

129. *Electrolytic Dissociation Processes. Part IV. The Ionisation of a Carbon-Halogen Bond by Inorganic Halides.*

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The ionisation of a carbon-bromine bond by an electrophilic inorganic halide dissolved in a non-polar solvent is in general very small. Measurements have been made of the dielectric polarisation of solutions in non-polar solvents, of several organic bromides mixed with electrophilic inorganic bromides. Ethyl bromide in *cyclohexane* solution shows an increase of polarisation in the presence of aluminium bromide corresponding to the ionisation of a few per cent. of the ethyl bromide. Benzyl bromide in the presence of stannic bromide, and *tert.*-butyl bromide in the presence of stannic bromide or boron tribromide, show no measurable increase of polarisation. Triphenylmethyl bromide in benzene solution is ionised to a small extent by stannic and boron bromides. The small degree of the ionisation of the triphenylmethyl bromide is confirmed by the colour of the solutions.

IN Part III of this series (J., 1941, 293) the rates of radio-isotopic exchange of bromine between a number of inorganic and organic bromides were compared, and a general correlation obtained between the rates of exchange of radio-bromine and the catalytic activity of the metal bromide on the one hand, and the ease of ionisation

of the covalent carbon-halogen bond on the other. This exchange was discussed on the basis of a mechanism involving the transition of a covalent carbon-bromine bond into an ionic bond, the resulting bromine ion being detached as part of a complex anion by the electrophilic metal bromide: $MBr_n + RBr = MBr_{n+1}^- + R^+$.

The energy relationships involved in such a transition of a covalent bond between two atoms X, Y into an ionic bond X^+, Y^- may be represented diagrammatically as in Fig. 1, in which *A* represents the potential energy of a given covalent state as a function of the nuclear separation of the two adjacent atoms X and Y where fission of the molecule occurs, and *B* that of the corresponding ion-pair. The difference between the asymptotic values of *A* and *B*, *i.e.*, of the energies at large values of *r* of the gaseous molecule and the ion-pair, respectively, is given by the difference between the ionisation potential of $\cdots X$ and the electron affinity of $Y \cdots$. In all cases in which the mainly covalent state is the normal one for the bond X-Y in the gaseous molecule, *B* will lie above *A*, the ionisation potential of an electropositive atom or radical usually exceeding the electron affinity of the electronegative partner. Any process which will lower the potential energy of the ion-pair to some state as represented by *C*, where a crossing from one state to another becomes possible without too high an activation energy or endothermicity, will result in the transition of a small proportion of the molecules into ion-pairs, the actual proportion depending on the energy change involved. A further lowering of the potential energy of the ion-pair to such a state as represented by *D*, where the minimum falls below the minimum of *A*, would result in the spontaneous transition of most of the covalent molecules into ion-pairs.

The two processes by which such lowering of the potential energy of an ion-pair is most frequently brought about are (a) solvation, involving mainly coulombic attraction between the ions and solvent molecules, and (b)

complex formation by one or both ions with solvent molecules or a third component, involving the formation of additional electron-pair bonds.

This paper deals principally with the question of the extent of this transition, *i.e.*, of the concentration of ion-pairs formed when an electrophilic metal halide is added to a solution of an organic halide in a non-polar solvent.

In Part III of this series (*loc. cit.*) an attempt was made to calculate the heat changes involved in the reaction between aluminium bromide and ethyl bromide, leading to the formation of a carbonium cation and a complex metal halide anion, $AlBr_3 + C_2H_5Br \rightleftharpoons (AlBr_4)^- + C_2H_5^+$, and in spite of the uncertainty of the exact magnitude of some of the terms involved, it seemed that such a formation of ions by an organic halide and a metal halide catalyst must in general be an endothermic process, and that therefore only a small proportion of the components would be present in the form of separate ions at equilibrium. Even the formation of undissociated ion-pairs, by which radioactive isotopic exchange might occur, by relative rotation of the ions without separation, would also usually appear to be an endothermic process.

In the present work the question of the formation of ion-pairs when organic and metal halides are dissolved together in a non-polar solvent has been studied by dielectric polarisation measurements and, in the case of the triphenylmethyl halides, also colorimetrically. The results confirm the previous conclusions that the concentration of ion-pairs in such solutions is very small.

Evidence has also been found that the higher energy of formation of a solid ionic lattice may be able to bring about that which simple pairing or solvation of the ions cannot, *viz.*, the formation of an ionic solid from components which are mainly non-ionic in solution.

A few preliminary measurements of the dielectric polarisation of mixed solutions of aluminium bromide and ethyl bromide in *cyclohexane* solution (Fairbrother, *Trans. Faraday Soc.*, 1941, **37**, 763) indicated by the rise of polarisation that some ion formation had occurred. These measurements have now been extended, the $AlBr_3/C_2H_5Br$ molar ratio being kept approximately constant and the apparent polarisation of the ethyl bromide being calculated on the assumption of a constant polarisation of the aluminium bromide. This is preferable to the inverse procedure, especially in solutions of different concentrations, since the change of polarisation with concentration is much less in the case of the almost non-polar metal halide than of the organic halide. A similar procedure has been adopted for systems involving other inorganic bromides. The results of the aluminium bromide-ethyl bromide measurements are given in Table I, in which f_3 denotes the mol.-fraction of aluminium bromide and f_5 that of ethyl bromide, the other symbols having their usual significance.

Aluminium bromide in *cyclohexane* solution is present almost wholly as the dimer (cf. *Trans. Faraday Soc.*, 1941, **37**, 763), but the solution in ethyl bromide contains the monomer (Wertyporoch, *Ber.*, 1931, **64**, 1371). In the present solutions we probably have a mixture of both forms—chiefly dimer—but the polarisations have

FIG. 1.

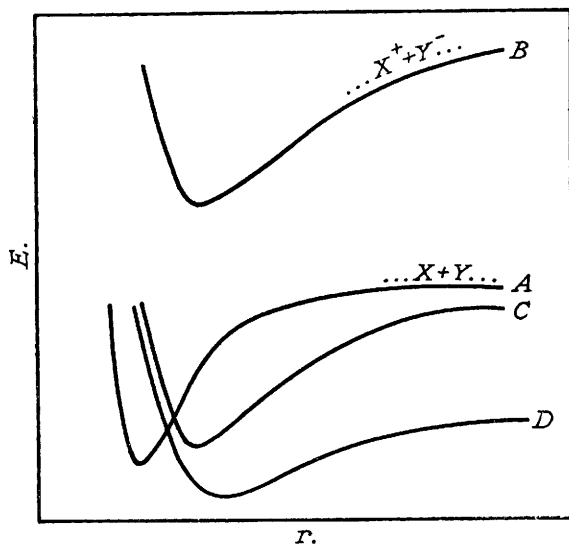


TABLE I.
Solutions in cyclohexane.
Aluminium bromide (AlBr₃).

f_2 .	ϵ .	d .	P_2 (c.c.).	f_2 .	ϵ .	d .	P_2 (c.c.).
0.00000	2.0153	0.7736	—	0.03711	2.0547	0.8397	45.3
0.03541	2.0521	0.8367	44.8				Mean 45.1

Aluminium bromide and ethyl bromide.									
f_2 .	f_3 .	ϵ .	d .	P_3 (c.c.).	f_2 .	f_3 .	ϵ .	d .	P_3 (c.c.).
0.00000	0.03635	2.1593	0.7900	96.3	0.01463	0.01562	2.1387	0.8073	153
0.00000	0.06548	2.2727	0.8035	93.0	0.02218	0.02545	2.2312	0.8256	162
0.00000	0.09334	2.3858	0.8165	91.3	0.02264	0.02346	2.2185	0.8253	164
0.01363	0.01952	2.1607	0.8071	149	0.02449	0.02475	2.2358	0.8293	167
0.01394	0.01393	2.1229	0.8051	149					

been calculated on the basis of the simple formula AlBr₃ since it is probably in this form that the aluminium bromide becomes attached to a donor molecule.

The solutions of aluminium bromide and ethyl bromide in cyclohexane were, provided that the concentration was not too high, just sufficiently stable to permit of the measurement of the dielectric constant and density. The aluminium bromide was first completely dissolved in the dry solvent, the ethyl bromide added, the flask quickly reweighed, and the solution transferred as quickly as possible to the dielectric-constant cell and pycnometer. These had been standing in the thermostat at 25.00° for some time; the initial temperature of the solutions was about 18—20°. Measurements of the dielectric capacity of the filled cell were started immediately and made at one minute intervals. These measurements fell slightly at first, as the solutions came to thermal equilibrium with the bath, remained steady at a minimum value for some minutes and then rose slowly. Coincident with this rise of dielectric constant the solutions became peach-coloured and turbid, and the dielectric losses so increased that after some 20—30 mins. measurements were no longer possible. The values of ϵ given in the above table are in all cases those of the flat minima. On standing for some hours, the liquid cleared and a small quantity of a deep red oil separated at the bottom of the dielectric cell and pycnometer. This red oil, which was not further investigated, was soluble in excess of ethyl bromide, and therefore its formation was not observed when the molar ratio of ethyl bromide to aluminium bromide was much greater than unity, as in the preliminary experiments, though the same gradual increase of dielectric loss was apparent.

It is clear from these figures that the presence of aluminium bromide brings about a substantial increase in the apparent polarisation of ethyl bromide in cyclohexane solution, but in the absence of any definite information as to the magnitude of the molar polarisation of the ion-pairs it is not possible to calculate their concentration. On the other hand, if we assume a molar polarisation of 2000 c.c. for the ion pairs, which is near the lower limit of that obtained by Kraus (*Science*, 1939, 90, 281) for the molar polarisation of a number of electrolytes in benzene solution, the present increase of polarisation would correspond to the ionisation of about 3—4% of the ethyl bromide. A smaller assumed molar polarisation would mean a larger concentration, and *vice versa*, but it is evident in any case that only a small fraction of the ethyl bromide has been ionised by the aluminium bromide in these solutions. The increase of dielectric constant of the solutions on standing, which could not be measured on account of a simultaneous increase in conductivity, indicates the formation of a more ionic system; it is this stage which should be compared with the conducting solutions of aluminium bromide in ethyl bromide obtained by Wertyporoch (*loc. cit.*, p. 1369), who also observed that the conductivity of the solutions increased with time, taking as long as 45 mins. to reach equilibrium, in dilute solutions.

The extension of polarisation measurements with aluminium bromide to other aliphatic bromides with which exchange of radioactive bromine occurs is not possible on account of the even more rapid decomposition of the solutions with evolution of hydrogen bromide, presumably as a result of the instability of the carbonium ions. Attention was therefore turned to some less electrophilic inorganic bromides, *e.g.*, stannic bromide and boron tribromide, which also exchange bromine atoms with a number of organic bromides, including *tert.*-butyl bromide and benzyl bromide, but without any apparent decomposition of the solutions. The polarisations of the inorganic and organic components were first measured separately in cyclohexane solution, and then together in the same solvent. The results are given in the following tables in which the symbols have the same significance as before, f_2 and P_2 referring in each case to the inorganic bromide and f_3 and P_3 to the organic bromide.

It may be noted that the polarisation of stannic bromide in cyclohexane (58.7 ± 0.4 c.c.) is slightly higher than the value obtained by Coop and Sutton (55.6 c.c.) for the vapour state (J., 1938, 1269) and may be due to a distortion of the tetrahedral symmetry of the molecule by the adjacent solvent molecules, producing a small effective moment in the same manner as the flexing of the Sn-Br bonds may be supposed to give rise to the large atomic polarisation (*cf.* Coop and Sutton, *loc. cit.*), or to a small formation of an ionic autocomplex SnBr₃⁺-SnBr₅⁻.

Boron tribromide in cyclohexane (32.3 ± 0.4 c.c.) and in benzene (32.2 ± 0.4 c.c., see below), together with Lowery's data for the refractivity of boron tribromide vapour (*Proc. Roy. Soc.*, 1931, A, 133, 188) leading to an electron polarisation of 30.03 c.c. at $\lambda = 5461 \text{ \AA}$., are consistent with a zero moment for this molecule and a planar structure as shown by electron-diffraction measurements (Levy and Brockway, *J. Amer. Chem. Soc.*, 1937, 59, 2085).

TABLE II.
 Solutions in cyclohexane.

Stannic bromide.				Boron tribromide.					
f_2 .	ϵ .	d .	P_2 , c.c.	f_2 .	ϵ .	d .	P_2 , c.c.		
0-00000	2-0153	0-7736	—	0-00000	2-0153	0-7736	—		
0-01739	2-0364	0-8268	58-5	0-01248	2-0201	0-7934	32-9		
0-02094	2-0409	0-8376	58-7	0-01437	2-0208	0-7967	32-2		
0-02343	2-0448	0-8452	59-4	0-02169	2-0230	0-8080	32-5		
0-06747	2-0969	0-9782	58-1	0-03563	2-0273	0-8309	31-6		
Mean 58-7				Mean 32-3					
<i>tert.</i> -Butyl bromide and stannic bromide.					<i>tert.</i> -Butyl bromide and boron tribromide.				
f_2 .	f_3 .	ϵ .	d .	P_3 .	f_2 .	f_3 .	ϵ .	d .	P_3 .
0-00000	0-04556	2-2514	0-7942	127-9	0-01557	0-04597	2-2578	0-8186	127-5
0-00000	0-04626	2-2522	0-7944	126-8	0-01870	0-04659	2-2628	0-8245	126-3
0-00000	0-04628	2-2531	0-7944	127-1	0-02931	0-04589	2-2640	0-8413	127-2
0-007560	0-04595	2-2634	0-8178	127-7	Benzyl bromide and boron tribromide.				
0-01969	0-04547	2-2763	0-8545	127-7	0-00000	0-04639	2-2049	0-8059	110-4
0-02377	0-04657	2-2886	0-8676	127-9	0-00000	0-05194	2-2276	0-8098	110-0
0-02584	0-04704	2-2890	0-8729	126-9	0-01871	0-04577	2-2070	0-8363	108-5
					0-02601	0-05172	2-2337	0-8517	108-3
					0-02936	0-03836	2-1794	0-8476	108-5

It is evident from the figures in the above table, that the increase in dielectric polarisation observed with aluminium bromide and ethyl bromide does not occur with *tert.*-butyl bromide or benzyl bromide in the presence of stannic or boron bromides, although exchange of radioactive bromine occurs fairly easily in such systems.

Since, as shown by the work of Ingold and his collaborators on the mechanism of organic substitution reactions, *tert.*-butyl and benzyl are groups which would be expected to facilitate the ionisation of the carbon-bromine bond by the electrophilic metal bromide, and which in fact do facilitate the exchange of radioactive bromine, *e.g.*, in comparison with ethyl bromide, the next question was whether a further increase in the ionisability of the organic bromide might lead to the formation of a measurable amount of ion-pairs by these less electrophilic metal bromides. Measurements were therefore made of the dielectric polarisation of benzene solutions of triphenylmethyl bromide with stannic and boron bromides. (The use of benzene as solvent was necessary on account of the very low solubility of the double compounds in cyclohexane.)

The ionisation of triphenylmethyl halides in certain solvents has been noted by many workers. For instance, Walden (*Ber.*, 1902, **35**, 2018) and Gomberg (*ibid.*, p. 2397) observed that a number of triphenylmethyl compounds and double compounds gave well-conducting solutions in liquid sulphur dioxide. It has also long been known that triphenylmethyl halides form stable double compounds with a number of metallic halides, some being well defined and crystalline (cf. Schmidlin, "Das Triphenylmethyl," Stuttgart, 1911, p. 111). In particular, Kehrman and Wentzel (*Ber.*, 1901, **34**, 3815) and Gomberg (*Ber.*, 1902, **35**, 1822) observed that triphenylmethyl chloride and stannic chloride formed a crystalline compound $\text{CPh}_3\text{Cl}, \text{SnCl}_4$, which was later shown by Walden (*loc. cit.*) to behave as an excellent electrolyte when dissolved in liquid sulphur dioxide. The corresponding bromide $\text{CPh}_3\text{Br}, \text{SnBr}_4$ has now been prepared and used in the present work. Most of these metal halide double compounds are insoluble or sparingly soluble in non-polar solvents, but the double compounds of triphenylmethyl bromide with stannic and boron bromides, severally, possessed sufficient solubility in benzene to permit of the measurement of the dielectric polarisation. The results of these measurements are given in Table III. As in the former cases, the polarisations of the separate components were also measured, but in the values given for the solutions of the double compounds, f_2 and P_2 refer respectively to the mol.-fraction and apparent polarisation of the double compound supposed to be present as such in the solution.

Attempts to prepare a crystalline double compound of triphenylmethyl bromide and boron tribromide of definite composition, failed. Addition of equivalent amounts of the components in benzene solution, even as dilute as 1%, produced a yellow precipitate which did not redissolve on dilution, and which, together with the mother-liquor, darkened on standing. Solutions of this compound were therefore prepared by dissolving a small known weight ($\ll 0.1$ g.) of boron tribromide in 70–80 ml. of pure benzene and adding the equivalent amount of triphenylmethyl bromide, as a 2% solution in benzene, drop by drop from a burette in a stream of dry nitrogen, the final amount of benzene present being obtained from the weight of the solution. This procedure gave a deeply orange-coloured solution which was stable for some hours, but as a result of the method of preparation, the polarisation measurements of this compound are probably not better than $\pm 10\%$.

The polarisation of boron tribromide in benzene differs from that in cyclohexane by less than the experimental error: the polarisation of stannic bromide is significantly greater in benzene, indicating a certain amount of interaction with the aromatic molecules, but much less than in the case of aluminium bromide, which in benzene possesses a polarisation of 550 c.c. and a moment of 4.89 D. (Ulich and Nespital, *Z. Elektrochem.*, 1931, **37**, 559).

The refractivities of the triphenylmethyl bromide solutions were measured with a Pulfrich refractometer at 25.00° and $\lambda = 5461 \text{ \AA}$. (Hg), giving $P_e = 91.9$ c.c. This value being taken for the electron polarisation and

TABLE III.
Solutions in benzene.

Triphenylmethyl bromide.				Stannic bromide.			
f_2 .	ϵ .	d .	P_2 (c.c.).	f_2 .	ϵ .	d .	P_2 (c.c.).
0.00000	2.2727	0.8737	—	0.00000	2.2727	0.8737	—
0.004158	2.3031	0.8788	179.9	0.01410	2.2920	0.9236	62.1
0.007363	2.3241	0.8821	177.6	0.01446	2.2935	0.9248	61.0
0.01006	2.3455	0.8867	176.4	0.01725	2.2970	0.9344	61.9
0.01361	2.3680	0.8900	175.8	0.02149	2.3028	0.9496	61.3
0.02063	2.4157	0.8986	174.1	0.03866	2.3275	1.0092	61.5
0.02821	2.4677	0.9077	173.4				
$\infty P_2 = 183.5$ c.c.; $P_0 = 91.9$ c.c.; $\mu = 2.1$ D.							Mean 61.6
Boron tribromide.				Triphenylmethyl bromide-stannic bromide.			
0.00000	2.2727	0.8737	—	0.00000	2.2727	0.8737	—
0.007370	2.2735	0.8871	31.5	0.000636	2.2779	0.8757	283
0.01591	2.2752	0.9025	32.4	0.000881	2.2804	0.8771	270
0.01642	2.2754	0.9032	32.9	0.001267	2.2840	0.8789	265
0.02536	2.2765	0.9199	31.9	0.001316	2.2855	0.8791	277
			Mean 32.2	0.002580	2.2968	0.8849	264
$\infty P_2 = 290$ c.c.; $P_0 = 153.5$; $\mu_{app.} = 2.7$ D.							
Triphenylmethyl bromide-boron tribromide.							
0.00000	2.2727	0.8737	—	0.000427	2.2917	0.8744	775
0.000403	2.2908	0.8744	779	0.000653	2.3002	0.8751	732

the atomic polarisation being neglected, the above figures indicate a moment of 2.1 D. for triphenylmethyl bromide.

The figures in Table III also show that double compound formation between these inorganic bromides and triphenylmethyl bromide is accompanied by an increase in polarisation, but this is still too small to indicate any considerable formation of ion-pairs. This increase of polarisation is again almost certainly due to the presence of a relatively few ion-pairs which have a large moment.

The use of triphenylmethyl compounds, however, permits an alternative approach to this question of ion-pair formation, *viz.*, by a consideration of the colours of the solutions. Anderson (*J. Amer. Chem. Soc.*, 1935, 57, 1673), who has also reviewed the earlier work on the colours of solutions of triphenylmethyl compounds, has made a quantitative study of the light absorption of solutions of the free triphenylmethyl radical and several of its compounds in liquid sulphur dioxide, sulphuric acid, and other solvents. He has shown that the light absorption curve for a solution of triphenylmethyl bromide in sulphur dioxide, which is the absorption curve for the triphenylmethyl cation, is very similar to the absorption by this cation in solution in sulphuric acid, perchloric acid, or methyl sulphate. In sulphur dioxide solution the frequencies of maximum absorption are shifted a little towards the longer wave-lengths, but otherwise the shape and height of the curves are almost identical in the various solvents. From the temperature independence of the light absorption by triphenylmethyl bromide in sulphur dioxide he concluded that it was completely dissociated in dilute solution.

The significance of this work for the present purpose is that the measurement of the light absorption permits of an independent estimate of the concentration of triphenylmethyl cations and therefore of ion-pair formation.

The double compounds of metal halides and triarylmethyl halides are all coloured, many of them very deeply, and even dilute solutions of the sparingly soluble ones are strongly coloured; but the quantitative light absorption of these solutions does not seem to have been studied. Hammett ("Physical Organic Chemistry," New York, 1940, p. 54) has compared the formation of these compounds to the ionisation of an acid or base, chloride ion being transferred instead of hydrogen ion: $\text{CPh}_3\text{Cl} + \text{SnCl}_4 \rightleftharpoons \text{Ph}_3\text{C}^+ + \text{SnCl}_5^-$. The equilibrium constants of this ionogenic reaction in various solvents are, however, not known. If one compares, *e.g.*, a 1% solution of triphenylcarbinol or a triphenylmethyl halide in sulphuric acid or perchloric acid with a solution of triphenylmethyl bromide-stannic bromide in benzene, of equivalent concentration, the difference in colour is very striking, corresponding to about a thousandfold greater concentration of carbonium ion in the former case. Dr. A. E. Gillam has kindly photographed the absorption spectra of several of the solutions used in the present work, by means of a Hilger Type E quartz spectrograph and Spekker photometer. The yellow solutions show an absorption band with a maximum in exactly the same region as that found by Anderson (*loc. cit.*) for solutions of triphenylmethyl cation in various solvents. For triphenylmethyl bromide-stannic bromide in benzene the maximum absorption occurs at $\tilde{\nu} = 2300$ mm^{-1} , and for triphenylmethyl bromide-boron tribromide at $\tilde{\nu} = 2400$ mm^{-1} . The values of the molar extinction coefficients, which varied slightly, probably on account of the shift in equilibrium with change of concentration, were, *e.g.*, about 50 for a 0.017M-solution of triphenylmethyl bromide-stannic bromide and about 400 for a 0.0034M-solution of triphenylmethyl bromide-boron tribromide. These may be contrasted with the extinction coefficients found by Anderson (*loc. cit.*) for salts of the triphenylmethyl cation in sulphur dioxide, sulphuric acid, methyl sulphate, and 72% perchloric acid solutions, all of which show maximum extinction coefficients of 16,000—40,000 in the region $\tilde{\nu} = 2300$ —2600 mm^{-1} . Hence, the concentration of carbonium ions in the present solutions is relatively

very small, amounting only to about 0.1% of the stannic bromide compound and about 1% of the boron tribromide compound. Both dielectric polarisation and light absorption indicate a somewhat greater ionisation of the boron tribromide compound.

In the solid state the double compounds may be more ionic; single crystals of the stannic bromide compound are deep orange-red in colour. In the formation of such an ionic solid, however, there is available, in addition to the energy of complex metal anion formation, also the energy of formation of the ionic lattice, which may be greater than the energy of formation of single ion-pairs in solution. In this connexion the case of arsenic tribromide is of particular interest. If a dilute solution of arsenic tribromide in benzene is added to an equivalent amount of triphenylmethyl bromide, also in solution, there is no visible colour development; but if the solvent is removed in a vacuum at room temperature, a deeply orange-coloured solid separates, which will again dissolve in benzene to give a colourless solution. In this case it may be presumed that the energy of formation of the complex metal anion is low, and that it is only in the solid state that ionisation is observed.

The non-ionic fraction of the solute in these solutions of double compounds is probably present both as a covalent complex and as uncombined component halides, chiefly the latter. There are several pieces of evidence which support this conclusion. The very small concentration of phenylmethylcarbonium ion, as indicated by the colours of the solutions, makes it necessary to assume also the presence of a small amount of a polar

non-ionic complex, unless the moments of the ion-pairs are improbably high—over 40 D. in both cases. On the other hand, any massive formation of such a covalent complex would give rise to a much larger polarisation than actually observed. In the case of the stannic bromide compound its formation could only take place by the distortion of the symmetrical tetrahedron of the stannic bromide molecule, with an approach to a more or less symmetrical trigonal bipyramid and the consequent unbalancing of the large Sn-Br moments. The 5-co-ordination compounds of stannic and titanium halides with nitriles and other molecules possess large moments, of the order of 6 D. (Ulich and Nespital, *Z. physikal. Chem.*, 1932, B, 17, 21). Also, the solutions of the boron tribromide compound, although very dilute, fume strongly in the air, indicating the presence in solution of the free components.

In general, therefore, the equilibria ($X = \text{halogen}$) in solution are $\text{MX}_n + \text{Ar}_3\text{CX} \rightleftharpoons (\text{MX}_n, \text{Ar}_3\text{CX}) \rightleftharpoons (\text{MX}_{n+1}^-, \text{Ar}_3\text{C}^+)$, with in all cases a small equilibrium concentration of the covalent complex ($\text{MX}_n, \text{Ar}_3\text{CX}$) and of ion-pairs $\text{MX}_{n+1}^-, \text{Ar}_3\text{C}^+$. In a polar solvent, as a result of the greater solvation energy of the ions, the degree of ionisation may be greater than in a non-polar solvent.

The study of such ionogenic equilibria, involving triarylmethyl compounds and metal halides, by light-absorption and polarisation measurements, offers an equilibrium method of comparing the electrophilic character of such metal halides and substituted metal halides as give rise to double compounds soluble in non-polar solvents. The study of rates of radioactive isotopic exchange offers a kinetic approach to the same problem.

Even when metal halide and double compound are both insoluble, the surface colour developed on addition of a solution of a triarylmethyl halide to a white inorganic halide may be used as a qualitative test of the electrophilic character of the latter. For example, in addition to those already mentioned, yellow solutions or precipitates, or yellow coloration

of the solid, were observed on the addition of the corresponding triphenylmethyl halide in benzene or cyclohexane solution to anhydrous BeBr_2 , ZnBr_2 , CdBr_2 , HgBr_2 , YCl_3 , CeCl_3 , GaBr_3 , InBr_3 , TiCl_4 , ZrCl_4 , ThCl_4 , TeCl_4 , or TaCl_5 , but not with halides of the alkali or alkaline-earth metals, thallos halides, or the halides of carbon, silicon, or phosphorus.

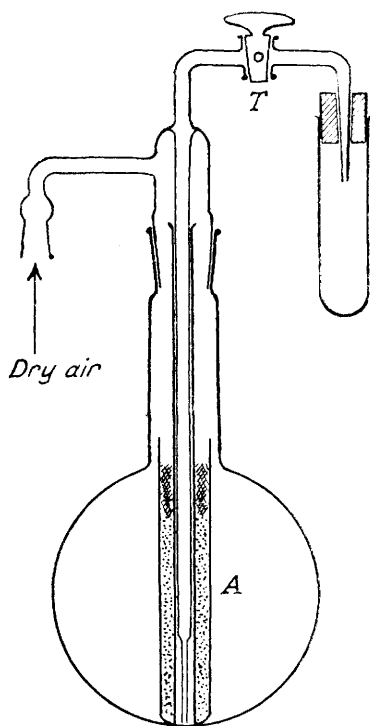
EXPERIMENTAL.

Materials.—*cycloHexane*. A commercial product was shaken with concentrated sulphuric acid to which a little fuming acid had been added, until it no longer showed the benzene absorption bands in the ultra-violet. It was then washed, roughly dried over potassium hydroxide pellets, set aside for several weeks in contact with phosphoric oxide, and fractionated through an efficient column in a stream of nitrogen, dried by passage through a coil immersed in liquid air; b. p. $80.0^\circ \pm 0.1^\circ/752 \text{ mm}$.

Benzene. "AnalaR" Benzene was fractionally frozen three times to remove homologues, kept for several months over phosphoric oxide, and fractionated as above in dry nitrogen; b. p. $80.9^\circ \pm 0.1^\circ/778 \text{ mm}$.

The pure solvents were stored in vessels of the form shown in Fig. 2, constructed entirely of Pyrex glass, with standard "Quickfit" ground joints; the latter were pressed together by metal collars and rubber bands (not shown). The delivery tap *T* was ungreased and the outlet tube capped when not in use. The loose annular vessel *A*, surrounding the central delivery tube, was partly filled with anhydrous magnesium perchlorate (freshly dehydrated by heating in a vacuum) kept in place by a plug of glass wool. The same drying agent was used in the air inlet tube connecting the vessel with the compressed-air line. This method of storage prevented contact between the drying agent and liquid: its efficiency was shown by the fact that the dielectric constants of the liquids remained unchanged over several months.

FIG. 2.



Boron tribromide. This was prepared by reaction between boron trifluoride and aluminium bromide (Gamble, Gilmont, and Stiff, *J. Amer. Chem. Soc.*, 1940, **62**, 1257). After fractionation, the extremely hygroscopic liquid was redistilled under low pressure (a few μ Hg), with rejection of the first part which contained any hydrogen bromide, and filled, without removal from the vacuum apparatus, into small ampoules provided with long fine capillaries at each end, one of these being sealed before filling with the liquid. The other capillary was then sealed by a small flame, at a point where it contained only boron tribromide vapour. In use, one capillary was cut near its end and placed just above the surface of the solvent; the upper capillary was then cut, and the boron tribromide allowed to flow into the solvent with a minimum contact with the atmosphere.

Stannic bromide. A commercial product was redistilled and filled in a similar manner into larger ampoules with a single capillary. These ampoules were only partly filled, and the molten stannic bromide was allowed to solidify with the sealed capillary uppermost. In use, the ampoules were cut near to the surface of the solid and quickly slipped into the solvent.

Aluminium bromide. Haen's "pro Synth." product was freshly sublimed in small portions in a vacuum at about 1μ Hg, and melted under dry nitrogen at atmospheric pressure into small tubes; after solidification of the bromide, these were cut close to the surface of the solid and quickly added to the solvent.

Triphenylmethyl bromide. Prepared from triphenylcarbinol and hydrogen bromide in glacial acetic acid (Wieland, *Ber.*, 1911, **44**, 3024), and recrystallised from carbon disulphide and three times from dry *cyclohexane*, this had m. p. 151° .

Other organic bromides were commercial products, purified, dried over phosphoric oxide, and fractionally distilled.

The triphenylmethyl bromide-stannic bromide double *compound* was prepared in a well-crystallised condition by mixing equimolar quantities of the components dissolved in sufficient warm benzene to prevent immediate precipitation, and allowing the solution to cool slowly (Found: C, 30.0; Sn, 15.5. $C_{19}H_{15}Br_2Sn$ requires C, 30.0; Sn, 15.6%). This compound is soluble only to the extent of about 2% by weight in cold benzene.

Measurements.—The dielectric constants were measured at about 100 kc. by means of a Muirhead Type 3-A Heterodyne Capacity Meter. This instrument was first calibrated by the step-by-step method, for linearity of scale, at 50 points, a 11μ F. fixed-capacity air condenser being used. The capacities could be measured to about $\pm 0.02\mu$ F. or about 1 part in 10,000 of the smallest capacity used, that of the dielectric cell when filled with dry air. The latter was a 3-plate platinum-glass cell of about 215μ F. capacity, of a type previously described (Fairbrother, *Proc. Roy. Soc.*, 1933, *A*, **142**, 173). Densities were measured in a glass-capped Sprengel-type pycnometer of about 11 c.c. capacity. Both dielectric cell and pycnometer were immersed in the same medicinal paraffin oil thermostat at 25.00° . The dielectric cell was calibrated in the usual manner with the dry benzene, the dielectric constant of the latter being assumed to be 2.2727 at 25° (Hartshorn and Oliver, *ibid.*, 1929, *A*, **123**, 664).

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