Addition Compounds of Aluminum Halides with Alkyl Halides[1]

BY HERBERT C. BROWN AND WILLIAM J. WALLACE[2]

The methyl bromide–aluminum bromide system has been examined at -78.5, -64.4, -45.8, -31.3 and $0°$. Aluminum bromide possesses the monomeric formula in methyl bromide solution and the molecular weight data support the existence of a 1:1 addition compound, $CH_3Br:AlBr_3$, in solution. At $-78.5°$ the only solid phase which exists in the presence of methyl bromide appears to be the 1:1 addition compound. At -64.4 and $-45.8°$, two solid phases exist: $CH_3Br:AlBr_3$ and $CH_3Br:Al_2Br_6$. At $31.3°$ only the second of these appears in the phase diagram, while at $0°$, crystalline aluminum bromide separates from the solution. Aluminum chloride is only slightly soluble in liquid methyl and ethyl chlorides. Molecular weight data support a dimeric formula for aluminum chloride in such solutions. On the other hand, aluminum iodide dissolves in methyl iodide to give deeply colored solutions which contain monomeric aluminum iodide, presumably in the form of a 1:1 addition compound, $CH_3I:AlI_3$. Ethyl bromide also dissolves aluminum bromide to give a solution containing monomeric aluminum bromide. The solutions slowly liberate hydrogen bromide. A liquid 1:1 complex separates from these solutions at -80, -45.8, -31.3 and $0°$. Isopropyl bromide and n-propyl bromide dissolve aluminum bromide. The solutions are unstable and rapidly liberate hydrogen bromide with the formation of a complex "red oil." Under these conditions the n-propyl bromide is isomerized to isopropyl bromide and the rate of isomerization is greater than the rate of decomposition. The isomerization occurs at $-80°$ without appreciable decomposition and the rate is not affected by hydrogen bromide. Methyl chloride–aluminum bromide, methyl chloride–aluminum iodide and methyl bromide–aluminum iodide exchange halogen. The reactions go essentially to completion, whereas the reverse reactions, involving the alternative pairs of reactants, do not proceed. It is proposed that the isomerization of n-propyl bromide and the exchange of the methyl halides proceed without prior ionization of the addition compounds.

Introduction

The literature with respect to the existence of stable addition compounds between alkyl halides and aluminum halides, $RX:AlX_3$, is quite confused —a situation which has been characteristic of much of the literature concerned with Friedel–Crafts catalysts.

Physical measurements on solutions of aluminum halides in alkyl halides (mainly the bromides) show that such solutions have markedly different properties from the pure solvents and suggest that these solutions contain the addition compounds. Thus, a strong dipole is produced when aluminum bromide and ethyl bromide are brought together[3] and the absorption spectrum of this solution is markedly different from that of the pure solvent.[4]

On the other hand, Van Dyke recently examined the vapor pressure–composition phase diagrams for systems of aluminum bromide with methyl and ethyl bromides and concluded that no addition compounds are formed in these systems.[5] We had recently investigated the methyl chloride–gallium chloride system and had obtained convincing data in favor of a 1:1 compound, $CH_3Cl:GaCl_3$. It therefore appeared desirable to examine the methyl bromide–aluminum bromide system and related systems in order to establish whether such 1:1 addition compounds are formed by the aluminum halides.

Results and Discussion

The System: Methyl Chloride–Aluminum Chloride.—Aluminum chloride is only very slightly soluble in methyl chloride. The low solubility precluded a detailed examination of the system. The solubility of aluminum chloride in methyl chloride at $-31.3°$ was established as 0.18 mole per cent. by the vapor pressure lowering. The

direct determination of the solubility indicates that aluminum chloride dissolves as the dimer, in contrast to the behavior of the bromide and iodide. It therefore appears that aluminum chloride shows no tendency to form simple 1:1 addition compounds of the type formed by gallium chloride.[6]

Aluminum chloride was also insoluble in ethyl chloride. However, on standing it slowly dissolved with evolution of hydrogen chloride. The low solubility was quite surprising in view of the numerous references in the patent literature to the use of solutions of aluminum chloride in these solvents.[7] It is apparent that the "solutions" must be the result either of impurities originally present in the alkyl chlorides or formed by the decomposition of the halides.

The System: Methyl Bromide–Aluminum Bromide.—Aluminum bromide dissolves in methyl bromide to give a clear colorless solution which is stable for a considerable time. Only after several days did the solutions become slightly yellow in color, apparently an indication of a slow decomposition. For this reason all measurements were made with clear, freshly prepared solutions.

The molecular weight of aluminum bromide in methyl bromide was determined from the vapor pressure lowering. Typical results are reported in Table I.

The molecular weights evidently correspond to the monomeric formula. If it is assumed that aluminum bromide exists in solution as a stable 1:1 addition compound, $CH_3Br:AlBr_3$, effectively removing one mole of solvent from the solution, the calculated molecular weight is essentially independent of concentration and in excellent agreement with the theoretical value.

Vapor pressure–composition studies were made at -80, -64.4, -45.8, -31.3 and at $0°$ (Fig. 1). At $-80°$ solid appeared at a $CH_3Br/AlBr_3$ mole ratio of 4.65 and the pressure remained constant

(1) The Catalytic Halides. VIII.

(2) Standard Oil Company (Indiana) Fellow, 1950–1952.

(3) F. Fairbrother, *Trans. Faraday Soc.*, **37**, 763 (1941); *J. Chem. Soc.*, 503 (1945).

(4) V. V. Korshak and N. N. Lebedev, *J. Gen. Chem. (USSR)*, **18**, 1766 (1948).

(5) R. Van Dyke, THIS JOURNAL, **72**, 3619 (1950).

(6) H. C. Brown, L. P. Eddy and R. Wong, *ibid.*, **75**, 6275 (1953).

(7) C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," A.C.S. Monograph No. 87, Reinhold Publ. Corp., New York, N. Y., 1941.

TABLE I

MOLECULAR WEIGHT OF ALUMINUM BROMIDE IN METHYL BROMIDE

Temp.,[a] °C.	Decrease in press., mm.	Mole fraction	Molecular weight[b] Assuming no complex	As- suming 1:1 complex
−64.0	2.00	0.0980	264	293
−45.8	7.55	.0999	243	270
−30.9	18.05	.1033	244	273
0.0	73.75	.1009	249	268
.0	94.50	.1256	234	266
.0	133.10	.1656	219	263
.0	171.40	.2082	214	270

[a] Pressure of methyl bromide: 6.30 mm. at −64.0°; 69.3 mm. at −45.8°; 151.1 mm. at −30.9°; 659.5 mm. at 0°. [b] Calcd. for $AlBr_3$: 266.7.

at 4.9 mm. At a mole ratio of 1.0 there was a sudden drop in the pressure to 0.5 mm. and the pressure remained at this level until all of the methyl bromide had been removed. This plateau evidently corresponds to a solid phase of the 1:1 addition compound, $CH_3Br:AlBr_3$, and the previous plateau to a saturated solution of the addition compound in methyl bromide.
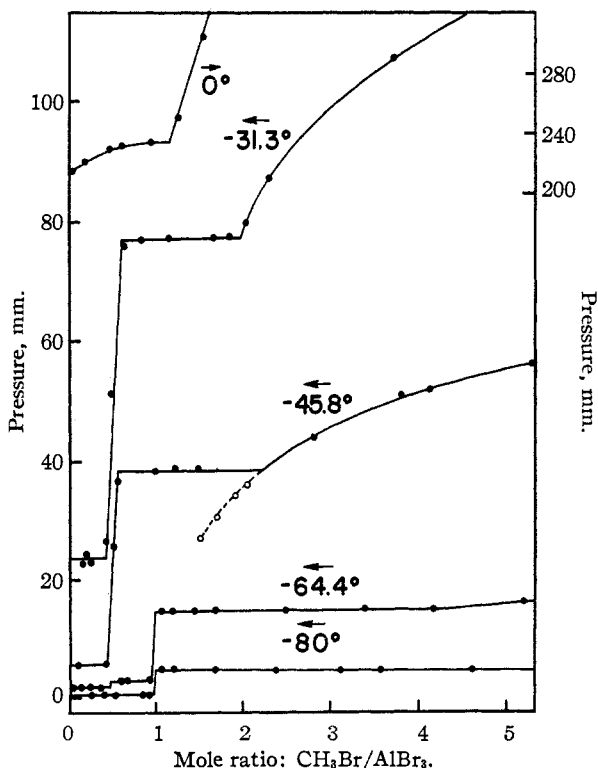

Fig. 1.—Vapor pressure composition diagrams for the methyl bromide–aluminum bromide system. (The arrows over the temperature value refer to the ordinate scale used.)

At −64.4° two plateaus appear, corresponding to compositions of $CH_3Br:AlBr_3$ and $CH_3Br:Al_2Br_6$. At the higher temperatures, −45.8 and −31.3°, only plateaus corresponding to the 1:2 compound, $CH_3Br:Al_2Br_6$, appear. Finally, at 0° no well-defined plateau, corresponding to compound formation in the solid phase, appears.

It was possible to determine the solubility of aluminum bromide from the phase diagram at each

of the temperatures involved. The data are summarized in Table II and Fig. 2. From the data the heat of solution or heat of fusion of the solid is calculated to be 1.83 kcal./mole.

TABLE II

SOLUBILITY OF ALUMINUM BROMIDE

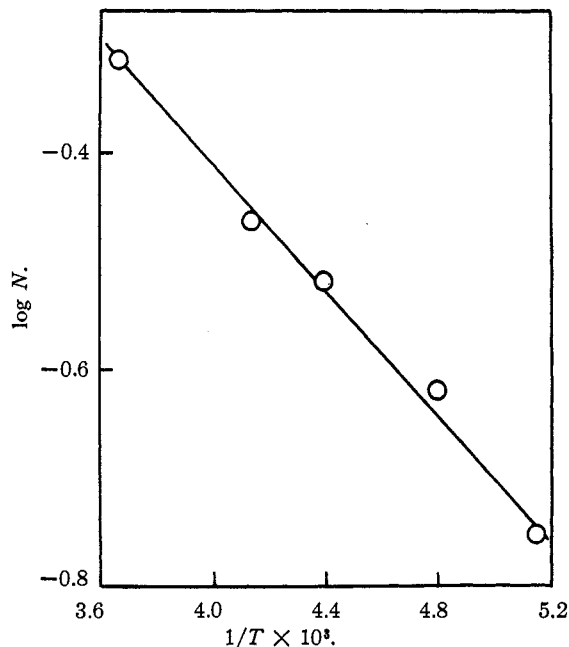| Temp., °C.	−80	−64.4	−45.8	−31.3	0
Mole fraction, N	0.177	0.240	0.303	0.343	0.484

Fig. 2.—Solubility of aluminum bromide in methyl bromide as a function of temperature.

The 1:1 addition compound was prepared at −80° and the pressure measured as the temperature was slowly allowed to rise. The data (Fig. 3) indicate a transition point at approximately −43°.
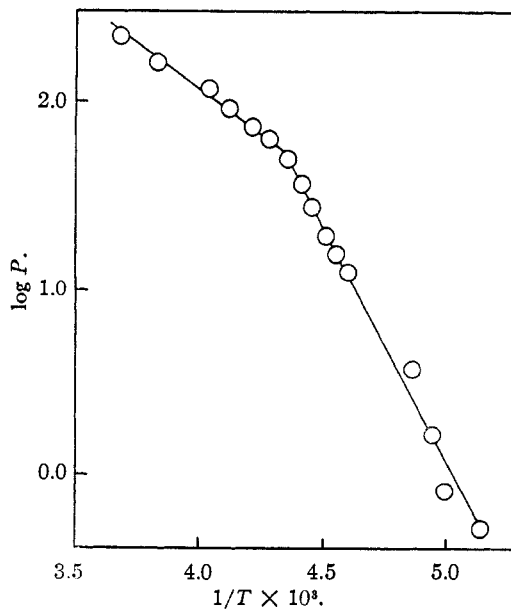

Fig. 3.—Vapor pressure of a 1:1 methyl bromide–aluminum bromide compound as a function of temperature.

The molecular weight data definitely support the existence of a 1:1 addition compound in solution. At $-78.5°$ and at $-64.4°$ the vapor pressure–composition curves show an arrest at the composition corresponding to the 1:1 compound. It follows that the solid which first separates from the solution possesses this composition. The linear relationship between log N and $1/T$ (Fig. 2) suggests that at each of the temperatures the solid phase which first separates and is in equilibrium with the saturated solution must be the same 1:1 compound. Both the discontinuity in the vapor pressure curve (Fig. 3) and the phase diagrams (Fig. 1) indicate that above approximately $-45°$, in the absence of a liquid phase of methyl bromide, the 1:1 compound is unstable with respect to the 1:2 compound. Moreover, at 0° the 1:2 compound appears to be unstable with respect to aluminum bromide and to form solid solutions with it.

It follows that at $-80°$ the 1:1 complex, CH_3-$Br:AlBr_3$, separates and is stable at this temperature. There may also be a drop in vapor pressure corresponding to a phase with the composition of the 1:2 compound, $CH_3Br:Al_2Br_6$. Unfortunately, the pressures are so low that no definite statement on this point can be made. At $-64.4°$ solid phases corresponding to both the 1:1 and 1:2 compounds are apparent. As the temperature is raised, the 1:1 complex apparently becomes less stable with respect to the 1:2 compound, and only the 1:2 solid phase appears in the phase diagrams at -45.8 and $-31.3°$. At 0°, there does not appear to be any stable complex. There is a brief arrest in vapor pressure when solid starts to separate, followed by a slow drop in pressure until all of the methyl bromide has been removed. This must be interpreted in terms of solid solutions of methyl bromide, or of the methyl bromide–aluminum bromide complexes, in aluminum bromide.

As a matter of fact, a careful examination of the curves above $-80°$ reveals an evident decrease in the vapor pressure of the $CH_3Br:Al_2Br_6$ compound as the methyl bromide present is reduced. This suggests that the 1:2 complex, $CH_3Br:Al_2Br_6$, and Al_2Br_6 form a series of solid solutions. A careful re-examination of the vapor pressure–composition relationships in the region $CH_3Br/AlBr_3$ between 0 and 0.5 will be required to check this point.

The System: Methyl Iodide–Aluminum Iodide.
—White crystalline aluminum iodide dissolved in colorless methyl iodide to give a solution which was red in color and which slowly evolved a gaseous product. Unfortunately, the amounts of this gas which were formed were too small to permit identification, but were sufficiently large to complicate the molecular weight determinations and the vapor pressure–composition studies. The data obtained with this system are necessarily less satisfactory than in the case of the corresponding aluminum bromide–methyl bromide system.

In spite of the lower precision, the molecular weight data (Table III) definitely support the conclusion that aluminum iodide is monomeric in methyl iodide. Moreover, although with less certainty than in the case of the methyl bromide–

aluminum bromide system, the data favor the existence of a 1:1 complex in solution.

TABLE III

MOLECULAR WEIGHT OF ALUMINUM IODIDE IN METHYL IODIDE

Temp.,[a] °C.	Decrease in press., mm.	Mole fraction (AlI₃)	Molecular weight[b] Assuming no complex	Assuming 1:1 complex
0.0	13.5	0.092	394	434
.0	17.9	.104	335	374
.0	20.1	.118	339	384
.0	26.5	.170	371	447

[a] Pressure of methyl iodide: 141.7 mm.   [b] Calcd. for AlI₃: 408.

Vapor pressure–composition studies were made at 0 and $-31.3°$. Because of the low vapor pressures of methyl iodide, studies at lower temperatures did not appear practical. The results (Fig. 4) show that at these temperatures neither 1:1 nor 1:2 complexes separate as a stable solid phase.
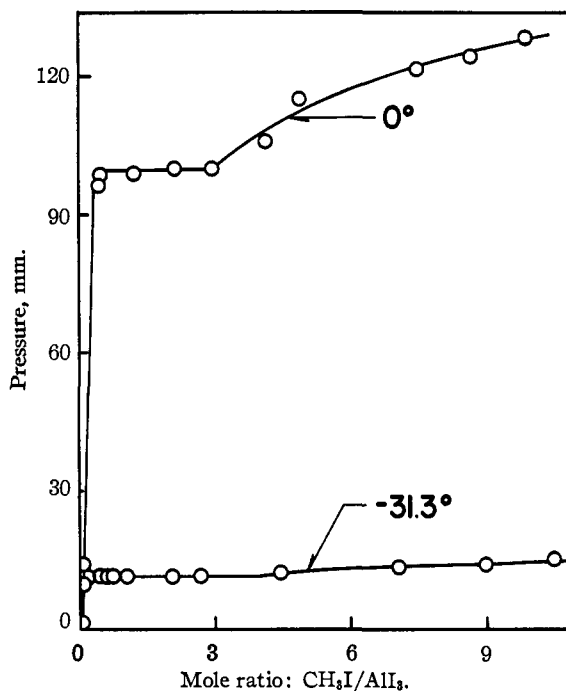

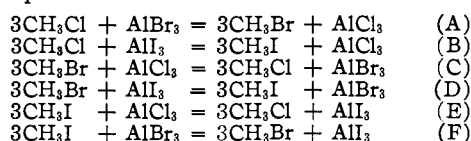Fig. 4.—Vapor pressure-composition diagram for the methyl iodide–aluminum iodide system.

At the present time there are no good experimental data on which to base a decision as to the relative acid strengths of the aluminum halides. If one may extrapolate from the acid strengths of the boron halides ($BF_3 < BCl_3 < BBr_3$),[8] one would expect AlI_3 to be a stronger acid than $AlBr_3$. Yet aluminum iodide is much less soluble in methyl iodide than aluminum bromide in methyl bromide. At 0° the solubility of the iodide is 0.251 mole fraction as compared to 0.484 for the bromide (the mole fraction is expressed as Al_2X_6). Moreover, the iodide separates from solution as the unsolvated compound, whereas the bromide separates as the addition compound.

These differences may be due to the higher heat of fusion of the aluminum iodide (3.8 kcal./mole

(8) Unpublished work with Robert Holmes.

for the iodide *vs.* 2.7 for the bromide).[9] Another possible factor is the relative base strengths of methyl bromide and iodide. It is known that the ability to donate an electron pair to typical Lewis acids falls off sharply in groups V and VI with increasing atomic number[10]: $(CH_3)_3N > (CH_3)_3P > (CH_3)_3As > (CH_3)_3Sb$. It follows that the failure to isolate 1:1 or 1:2 crystalline compounds from the iodide system may largely be a result of the relatively weak basic properties of methyl iodide, augmented by the higher crystal lattice energy of aluminum iodide.

Mixed Systems: Methyl Halide–Aluminum Halide.—Ampules were prepared containing all six possible combinations of the methyl halides (in excess) with the aluminum halides. After 24 hours at 0° the ampules were opened and analyzed. Of the six possible reactions

$$3CH_3Cl + AlBr_3 = 3CH_3Br + AlCl_3 \quad (A)$$
$$3CH_3Cl + AlI_3 = 3CH_3I + AlCl_3 \quad (B)$$
$$3CH_3Br + AlCl_3 = 3CH_3Cl + AlBr_3 \quad (C)$$
$$3CH_3Br + AlI_3 = 3CH_3I + AlBr_3 \quad (D)$$
$$3CH_3I + AlCl_3 = 3CH_3Cl + AlI_3 \quad (E)$$
$$3CH_3I + AlBr_3 = 3CH_3Br + AlI_3 \quad (F)$$

three (A, B and D) proceeded essentially to completion, whereas three (C, E and F), the reverse of the previous reactions, did not take place. From available thermochemical data it is possible to calculate the heats of the exchange reactions: A, $\Delta H = -32.0$ kcal./mole; B, $\Delta H = -82.6$; D, $\Delta H = -38.3$. Since the entropy changes in these reactions should be small, the changes in enthalpy should be a satisfactory measure of the relative positions for the equilibria.

Several attempts were made to force reactions C and F to proceed by carrying the reactions out under reflux and permitting any of the more volatile methyl halides formed as product to escape from the reaction vessel. However, no evidence
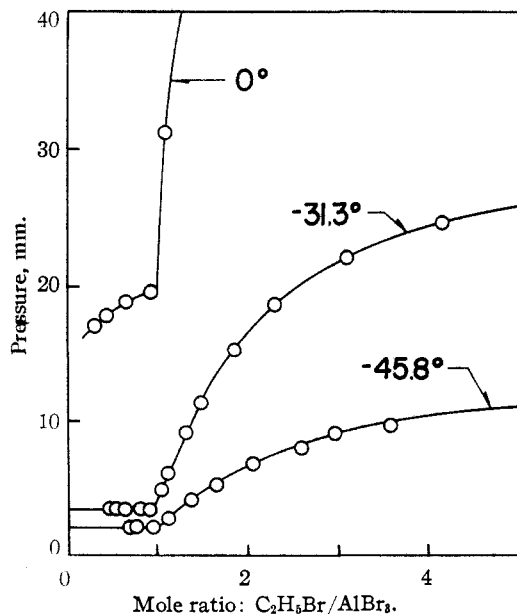
was obtained for any simple exchange even under these conditions.

A number of experiments were carried out in an attempt to measure the rate of exchange at −80° between alkyl chlorides (methyl, ethyl, *n*-propyl and isopropyl) and aluminum bromide. Unfortunately the results were erratic and will therefore not be reported at this time. We plan to continue our study of this phase of the problem.

The System: Ethyl Bromide–Aluminum Bromide.—A solution of aluminum bromide in ethyl bromide is yellow in color and slowly evolves hydrogen bromide. This slow decomposition made it impossible to determine the molecular weight of aluminum bromide in this solvent. However, by operating rapidly, it was possible to make vapor pressure–composition studies at −45.8, −31.3 and 0° (Fig. 5). The vapor pressure at −80° is too low to permit a direct measurement of the vapor pressure–composition curve. However, it was established that the rate of evaporation is proportional to the vapor pressure and the rate of evaporation of ethyl bromide from an aluminum bromide solution at −80° was determined (Fig. 6).
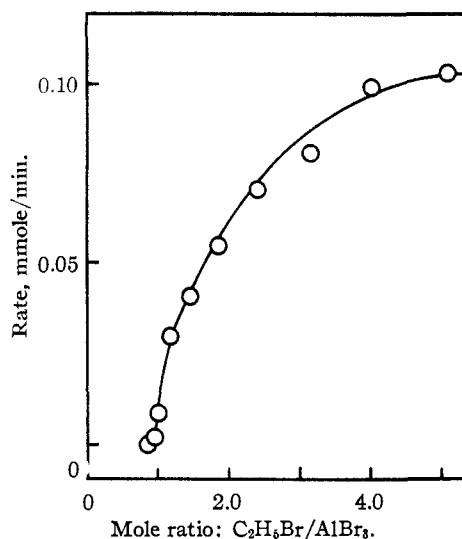
Fig. 6.—Rate of evaporation of ethyl bromide from a solution of aluminum bromide in ethyl bromide at −80°.

All of the phase diagrams show that a 1:1 ethyl bromide–aluminum bromide complex exists, with no evidence for a 1:2 complex similar to that observed in the methyl bromide–aluminum bromide system. The vapor phase–composition curves are quite different in the ethyl bromide system. It appears that the 1:1 complex is a liquid, completely miscible with ethyl bromide at all temperatures down to −80°. Therefore a pressure plateau is first observed after all of the excess ethyl bromide has been removed and ethyl bromide begins to leave the 1:1 complex with concurrent precipitation of aluminum bromide.

The difference in the two systems is readily explicable in terms of the greater steric requirements of ethyl bromide. Examination of a model of the aluminum bromide lattice[11] showed that it

Fig. 5.—Vapor pressure–composition diagrams for the ethyl bromide–aluminum bromide system.

(9) W. Fischer, *Z. anorg. allgem. Chem.*, **200**, 332 (1931).
(10) Unpublished work with Robert H. Harris.

(11) P. A. Renes and C. H. MacGillavry, *Rec. trav. chim.*, **64**, 275 (1945).

might accommodate methyl bromide without serious distortion or expansions of the lattice, but that ethyl bromide could not be similarly accommodated.

It has been mentioned that the solutions of aluminum bromide in ethyl bromide were faintly yellow at the start. Hydrogen bromide was slowly evolved and the intensity of the color increased. Removal of the ethyl bromide by evaporation always resulted in a small loss, and the colored material remained with the aluminum bromide as a non-volatile product. Hydrolysis of such residues liberated an unsaturated oil. It is probable that these colored products are σ-complexes[12] in which the organic base is an olefinic material formed from the ethyl bromide.

## The Action of Aluminum Bromide on n-Propyl and Isopropyl Bromides.

—Aluminum bromide dissolves at 0° in n-propyl and in isopropyl bromides to give solutions which evolve hydrogen bromide and become red in color. The rate of evolution of hydrogen bromide is far greater than that previously observed in the ethyl bromide system and precluded any molecular weight or vapor pressure–composition studies. It is of particular interest that under similar conditions the evolution of hydrogen bromide proceeds at essentially the same rate from both iso- and n-propyl bromide.

Two reaction mixtures were prepared: 0.807 mmole AlBr$_3$ in 3.177 mmole isopropyl bromide; 1.154 mmole AlBr$_3$ in 4.871 mmole n-propyl bromide. After 9 hours at 0° the hydrogen bromide evolved corresponded to 40.7% of the isopropyl bromide in the first case and to 45.5% of the n-propyl bromide in the second. Moreover, the only alkyl bromide recovered in both experiments was isopropyl bromide. Material balances in both cases were 95%.

At −80° a solution of aluminum bromide in n-propyl bromide becomes only slightly colored and there is little or no evolution of hydrogen bromide. However, under these conditions the n-propyl bromide is slowly isomerized to isopropyl bromide (27.6% in 11.7 hours). A similar experiment in the presence of hydrogen bromide gave essentially identical results (38.3% in 17.6 hours). It may be concluded that the isomerization is not affected by hydrogen bromide.

Doering and his co-workers[13] have shown that the isomerization of n-propyl chloride by aluminum chloride in the presence of deuterium chloride does not result in the introduction of deuterium in the product. This result conclusively demonstrates that the isomerization does not involve dehydrohalogenation to the olefin, followed by addition of the hydrogen halide to produce the secondary halide.

The observation that hydrogen bromide is produced from n-propyl bromide far more rapidly than from ethyl bromide suggests that the simple ionization of the addition compound cannot be the rate determining stage.
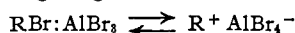
$$RBr:AlBr_3 \rightleftharpoons R^+ AlBr_4^-$$

The rates of ionization would not be expected to differ markedly for ethyl and n-propyl halides unless the ionization is facilitated by simultaneous transfer of a hydride ion—a neighboring group effect of the kind which has been investigated so brilliantly by Professor Winstein and his students.[14]
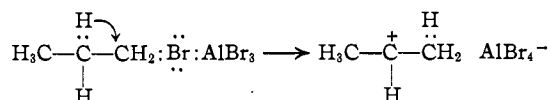
There also remains the possibility that the isomerization occurs without ionization of the addition compound.
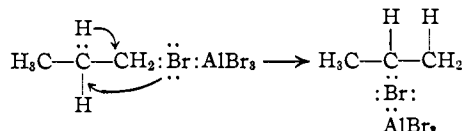
Such a mechanism could account very nicely for the observation that the isomerization of n-propyl bromide is considerably faster than the rate of dehalogenation. It also offers a reasonable explanation for Doering's results.[13] A comparison of the rate of exchange of the halogen in n-propyl halide with the rate of isomerization should afford conclusive data on which to base a decision between the two alternative mechanisms.

Conclusions

As a result of vapor pressure–composition studies, Van Dyke decided that 1:1 addition compounds of the type RBr:AlBr$_3$ do not exist. We are puzzled at his conclusion. In our opinion, the data presented in his paper support the conclusion that 1:1 compounds exist. Moreover, a recalculation of his molecular weight data on the basis of the existence of a 1:1 complex also yields results in agreement with this conclusion.[5]

We believe, then, that it can be considered definitely established that aluminum bromide forms 1:1 addition compounds with alkyl bromides and this probably constitutes the first step in Friedel–Crafts reactions.

$$RBr + \frac{1}{2}Al_2Br_6 \rightleftharpoons RBr:AlBr_3$$
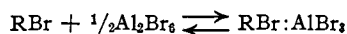
The question of the possible ionization of these addition compounds to carbonium ions

$$RBr:AlBr_3 \rightleftharpoons R^+ AlBr_4^-$$
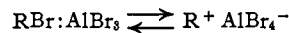
is in a much less satisfactory state. Fairbrother[3] has estimated from measurements of the dielectric polarizability of solutions of aluminum bromide in ethyl bromide that ionization to the extent of 3–4% occurs. However, we have pointed out that such solutions are unstable and liberate hydrogen bromide with the formation of non-volatile colored products, presumably σ-complexes. It is significant that in the case of the triphenylmethyl bromide–stannic bromide system, where one would anticipate the ready formation of the stable triphenylcarbonium ion, he concluded from absorption spectra studies, that the ionization must be less than 0.1%.

The literature contains numerous reports of con-

(12) H. C. Brown and J. D. Brady, This Journal, 74, 3570 (1952).
(13) L. M. Nash, T. I. Taylor and W. von E. Doering, ibid., 71, 1516 (1949).
(14) S. Winstein, et al., ibid., 74, 1127 (1952) and numerous earlier papers in This Journal.

ductivity measurements on aluminum halide–alkyl halide systems.[15-18] Unfortunately, most of the work was done with ethyl bromide and there is little agreement between individual workers, probably a result of the instability of such solutions. Only Jacober and Kraus[18] examined the conductivity of solutions of aluminum bromide in methyl bromide and report conductivities far less than those previously noted by other workers for systems involving higher halides. Moreover, the conductivities of solutions of aluminum bromide in methyl bromide were considerably less than for solutions in dimethyl ether. It appears safe to conclude that any ionization

$$CH_3Br:AlBr_3 \rightleftarrows CH_3{}^+ AlBr_4{}^-$$
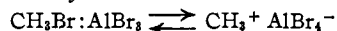
must be quite small, if it occurs at all. Further work will be necessary to establish the importance of such ionization in the reactions of alkyl halide–aluminum halide systems.

Experimental Part[19]

Apparatus.—All experiments were carried out with high vacuum apparatus and techniques in which the materials came in contact only with glass and mercury. The general techniques are described by Sanderson[20] and in previous papers of this series.

Solubility of Aluminum Chloride.—The solubility of aluminum chloride in methyl chloride was determined in a tube divided in two compartments by a sintered disk. Aluminum chloride was introduced into the lower compartment. The tube was then evacuated and methyl chloride condensed in it. The side arm was sealed and the tube maintained at $-31.3°$ for 7 hours, with occasional shaking to facilitate solution of the aluminum chloride. The tube was then quickly inverted to permit the methyl chloride solution to filter through the sintered glass disk. The tube was removed from the bath, the tip containing the solution placed in a bath at $-80°$, and the side arm cooled in liquid nitrogen. In this way the methyl chloride was separated from the dissolved aluminum chloride. The lower section containing the aluminum chloride was then removed by carefully sealing at the constriction. The weight of the aluminum chloride was determined by direct weighing of the sealed ampule before and after it was opened and the crystals removed. The identity of the material was established by a chloride ion analysis. In a typical experiment 0.0030 g. of aluminum chloride dissolved in 6.24 mmole of methyl chloride (0.0036 mole fraction as $AlCl_3$ or 0.0018 as Al_2Cl_6). At $-31.3°$ the vapor pressure lowering observed for the saturated solution was 1.00 mm., or 0.00176 mole fraction. Thus, aluminum chloride must be present in solution as Al_2Cl_6.

Molecular Weight Determinations.—The molecular weights were determined by vapor pressure lowering, using a differential method in which the pure solvent and the solution were maintained in the same bath and exerted their pressures on the two limbs of a single manometer. The method was checked with two substances, t-butylbenzene and silicon tetrabromide, which do not form complexes with methyl bromide. Typical results are reported in Table IV. Very good results were obtained with t-butylbenzene. The silicon tetrabromide results averaged approximately 5% high.

Materials.—Aluminum bromide was prepared and handled as described previously.[21] Aluminum iodide was prepared by heating a weighed sample of purified sublimed iodine with an excess of aluminum wire in a sealed evacuated tube. The aluminum iodide was obtained as a white crystalline product which was sublimed into place for the particular experiment without exposure to air.

Methyl chloride was purified by distillation from aluminum chloride at $-80°$. Methyl bromide was similarly purified by distillation from aluminum bromide at $-80°$. Methyl iodide (b.p. 42.4°), ethyl bromide (b.p. 37.6° at 744 mm., $n^{20}D$ 1.4243), n-propyl bromide (b.p. 70.0° at 736 mm., $n^{20}D$ 1.4340) and isopropyl bromide, (b.p. 59.3° at 744 mm., $n^{20}D$ 1.4252) were each purified by distillation through an efficient column and the purity established in the high vacuum apparatus by vapor pressure measurements (Table V).

TABLE IV

MOLECULAR WEIGHT DETERMINATIONS IN METHYL BROMIDE

t-Butylbenzene[a]			Silicon tetrabromide[b]		
Temp., °C.	Mole fraction	Mol. wt.	Temp., °C.	Mole fraction	Mol. wt.
0.0	0.104	131	0.0	0.128	370
.0	.108	133	.0	.128	373
.0	.104	132	.0	.097	365
.0	.160	133	−30.7	.092	371
−30.7	.095	131	−30.7	.081	369
−30.7	.097	134	−45.8	.092	356
−30.7	.094	134	−45.8	.092	371
−30.7	.139	137	−45.8	.073	389
−30.7	.214	140	−64.4	.089	357
−45.8	.210	139	−64.4	.071	348
−64.6	.203	141			
−64.5	.092	125			

[a] Calcd. 134.2. [b] Calcd. 348.

TABLE V

VAPOR PRESSURE DATA

Methyl chloride	$\log P(mm.) = -1190/T + 7.667$				
Temp., °C.	−78.5	−64.6	−45.8	−30.9	
Press., mm.	34.00	93.60	277.7	568.9	
Methyl bromide	$\log P(mm.) = -1348/T + 7.756$				
Temp., °C.	−79	−64.4	−45.8	−32.1	0.0
Press., mm.	6.30	20.0	69.3	151.1	659.5
Methyl iodide					
Temp., °C.	0.0				
Press., mm.	141.7				
Ethyl bromide	$\log P(mm.) = -1521/T + 7.7776$				
Temp., °C.	−45.6	−39.6	0.0	5.8	
Press., mm.	12.15	18.25	165.1	212.1	
Silicon tetrabromide	$\log P(mm.) = -2044/T + 7.613$				
Temp., °C.	3.3	12.3	17.2	20.9	24.5
Press., mm.	1.70	2.70	3.70	4.60	5.60

Exchange Reactions of the Methyl Halides.—Excess methyl bromide was condensed on a sample of aluminum chloride and allowed to stand for 24 hours at 0°. A slight lowering of the vapor pressure was observed, corresponding to a solubility of 1.1 mole %. If any exchange had occurred, a marked increase in pressure would have been expected as a result of the formation of the more volatile methyl chloride.

Weighed samples (approximately 0.7 mmole) of the aluminum halide were introduced into small tubes. A measured excess of the alkyl halide (about 5 mmoles) was introduced, the tube sealed and maintained at 0° for 24 hours. The tube was then opened, the volatile products recovered, and the extent of exchange estimated from the weight of the volatile products. In this way aluminum bromide dissolved in methyl bromide, but the methyl halide recovered after 24 hours contained no more than 1% of methyl iodide. On the other hand, a solution of aluminum iodide in methyl bromide generated a product which contained sufficient methyl iodide to correspond to 99.3–101.1% exchange.

Aluminum Bromide with the Propyl Bromides.—Aluminum bromide, 0.807 mmole, was dissolved in 3.177 mmoles of isopropyl bromide and the reaction mixture maintained

(15) J. W. Walker, J. Chem. Soc., **85**, 1082 (1904).

(16) A. Wohl and E. Wertyporoch, Ber., **64**, 1357 (1931).

(17) I. L. Katsnel'son, Mem. Inst. Chem., Acad. Sci. Ukrain, S.S.R., **4**, 393 (1938).

(18) W. J. Jacober and C. A. Kraus, THIS JOURNAL, **71**, 2405, 2409 (1949).

(19) For the experimental values of the vapor pressure–composition studies and the diagrams of the apparatus used in these studies consult W. J. Wallace's Ph.D. thesis, Purdue University Library.

(20) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

(21) H. C. Brown and W. J. Wallace, THIS JOURNAL, **75**, 6265 (1953).

at 0°. A rapid increase in pressure was observed (Fig. 7). After 9.5 hours, the volatile material was removed and analyzed. There was obtained 1.29 mmoles (41% conversion) hydrogen bromide (v.p. 35.0 mm. at −112°) and 1.74 mmoles isopropyl bromide (v.p. 70.1 mm. at 0°, n^{20}D 1.4260). The hydrogen bromide and isopropyl bromide represent a 95% recovery of the bromine originally present in the alkyl halide. During the reaction the solution was red in color. During the removal of the products, the residue in the tube became much deeper red and very viscous. It possessed the appearance of a typical Friedel–Crafts "red oil."

A similar experiment was carried out using 1.154 mmoles of aluminum bromide in 4.87 mmoles of n-propyl bromide. The evolution of hydrogen bromide proceeded much as in the previous experiment (Fig. 7). (The higher pressures are approximately of the magnitude to be anticipated from the larger amount of catalyst present.) After 9 hours, the volatile materials were removed. There was obtained 1.92 mmoles (40% conversion) of hydrogen bromide and 2.70 mmoles of isopropyl bromide. No significant concentration of the original n-propyl bromide could be detected. Again the hydrogen bromide and isopropyl bromide represent a material recovery of 95%.

When n-propyl bromide and aluminum bromide were maintained at −80°, the solution was only slightly colored and there was little or no evolution of gas. After 11.7 hours, trimethylamine was added to deactivate the catalyst and permit recovery of the alkyl halide. The product, analyzed by refractive index, contained 27.6% isopropyl bromide. In another experiment, the isomerization contained hydrogen bromide. After 17.6 hours, the hydrogen bromide was removed, the aluminum bromide deactivated
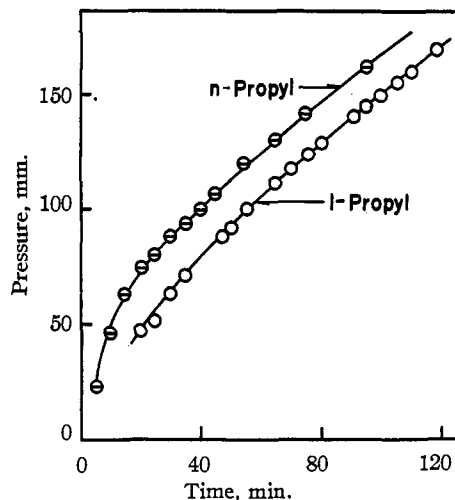

Fig. 7.—Pressure increase above solutions of aluminum bromide in the propyl bromides at 0°.

with trimethylamine, and the product recovered. In this experiment the product contained 38.3% isopropyl bromide. Considering the difference in reaction times it is apparent that the reaction rates were approximately the same in the two experiments.

LAFAYETTE, INDIANA

Kinetics of the Reaction of Representative Benzyl Halides with Aromatic Compounds; Evidence for a Displacement Mechanism in the Friedel–Crafts Reactions of Primary Halides[1,2]

By Herbert C. Brown and Martin Grayson[3]

Received March 11, 1953

A kinetic study has been made of the reactions of several benzyl halides with various aromatic compounds under the catalytic influence of aluminum chloride in nitrobenzene solution. Both benzyl chloride and p-chlorobenzyl chloride react too rapidly for convenient measurement; therefore 3,4-dichloro- and p-nitrobenzyl chlorides, which react at more convenient rates, were primarily utilized in the kinetic studies. The rate data reveal that the reaction is third order—first order in aromatic component, first order in aluminum chloride (AlCl₃), and first order in the benzyl halides. The rate increases with increasing basic properties of the aromatic component: $ClC_6H_5 < C_6H_6 < CH_3C_6H_5 < m\text{-}(CH_3)_2C_6H_4$. Slower, competitive dialkylation reactions were observed at low aromatic concentrations. The kinetic analysis of the consecutive reactions was confirmed by the preparation of 3,4-dichlorodiphenylmethane and measurement of its rate of reaction with 3,4-dichlorobenzyl chloride. The reaction is not very sensitive to the dielectric constant of the solvent. A displacement mechanism involving nucleophilic attack by the aromatic component on an alkyl halide–aluminum chloride addition compound is consistent with the observations. Moreover, this mechanism offers a simple, reasonable explanation for the observed formation of n-propylbenzene in the Friedel–Crafts alkylation of benzene with either n-propyl halides or alcohol.

Introduction

The mechanism which is generally accepted at the present time for the Friedel–Crafts reaction involves ionization of the alkyl halide under the influence of the catalyst, followed by the electrophilic substitution of the aromatic nucleus by the carbonium ion.[4]

$$RX + MX_3 \rightleftarrows R^+ + MX_4^-$$
$$ArH + R^+ \longrightarrow ArR + H^+$$
$$H^+ + MX_4^- \longrightarrow HX + MX_3$$
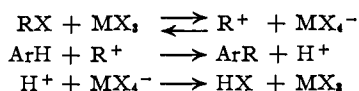
This theory is supported primarily by observations

that the reaction is enhanced by strong electrophilic catalysts and easily ionized alkyl halides[4] and rearrangements characteristic of carbonium ions are common during alkylation.[5]

This ionization mechanism, however, does not account for the high yields of n-propylbenzene obtained in the alkylation of benzene with n-propyl chloride[6] and the sole formation of the n-propyl isomer in the alkylation of benzene with n-propyl alcohol and aluminum chloride.[6] Moreover, the same workers also report that neopentylbenzene is formed in the alkylation of benzene with neopentyl alcohol and aluminum chloride.[7] These observations suggest a displacement mechanism.

(1) The Catalytic Halides. IX.

(2) Based upon a thesis submitted by Martin Grayson in partial fulfillment of the requirements for the Ph.D. degree.

(3) Standard Oil Company (Indiana) Fellow, 1949–1950; A.E.C. Fellow, 1950–1952.

(4) C. C. Price, Chem. Revs., 29, 37 (1941); "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., pp. 1–82.

(5) D. V. Nightingale, ibid., 25, 329 (1939).

(6) V. N. Ipatieff, H. Pines and L. Schmerling, J. Org. Chem., 5, 253 (1940).

(7) H. Pines, L. Schmerling and V. N. Ipatieff, THIS JOURNAL, 62, 2901 (1940).