr_3$	$C_2H_5Br^*$	10	vac.	—
PBr_5	$C_2H_5Br^*$	120	vac.	—
$InBr_3$	$tert.$-$C_4H_9Br^*$	30	vac.	+
$InBr_3$	$C_2H_5Br^*$	30	vac.	+
KBr	$C_2H_5Br^*$	15	vac.	—
$CaBr_2$	$tert.$-$C_4H_9Br^*$	60	vac.	—

[1] Exchange at 0° : some polymerisation and charring.   [2] 5% Allyl bromide solution in CS_2.
[3] 10% CBr_4 solution in CS_2.   [4] Room temp.   [5] 100°.   [6] Instantaneous condensation with evolution of HBr.   [7] Solubility small but considerable exchange.   [8] In 50% solution in ether.
[9] Refluxed : b. p. 132°.

All the organic bromides examined, with the exception of bromobenzene, very readily exchanged their bromine atoms with those of aluminium bromide. With bromobenzene, the exchange only occurs easily at higher temperatures. The dissolution of the aluminium bromide in nitrobenzene, in the proportion of about 1 mol. in $2\frac{1}{2}$ mols., effected a very large reduction in the rate of exchange with ethyl bromide. This may readily be attributed to the formation of the double compound between the nitrobenzene and the aluminium bromide, with a consequent reduction in the equilibrium concentration of the latter in the system.

Stannic bromide and antimony tribromide possess less power of exchange than aluminium bromide, and at room temperature are only able to exchange their bromine atoms with those of the more reactive organic bromides. The small exchange between stannic bromide and allyl bromide was unexpected in view of the reactivity of the latter, but repeated experiments confirmed that this exchange occurs very slowly at room temperature.

Auric bromide, though of limited solubility, appears to possess considerable exchange ability. This is not surprising in view of the similarity between its dimeric formula and that of aluminium bromide.
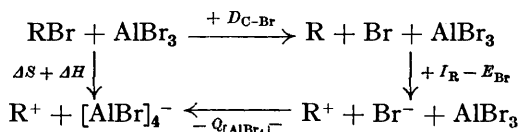
The exchange results marked $+$ refer to systems in which the solubility of the inorganic bromide was too small to permit of the quantitative measurement of the exchange. In these cases the exchange was confirmed by the presence of the 4·5-hr. period of ^{80}Br. It has already been observed (Fairbrother, *Nature*, 1939, **145**, 307) that many inorganic bromides will extract the 18-min. period of radio-bromine from active ethyl bromide. Probably any inactive inorganic bromide when shaken with any active organic bromide would show some radioactivity after separation : it is only when all the radio-bromine isotopes are transferred that a true exchange can be considered to have occurred. This in fact provides a convenient qualitative test of exchange, especially for insoluble inorganic bromides : a decay of the activity of the latter after separation with a pure half-life of 18 mins. and no " tail " indicates that no chemical exchange of the bromine atoms has occurred. Such results are indicated in the table by the $-$ sign.

DISCUSSION.

In the previous communication (*loc. cit.*) it was suggested that the radioactive exchange took place through the formation of a carbonium ion and a complex metal halide ion, *e.g.*, $2RBr + Al_2Br_6 \rightleftarrows 2R^+ + 2[AlBr_4]^-$. A similar mechanism has been postulated by Bodendorf and Böhme (*Annalen*, 1935, **516**, 1) to account for the catalytic racemisation of α-phenylethyl chloride by inorganic chlorides. In certain circumstances, as shown by Wohl and Wertyporoch (*Ber.*, 1931, **64**, 1357, 1369), it is actually possible for a weakly conducting system to be formed.

It is not necessary, however, for complete radioactive exchange to take place, that the equilibrium concentration of the carbonium ion–metal complex ion pair should be large. Indeed, a consideration of the energies involved in the change $RBr + MBr_n \longrightarrow R^+ + [MBr_{+1}]^-$ makes it appear probable that in many cases the net results would be a gain in free energy in the forward direction, and that therefore only a small equilibrium concentration of the carbonium ion will be formed, which may be quite undetectable by cryoscopic, ebullioscopic, or conductivity methods. Moreover, if a large concentration of carbonium ion were formed, there would be much decomposition with the liberation of hydrogen bromide and formation of olefin. This was observed in certain cases, notably with *tert.*-butyl bromide and aluminium bromide, and it has long been known that the action of aluminium chloride on aliphatic chlorides may give rise to olefins (Kerez, *Annalen*, 1885, **231**, 306; Monneyrat, *Ann. Chim.*, 1900, **20**, 530). Also, Ingold and his collaborators have shown (J., 1937, 1271) that olefin elimination accompanies those cases of halide hydrolysis in which the rate-controlling mechanism is halogen ionisation, *i.e.*, the formation of a carbonium ion.

The ionisation process may be represented by a cycle. In the case of aluminium bromide, which can be regarded as $AlBr_3$, since it is present in this form to some extent in many solvents and largely so in ethyl bromide (Wertyporoch, *Ber.*, 1931, **64**, 1371), the cycle would be

$$RBr + AlBr_3 \xrightarrow{\ + D_{C-Br}\ } R + Br + AlBr_3$$

$$\Delta S + \Delta H \downarrow \qquad\qquad\qquad\qquad \downarrow + I_R - E_{Br}$$

$$R^+ + [AlBr]_4^- \xleftarrow[\ - Q_{[AlBr_4]^-}\ ]{} R^+ + Br^- + AlBr_3$$

in which ΔH is the algebraic sum of D_{C-Br}, the C–Br bond energy, I_R, the ionisation potential of the free radical R, E_{Br}, the electron affinity of the bromine atom, and $Q_{[AlBr_4]^-}$, the energy of formation of $[AlBr_4]^-$ from $AlBr_3$ and Br^-. Since the process takes place in solution, to these must be added ΔS, the net change in solvation energies.

A consideration of these various magnitudes leads to the conclusion that the major factor determining the exchange process with a given inorganic halide is I_R; if a number of different metal halides are under review, the energy of formation of the complex metal ion is also a major factor.

Thermal and other data show that the bond energies of organic halides do not vary greatly with different organic radicals. For example, Butler and Polanyi (*Nature*, 1940, **146**, 129) suggest bond energies for a number of iodides which only vary by 8·9 kg.-cals./mol. between phenyl and *tert.*-butyl : one may expect a similar range to be found in the case of the bromides, with an average value of about 60 kg.-cals./mol. Any variation in the net solvation energy changes in the cases at present under consideration would also be too small to account for the observed variation in ease of bromine exchange.

Of the values of the other factors involved, the only one which is known with any certainty is E_{Br}, which may be taken as 81·5 kg.-cals./mol. (Mayer and Helmholz, *Z. Physik*, 1932, **75**, 19).

Klemm and Jacobi (*Z. anorg. Chem.*, 1932, **207**, 186) give the heat of formation of aluminium bromide as $Al + 3Br_{(liq.)} \longrightarrow AlBr_{3\,(solid)} + 121$ kg.-cals., and Fischer and Ralphs (*ibid.*, 1932, **205**, 1) calculate the heat of the reaction $Al_2Br_6 \longrightarrow 2AlBr_3$ as $-26·5$ kg.-cals. and the heat of volatilisation of Al_2Br_6 as 12·1 kg.-cals./mol. From these data and the heats of volatilisation of aluminium and dissociation of bromine molecules, it appears that the strength of each Al–Br bond in $AlBr_3$ is about 70 kg.-cals. This may be taken as the lower limit of formation of a fourth Al–Br bond, *i.e.*, of the formation of $[AlBr_4]^-$ from $AlBr_3$ and Br^-. The actual energy of formation may be somewhat greater than this on account of increased resonance in the ion, but it does not seem probable that it can be much greater than about 100 kg.-cals./mol. The energy of formation of a complex anion will be less in the case of the other inorganic bromides used.

The greatest uncertainty lies in the value of I_R. Only very few organic radicals have been studied in this connexion, and the values given for the ionisation potentials vary between wide limits. For example, for the methyl radical, Fraser and Jewitt (*Proc. Roy. Soc.*, 1937, *A*, **160**, 563), using a molecular beam technique, found 11·2 ± 0·8 volts, and for the ethyl radical, 10·6 ± 0·8 volts. On the other hand, Baughan, Evans, and Polanyi (private communication) conclude from chemical evidence that the ionisation potential of the methyl radical is about 7·8 volts (180 kg.-cals./mol.). Other estimates by physical and theoretical methods lie between these.

It appears, however, even within the probable limits of the values of these various factors, that the ionisation of an organic bromide by an inorganic bromide may often be an endothermic process. This supposition is borne out by the low conductivities of such solutions (cf. Wertyporoch, *loc. cit.*), which is indicative of a small equilibrium concentration of free ions. It is possible that a greater concentration of undissociated ion-pairs may be present, especially in view of the fairly low dielectric constants of most of the liquids. An answer to this question is being sought through the measurement of the dielectric polaris-abilities of mixed solutions of organic and inorganic halides, which should show an increase of polarisability if there is any appreciable formation of ion-pairs.

The effect of temperature on the exchanges between aluminium bromide and bromo-benzene and between antimony tribromide and ethylene dibromide shows that these exchanges possess an activation energy. This is probably general, and is in accord with the observations of other authors that various inorganic halide catalysts can be used in the Friedel–Crafts syntheses, but require higher temperatures than aluminium halides; *e.g.*, Menschutkin (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1710) in the case of antimony tri-chloride and Bredereck *et al.* (*Ber.*, 1939, **72**, 1414) in that of beryllium chloride.

It is to be expected that a similar effect will be observed in the corresponding radio-active exchanges. The study of the rates of halogen exchange over a range of temperatures, between various pairs of organic and inorganic bromides, and the evaluation of the activ-

ation energies of the process, offer a chemical method of comparing the ionisation potentials of different organic radicals and also of discriminating quantitatively between the potential catalytic properties of various inorganic bromides. In view of the more general use of chloride catalysts, a similar study of the exchange between organic and inorganic chlorides would be desirable, since it is not possible in all cases to extrapolate from the bromide to the chloride. This was not possible with the present technique, since irradiation of a chloride in the same manner leads only to a very weak product of radio-chlorine, which moreover has a relatively short half-life (37 mins.). Such experiments could be carried out by activation of the chloride by high-velocity deuteron bombardment, as with aluminium chloride in Part II of this series (J., 1937, 503).

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