592. *The Hydration and Hydrolysis of Anhydrous Aluminium Bromide.*

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A study has been made of the hydration and hydrolysis of anhydrous aluminium bromide, initially (*a*) in the vapour state, (*b*) as a crystalline solid, and (*c*) in solution in ether, with amounts of water ranging from traces up to that corresponding to $AlBr_3,6H_2O$.

The primary reaction appears to be a hydration which may or may not be followed by hydrolysis, depending upon the temperature of the reaction.

The results suggest a 3-stage hydration: (1) to a tetrahedrally co-ordinated $AlBr_3,H_2O$, followed by (2) the formation of an octahedrally co-ordinated $AlBr_3,3H_2O$ in which the aluminium–bromine bonds are still largely covalent, and (3) progressive displacement of the bromine atoms as negative ions by the co-ordination of additional molecules of water: $[AlBr_2,4H_2O]^+Br^-$; $[AlBr,5H_2O]^{2+}Br_2^{2-}$; $[Al,6H_2O]^{3+}Br_3^{3-}$, resulting finally in the formation of the hexahydrate, which is stable at room temperatures. Hydrolysis, which is very slow at room temperature, even with the most easily hydrolysable systems, and which becomes progressively slower and less in amount after 2—3 moles of water per mole of Al_2Br_6 have been added, is believed to be chiefly the result of the reaction of the still covalently bound bromine atoms with the adjacent water molecules.

The results indicate that the promoter effect of added aqueous hydrobromic acid on aluminium bromide or of aqueous hydrochloric acid on aluminium chloride, may be that of the water rather than that of the hydrogen halide.

It has long been known that addition of traces of water or of hydrogen halide to anhydrous aluminium chloride and aluminium bromide may materially improve their activities as catalysts in a number of reactions. Especially is this so in polymerisation and isomerisation reactions, in which indeed such an addition may be necessary in order to start the reaction. The rôle of the hydrogen halide has in the past usually been discussed in terms of the formation of a supposed hydrogen aluminium tetrahalide, $HAlCl_4$ or $HAlBr_4$, metallic salts of which are well known (cf. Leighton and Heldman, *J. Amer. Chem. Soc.*, 1943, **65**, 2276; Thomas, "Anhydrous Aluminium Chloride in Organic Chemistry," New York, 1941, Chapter 4).

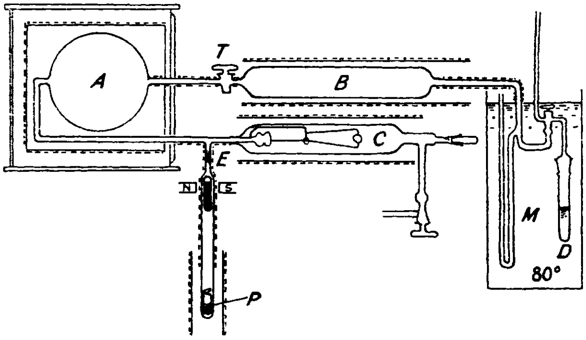
Recent work, however (Fontana and Herold, *J. Amer. Chem. Soc.*, 1948, **70**, 2881; Richardson and Benson, *ibid.*, 1951, **73**, 6096; Brown and Pearsall, *ibid.*, p. 4683), has shown that, at all events in binary systems of hydrogen halide and anhydrous aluminium halide, or in a ternary system involving also a saturated hydrocarbon such as *n*-butane, such halogeno-aluminium acids are in fact quite hypothetical and do not exist in any detectable amount even in circumstances which might be regarded as most favourable to their formation. It is only in the presence of a somewhat "basic" or electron-donor third component such as an olefinic or aromatic hydrocarbon that association of the hydrogen halide with the aluminium halide takes place. The action of added traces of water on these catalysts has also usually been interpreted as that of a hydrogen halide produced as the result of hydrolysis. Wackher and Pines, however (*ibid.*, 1946, **68**, 1642), have shown that not only does anhydrous hydrogen halide alone fail to promote the isomerisation of alkanes in the presence of aluminium chloride or bromide, but that the aluminium halides treated with various amounts of water and freed from uncombined hydrogen halide are quite effective catalysts, the most active being the one prepared by the action of 4 moles of water on one mole of aluminium bromide (Al_2Br_6). The same authors also showed that the amount of hydrogen bromide obtained by condensing water on to aluminium bromide at low temperatures and then heating to 100°, *decreased* as the proportion of water was increased, from 2·5 moles of HBr when 2 moles of water were added to one of Al_2Br_6, to zero when 12 moles of water were added.

We have now examined the reaction between anhydrous aluminium bromide and water in greater detail, with the aluminium bromide initially (*a*) in the vapour state, (*b*) as a crystalline solid, and (*c*) in solution in ether. The quantitative nature of the results varied over fairly wide limits as a consequence of the heterogeneity of most of the reactions involved; but the overall qualitative picture was always the same, namely, an initial hydration of the aluminium bromide, which may or may not be followed by hydrolysis and subsequent hydration of the products, according to the conditions of the reaction. At room temperature hydrolysis of a previously formed hydrate occurs only very slowly.

Vapour-phase Hydrolysis.—This aspect of the problem was of additional interest since it has been shown (Hudson, *Proc. I.U.P.A.C.*, 1947, **2**, 297) that a number of inorganic chlorides whose rapid hydrolysis in aqueous solution is a familiar phenomenon, *i.e.*, PCl_3, $SOCl_2$, S_2Cl_2, $SeOCl_2$,$SiCl_4$, do not in fact react easily with water vapour except as a heterogeneous reaction, whereas others such as BF_3 and $TiCl_4$ readily undergo a homogeneous reaction in the vapour phase.

A review of these limited results immediately suggests that it is only the " acceptor " or " Friedel–Crafts catalyst " type of halides which undergo vapour-phase hydrolysis and that they do so in the first place by co-ordination of a water molecule by the central atom. Accordingly, it was to be expected, and has been confirmed, that anhydrous aluminium bromide would readily undergo vapour phase hydrolysis.

FIG. 1.

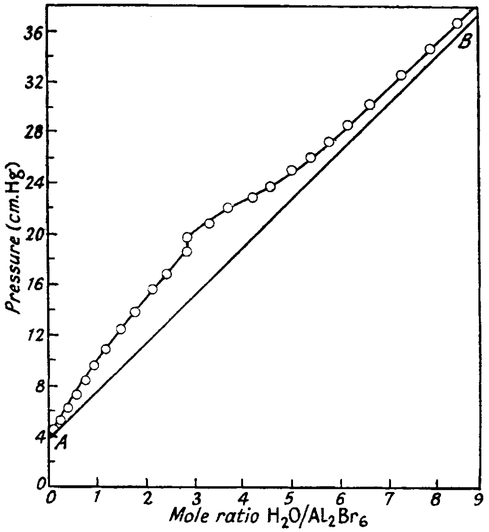


The apparatus used is shown in Fig. 1. The reaction vessel *A*, of about 1 l. capacity, the water-vapour reservoir *B*, of about 300 c.c., and the sensitive sickle gauge *C* were maintained at 160° ± 0·5° by three Cambridge thermocouple regulators. The sickle gauge was fitted with a mirror, operating on a torsional principle, which gave a 3-cm. deflection of a spot of light at 1 m. distance for a pressure difference of 1 mm. Hg; the deflection was linear with the pressure difference over a range of about ±15 mm. Hg. This gauge enabled instantaneous pressure readings to be made without the time lag associated with the adjustment of the external pressure in a simple sickle gauge. The gauge was brought to zero deflection before each addition of water vapour. The working temperature of 160° was chosen as being the lowest at which the vapour pressure of aluminium bromide (60 mm. Hg) was high enough to maintain sufficient halide in the reaction vessel in all experiments as an unsaturated vapour. A known amount of aluminium bromide, purified by at least six sublimations *in vacuo*, and sufficient to give an initial pressure in the reaction system of about 40 mm. Hg, was volatilised from the hook-ended ampoule *P* (Alexander and Fairbrother, *J.*, 1949, S223) into the reaction system, which was then sealed at *E*. Water vapour was admitted through the tap *T* (also maintained at 160°) in successive known small amounts which were calculated from the volume of *B* and its associated connecting tubes and the fall in pressure measured by the manometer *M*, which was kept at 80°. At the beginning of the experiment *B* was filled to a pressure of about 300 mm. Hg with water vapour from the reservoir of boiled distilled water *D*. The portion of the apparatus which gave the most trouble was the tap *T*. After many trials with a variety of devices, a well-fitting hollow-key Pyrex tap, wound with successive layers of copper foil, asbestos, and heating tape, and containing a thermometer bulb inside the connecting tube up against the key, was found to be the most suitable. The tap was greased with Dow Corning high-vacuum grease and could be kept for about 3 days at 160° and turned 30—40 times before sticking or leaking.

Measurements of the total pressure in the reaction system were made by the sickle gauge immediately after each addition of water vapour and at intervals thereafter up to ½ hour, when a further addition of water vapour was made. In Figs. 2 and 3 are plotted, against the molar proportion of water added in one such "run," (*a*) (Fig. 2) the total pressure in the reaction system, and (*b*) (Fig. 3) the differential pressure Δp, *i.e.*, the *excess* pressure over that which would have been observed if no reaction had taken place. Each point shown corresponds to the pressure observed at the end of a half-hourly period.

Certain facts emerge from these results. At the temperature of the reaction aluminium bromide is dimeric, so that we are dealing in the first place with the reaction of Al_2Br_6 molecules. If the net reaction had been of the form

FIG. 2.



$$Al_2Br_6 + H_2O = 2HBr + Al_2Br_4O \quad \ldots\ldots\ldots \quad \text{(i)}$$

no change in total pressure would have been observed, the oxybromide being assumed to be involatile (Line *AB*, Fig. 2; $\Delta p = 0$, Fig. 3). If the reaction had been

$$Al_2Br_6 + 2H_2O = 4HBr + 2AlBrO \quad \ldots\ldots\ldots \quad \text{(ii)}$$

the reaction would have followed the line *AB* on Fig. 3 whilst if it had been

$$Al_2Br_6 + 3H_2O = 6HBr + Al_2O_3 \quad \ldots\ldots\ldots\ldots \quad \text{(iii)}$$

i.e., a complete hydrolysis, the differential pressure would have been as at *AC*, Fig. 3. It will be observed that for the first few additions of water, up to something less than unity for the ratio H_2O/Al_2Br_6, whilst the aluminium bromide is still in large excess, the net reaction almost followed this course. The yield of hydrogen bromide, however, was never quite theoretical and soon fell below that of this simple hydrolysis reaction. Moreover, the reaction became gradually slower, so that in contrast to the early additions of water vapour, where the immediate increase of pressure was little less than that recorded after the lapse of ½ hour, even the half-hourly pressures recorded were no longer the limiting pressures. At *D*, where the differential pressure should have nearly double that observed if only the reaction (iii) had occurred, the half-hourly additions of water were interrupted and the system maintained at 160° for 10 hr., the pressure being noted at frequent intervals. Even after this lapse of time it was clear that the system had not reached equilibrium but was slowly approaching a less-than-theoretical yield asymptotically. A re-commencement of additions of water at *E* gave even less yields and eventually an apparent recession of the reaction set in. After a total of about 4 moles of H_2O per mole of Al_2Br_6 had been added the pressures observed at the end of the half-hourly periods were actually *less* than those at the beginning.

The most probable explanation of this course of events would appear to be as follows.

Since, especially at the pressures used, we can exclude simultaneous collisions of an aluminium bromide molecule with two or three molecules of water, and in view of the well-known behaviour of aluminium bromide towards electron-donor molecules, the first stage must be the formation of a monohydrate : $Al_2Br_6 + H_2O = AlBr_3,H_2O + AlBr_3$, support for which is given by later experiments and which, whilst stable at low temperatures, rapidly decomposes even below 100° to give in turn $AlBr_2{\cdot}OH$ and AlBrO. The system is now heterogeneous and the $AlBr_2{\cdot}OH$ and AlBrO almost certainly undergo, at this stage, a rapid disproportionation into Al_2Br_6 and Al_2O_3 on the surface of the reaction vessel. This kind of disproportionation of an oxyhalide has been observed in other cases where the halide is volatile and in this instance is facilitated by the high lattice energy of the aluminium oxide. Thus, the final net reaction at this stage approaches the complete hydrolysis of Eqn. (i). It is to be noted that this only occurs in practice when the aluminium bromide is still in great excess and the products of hydrolysis are small in amount. As more water is added, however, hydrogen bromide accumulates in the vapour phase and the layer of hydrolysis products on the inner surface of the reaction vessel becomes thicker. Other reactions then become progressively more significant. Among these, which cannot be identified separately, the most important are probably : (*a*) the experimentally observed slowing down of the heterogeneous reaction of initial hydrolysis products, (*b*) the formation, by disproportionation, of thermally more stable hydrates, such as the hexahydrate, (*c*) a reversal, in the later stages of the reaction of the hydrolysis equation (iii) [we have also demonstrated the reversibility of this reaction by passing anhydrous hydrogen bromide over heated γ-Al_2O_3,H_2O (Boehmite) which was prepared by dehydration of the precipitated hydroxide in a vacuum at 200°] ; (*d*) an absorption of part of the added water vapour by the alumina. It may be noted that a similar effect to (*d*) was observed by Hudson (*loc. cit.*) in the case of titanium tetrachloride, at 25—100°, an initial rapid hydrolysis leading to the formation of the intermediate $Ti(OH)_2Cl_2$, followed by a subsequent slow absorption of water vapour on this solid particulate.

FIG. 3.

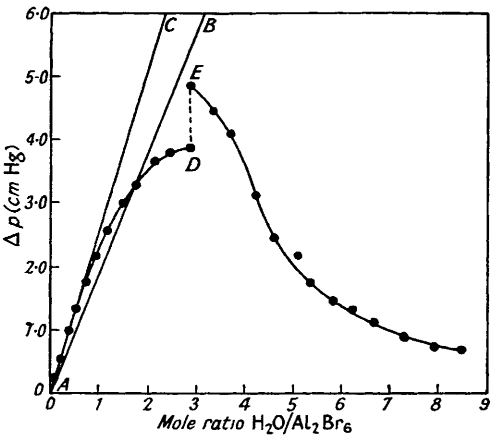
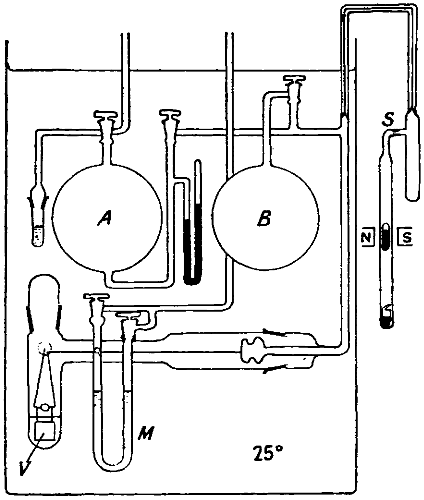


FIG. 4.



Solid-phase Hydrolysis.—These experiments consisted in the condensation of known amounts of water vapour on to crystalline aluminium bromide at −195°, followed by heating of the system to various temperatures up to 100° and the measurement of the pressure of the evolved hydrogen bromide.

The apparatus is illustrated in Fig. 4. Water vapour in known amounts, measured by the fall in pressure in the 1200-c.c. reservoir *A*, was condensed at −195° on to a known weight of pure aluminium bromide previously sublimed into the reaction vessel *L* which was sealed off at *S*. The reaction system, which included also a 1-l. bulb *B* (which could be used to increase the volume of the system when large amounts of hydrogen bromide were evolved), was otherwise evacuated and out-gassed. After the condensation of the required amount of water—which might require several fillings of the reservoir *A*—the reaction vessel *L* was surrounded by a constant-temperature bath at the desired temperature. In order to minimise dead space and the effects of variation in room temperature, the connection between *L* and the rest of the apparatus, and which was outside the thermostats, was made of capillary tubing. Pressure measurements were made by means of an extremely sensitive sickle gauge, based on a design by Lewis and Style (*Nature*, 1937, **139**, 631) and depending upon a bifilar suspension of the mirror for the amplification of small movements of the end of the sickle pointer. The movements of the mirror were damped by a vane *V* immersed in dibutyl phthalate. The pressure required to balance the gauge, which with its optical system was sensitive to $\pm 1{\cdot}5 \times 10^{-4}$ mm. Hg (for 1 mm. deflection at 1 m.) was measured by a mercury manometer, small pressure differences being measured directly by the gauge, which was calibrated for this purpose with the aid of the dibutyl phthalate manometer *M*.

A preliminary study in which, after condensation of the water on to the aluminium bromide at −195°, the vessel *L* was kept for 1 hr. at each of the following temperatures : −78° (acetone and solid carbon dioxide) ; −59° (melting chloroform) ; −44° (melting chlorobenzene) ; −33° (melting ethylene dichloride) ; −22° (melting carbon tetrachloride) ; −5·5° (ice and salt) ; 18° (room temperature), showed that hydrolysis began to take place, although extremely slowly, at temperatures as low as −40° : the amount, however, was sufficient to preclude the measurement of the dissociation of the hydrate, for which the sensitive gauge was designed.

As with the vapour-phase hydrolysis, small additions of water reacted relatively more completely and rapidly than larger ones. Even at room temperature, with sufficient water added to produce complete hydrolysis, less than 5% of hydrolysis (or 10% if the final product were hydroxy-halide) had occurred after 3 days. These points are illustrated below :

$H_2O : Al_2Br_6$	0·46	1·11	1·14	2·28	3·01
Reaction time (days)	4	2	2	1	3
Reaction % (on basis of 2 moles of HBr per mole of water added)	8·6	2·4	6·6	1·6	4·5

The quantitative variability of the results serves to illustrate the heterogeneous nature of the reaction. It is doubtless to such a slow hydrolysis at room temperature that must be ascribed the internal pressure developed in old ampoules of commercial aluminium chloride or bromide.

In all cases, the pressure in the reaction system in the early stages was less than the vapour pressure of water at the particular temperature of *L*, although sufficient water was present to saturate the volume of the system. This confirms the idea of initial hydration. The absorption of a trace of water to give a hydrate with a negligible dissociation pressure, stable at ordinary temperature but dissociating on heating, has been described in the cases of niobium (columbium) and tantalum halides (Alexander and Fairbrother, *J.*, 1949, S223, 2472).

A series of experiments was carried out on systems similar to those studied by Wackher and Pines (*loc. cit.*) in which mixtures of aluminium bromide with known amounts of water, made at −195°, were kept for some time at about 20° and then heated to 100°, at which temperature they were maintained for several hours and until no further increase of pressure could be observed during 1 hr. The results are given in the annexed Table.

Reaction time, hr. at 20°	48	14	18	40	6	18	60
Reaction time, hr. at 100°	2	2	16	8	6	6	2
Molar ratio, $H_2O : Al_2Br_6$	1·13	2·27	3·01	4·05	5·94	8·12	11·86
Molar ratio, $HBr : Al_2Br_6$	2·25	3·21	3·11	2·38	2·11	1·83	0·63

Very little hydrogen bromide was evolved from these mixtures at room temperature. When the reaction vessel was warmed in a water-bath, the evolution, which was still slow up to about 70—75°, thereafter became more rapid, often with melting of the reaction mixture to a liquid which was very viscous even at 100° and solidified on cooling to room temperature.

It may again be observed that with small amounts of added water a nearly theoretical yield of two moles of hydrogen bromide per mole of added water is obtained. As more water is added the yield of hydrogen bromide per mole of Al_2Br_6 passes through a maximum and then decreases, so that when an amount of water almost sufficient to form the stable hexahydrate $AlBr_3,6H_2O$ is initially condensed on to the aluminium bromide, little more than one-tenth of the bromine is evolved as HBr on warming, an amount which might be expected to be obtained by heating the separately prepared hexahydrate at 100° for the same length of time.

Hydrolysis in Ethereal Solution.—Vapour-phase and solid-phase hydrolyses gave no experimental evidence of the formation of any intermediate hydrate, such as a trihydrate, which might reasonably be expected to be formed as a stage between a tetrahedrally co-ordinated monohydrate and the octahedrally co-ordinated hexahydrate. Evidence in this direction, however, was secured from experiments on the hydration of aluminium bromide in non-aqueous solution.

Since the dissolution of aluminium bromide in a large excess of water is exothermic to the extent of about 85 kcal. per mole of $AlBr_3$ (Berthelot, *Ann. Chim. Phys.*, 1878, **15**, 185), a calorimetric study of the hydration provides a convenient means of following the reaction. A similar approach has been used by Voigt (*Compt. rend.*, 1951, **232**, 26) to investigate the hydrolysis of phosphorus trichloride.

The study of the action of water on anhydrous aluminium bromide in non-aqueous solution, however, is additionally complicated by the fact that water is only sparingly soluble in all solvents in which aluminium bromide will dissolve as uncomplexed dimeric molecules. Consequently, even minute added droplets of water dissolve but slowly and there persists for some time a local excess of water at the periphery of the droplets so that the individual stages of hydration become smoothed out and hardly recognisable. Curves obtained for solutions in benzene and in chlorobenzene were of this nature but, though not sufficiently clear-cut in themselves, nevertheless offered supporting evidence to the results described below.

The most significant results were obtained by the study of the hydration in ethyl ether solution. Anhydrous aluminium bromide dissolves in ethyl ether as the monomer $AlBr_3$ (Wertyporoch, *Ber.*, 1931, **64**, 1370). One is therefore really dealing with the hydration of the ether complex, rather than with the unco-ordinated bromide, but the considerable heat developed when water is added to a solution of aluminium bromide in excess of ether shows that water is much the more strongly held ligand, and the presence of ether is unlikely to affect the conclusions, regarding the stages of hydration, which may be drawn from the results.

FIG. 5.

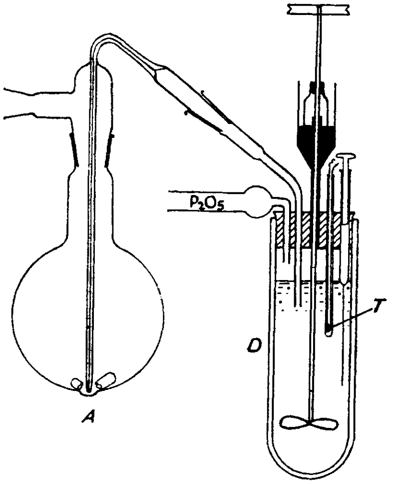
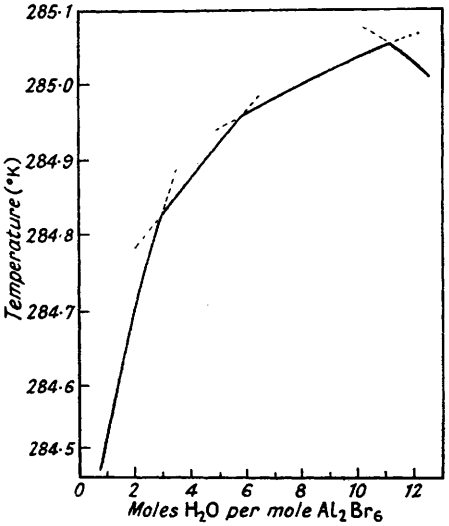


FIG. 6.



It is in the nature of the reaction that after the first addition of water, however small, the system becomes heterogeneous. Nevertheless, by adding the water very slowly and with rapid stirring, the precipitate can be obtained in a very finely dispersed condition, permitting a much closer approach to homogeneity than is possible when the products are deposited on the sides of the reaction vessel. Under these conditions, evidence has been obtained of hydration, *without hydrolysis* to the hexahydrate through a trihydrate and a lower hydrate, probably the monohydrate.

The apparatus used for hydrolysis in ether is shown in Fig. 5. About 250 c.c. of pure dry ethyl ether were distilled into the flask *A*, and a weighed quantity of pure aluminium bromide, contained in a small ampoule, added. After dissolution of the halide, the whole of the liquid contents of *A*, with the exception of a few drops, were driven over by a stream of dry nitrogen into the unsilvered Dewar vessel *D*. This vessel was sealed against ingress of moisture and evaporation of the ether by a large rubber stopper carrying a stirrer, thermistor, and micrometer syringe. The liquid was stirred at a constant rate, and temperature changes were measured by means of the thermistor *T*. The latter was a Stanel type F.2311/300 element and was mounted inside a thin glass protective shield. The temperature–resistance relationship of the thermistor was determined over the range 10—30° by calibration against a standard mercury thermometer: with the bridge arrangement employed, temperature changes of $\pm 0{\cdot}001°$ could be measured. There was observed a slight but steady upwards temperature drift due to the stirring, which however was small in comparison with the temperature rise due to hydration and was of no significance since we were only concerned with the relative temperature rises on the addition of equal amounts of water at the various stages of hydration. Water was added, as a liquid, by means of an all-glass micrometer syringe with an extremely fine tip which permitted the added water to be measured to 0·0002 c.c. Equal amounts of water (0·010 c.c.) were added at 5-min. intervals, and the temperature recorded after 2 and 4 min. and immediately before the next addition.

In Fig. 6 are shown the results of a typical experiment of this nature. The actual temperature rises in individual experiments varied with the concentration of the aluminium bromide used, but the breaks in the curves always occurred at the same place, namely, somewhat below 3 moles of H_2O per mole of Al_2Br_6, sharply at 6 moles, and again at about 11—12 moles. The formation of mono-, tri-, and hexa-hydrate respectively would require 2, 6, and 12 moles of water. It might be expected therefore that a break in the curve should occur at 2 moles of water. Superficially the break at something below 3 moles of water recalls the maximum HBr evolution around the same proportion in the two previous cases. Consideration, however, shows that the situation is quite different in that evolution of HBr involves hydrolysis, whereas the experiments in ethereal solution involve only hydration since practically no hydrogen bromide can be detected in the filtered ethereal solution at the conclusion of the experiment. Nevertheless, it seems probable that this break at 3 moles has this in common with the two previous cases, that it is the result of the onset of a subsequent reaction before a previous one is complete.

A precipitate begins to form in the ethereal solution immediately on the addition of the first drop of water and increases throughout the first stage, by the end of which the reaction mixture has become quite opaque. If this precipitate were substantially a tri- or higher hydrate, or a product of hydrolysis caused by the reaction of the whole of the drop of water with the minimum of bromide in its immediate neighbourhood, the temperature–composition curve would be unbroken in its early stages. It must be remembered, however, that the water will be momentarily in excess before the drop dissolves, even with vigorous stirring, so the precipitate will not be a pure monohydrate, though this may be the main product of reaction at this stage, but will contain traces of a higher hydrate, probably the trihydrate. The formation of a 5-co-ordinated dihydrate $AlBr_3,2H_2O$ seems unlikely, and there is no experimental evidence for its existence. Hence the first break in the curve, which probably occurs when all the aluminium bromide has been precipitated from the ethereal solution, must occur at a molar ratio somewhat greater than 2 and its near coincidence with 3, corresponding to the formation of a $1\frac{1}{2}$ hydrate, seems to be fortuitous.

Beyond this stage, further reaction is heterogeneous, and the risk of temporary local excess concentrations of water much diminished. The anticipatory formation of a trihydrate therefore will not so much affect the location of the next break in the curve which always occurs sharply at 6 moles of water per mole of Al_2Br_6, corresponding to the formation of a trihydrate $AlBr_3,3H_2O$.

Near the conclusion of the hydration, as the formation of the hexahydrate nears completion, the reaction slows down and the system begins to cool as water is added, somewhat before the full 12 moles of water have been added.

The addition of water to more concentrated solutions of aluminium bromide in ether, *e.g.*, 20 g./l., produced temperature rises which could be measured with a mercury thermometer, but the results were less reproducible and some hydrolysis took place. When concentrations of 4—6 g./l. were used in the present experiments, no evolution of hydrogen bromide was observed and the filtered liquid at the end of the experiment gave negative tests for the presence of bromide, whilst analysis of the precipitate showed that it contained almost as great a proportion of bromine to aluminium as the original aluminium bromide.

DISCUSSION

In the light of the foregoing results, the mechanism of hydration, whereby the anhydrous crystalline mass of Al_2Br_6 molecules passes into the stable, ionic, and catalytically inactive hexahydrate $AlBr_3,6H_2O$, would appear to be as follows.

The first molecule of water to react with the bromide molecule brings about its dissociation and the formation of a tetrahedrally co-ordinated monohydrate Br_3AlOH_2. This is in accord with the general " acceptor " properties of aluminium bromide which, as the monomer $AlBr_3$, reacts with, and forms double compounds with, a variety of " donor " molecules. Since the usual co-ordination number of aluminium is 6, the monohydrate can add further molecules of water up to a maximum of 3 without displacement of bromine, to form an octahedrally co-ordinated trihydrate, $AlBr_3,3H_2O$. These initial hydrates are stable at very low temperatures but decompose on heating, extremely slowly at room temperature, and fairly rapidly at 100°, to give a variety of hydrolysis products, which vary widely in composition according to the experimental conditions.

The corresponding slow hydrolysis of aluminium chloride has been known for a long time, it having been observed that " the reaction between moisture and aluminium chloride often does not take place at once but the hydrochloric acid is given off slowly on standing " (Ralston, Bureau of Mines Technical Paper, 321, 1923; *Chem. News*, 1923, **127**, 246). This behaviour was ascribed to a slow diffusion of the hydrate water of a surface hexahydrate " glaze " into the interior of the mass, with the formation of aluminium oxide and hydrochloric acid. Why a trace of moisture should immediately form, without hydrolysis, a hexahydrate which subsequently dissociates and the water molecules of which diffuse into the interior and react with other aluminium chloride molecules, *with* hydrolysis, is not obvious.

A clearer picture, however, is obtained if we assume that at ordinary and medium temperatures, *i.e.*, below 100°, the hydrogen bromide evolved on hydrolysis is the result of reaction between the water molecules ($\not> 3$ per $AlBr_3$) and the still mainly covalently bound bromine atoms attached to the same aluminium atom.

It has been shown by Palmer and Elliott (*J. Amer. Chem. Soc.*, 1938, **60**, 1852), by electron-diffraction measurements, that the lengths of the aluminium–bromine bonds in gaseous Al_2Br_6 molecules indicate that these already possess a considerable ionic character. Co-ordination of three water molecules to an $AlBr_3$ molecule would be expected still further to increase the ionic character of the Al–Br bonds and thus facilitate the displacement of a bromine atom as a negative ion on the approach of a fourth water molecule. Likewise, the addition of the fifth and the sixth water molecule finally results in a hexahydrated aluminium cation and three bromide ions. The hexahydrate is quite stable at ordinary temperatures, but decomposes on heating, slowly at 100° and more rapidly as the temperature is raised, with the simultaneous evolution of water and HBr. This hydrolysis on heating cannot be prevented by heating in HBr at atmospheric pressure.

The diminution in the amount of HBr evolved and the increasing slowness of the reaction as the amount of water is increased in the first two cases described above, can most easily be explained by the rearrangement in the solid phase of some of the water molecules to form a more stable hydrate with the accompanying ionisation of the bromine. The greater the number of water molecules present, the more likely would this be to occur before the hydrolysis of a lower hydrate was complete.

The above observations also suggest that in many cases, especially of isomerisation reactions or olefin alkylation, in which the addition of an aqueous solution of hydrogen halide has been observed to promote the reaction, the effect may not be that of the hydrogen halide but of the accompanying water. Aluminium chloride and bromide are excellent drying agents and will abstract water even from a hydrogen halide. In fact aluminium chloride was used by Burt and Gray (*Trans. Faraday Soc.*, 1911, **7**, 1) for this purpose in their determination of the atomic weight of chlorine from the density of hydrogen chloride.

Wackher and Pines (*loc. cit.*) suggested that the catalysts prepared by the action of water on aluminium halide probably consist of complexes which include aluminium halide, hydroxyaluminium halides, hydrogen halide, water, etc. It seems however, equally probable that the simple hydrates may be the effective catalysts in many reactions, by the formation of hydrogen-acids, *e.g.*, $[AlBr_3{\cdot}OH]^-H^+$, the proton then acting as a powerful positive ionogenic centre. This is similar to the action of water on boron trifluoride, the hydrates of which behave as $[BF_3{\cdot}OH]^-H^+$ or $[BF_3{\cdot}OH]^-OH_3^+$ (Greenwood and Martin, *J.*, 1951, 1795), and is also in accord with the well-known ability of various acids, *e.g.*, HF, H_2SO_4, H_3PO_4, to act as Friedel–Crafts catalysts, and with the behaviour of hydroxylic compounds as co-catalysts for the metal halide polymerisation of olefins.

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