more nearly correct than that of Strehlow and von Stackelberg.

These figures depend on the correctness of the coefficient 607 in equation (4a). Values of the diffusion coefficients of 5 mM ferricyanide in 0.1 F potassium chloride and of 5 mM silver in 0.1 F potassium nitrate, calculated from the work of Laitinen and Kolthoff,[13] lead, however, to the values 575 and 544, respectively. Therefore, the best available empirical modification of equation (1) is

$$I = 560nD^{1/2}[1 + 29D^{1/2}(t^{1/6}/m^{1/3})] \qquad (6)$$

The values predicted by this equation fall on the lines bb in Figs. 5 and 7, while the lines aa represent equation (1). The latter are plainly unsatisfactory: concerning the former, it is of interest to note that equation (6) reproduces the data to within about 0.5% if the values of D^0 calculated from equivalent conductance data[13] are used instead of the experimental values of Laitinen and Kolthoff. Whether this is due to experimental errors in the latter or to changes in D caused by the addition of gelatin is impossible to decide at this time.

Although the considerations outlined do not constitute a proof of the correctness of the factor 560 in equation (6), it does seem apparent that the value 607 is subject to considerable doubt pending further study.

It may be remarked that the values of I calculated from the Ilkovič equation, 2.533 for silver and 1.761 for ferricyanide, are found on Figs. 1 and 3 at drop times of 2.5 sec., but, again, not at equal values of $t^{1/6}/m^{1/3}$.

Acknowledgment.—The work described in this paper was supported by Contract Number AT (30-1)-842 between the U. S. Atomic Energy Commission and Yale University.

NEW HAVEN, CONN. RECEIVED JULY 28, 1950

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[13] H. A. Laitinen and I. M. Kolthoff, THIS JOURNAL, **61**, 3344 (1939).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

The Conductance of Methanol, Acetone, Ethyl Acetate and Acetic Anhydride Complexes of Aluminum Bromide in Nitrobenzene at 25°[1]

BY ROSS E. VAN DYKE

The conductance of aluminum bromide in nitrobenzene on addition of methanol, acetone, ethyl acetate and acetic anhydride has been determined. The curves for methanol and acetone are remarkably similar, while that for ethyl acetate was found to be similar to those obtained for dimethyl ether as complexing agent.[2a] The curves obtained with acetic anhydride are markedly different from any of the other curves obtained. The electrical conductivity of some of these complexes is considered in the light of their reported catalytic activity in alkylation reactions.[3]

I. Introduction

The conductance of aluminum bromide and of gallium chloride and gallium bromide on addition of dimethyl ether, trimethylamine and ammonia in nitrobenzene solution have been reported recently[2a,b] These studies have yielded new and interesting information concerning the nature and stability of these complexes in solution. Ipatieff and Schmerling[3] report that the monomolecular addition compounds of aluminum chloride with ethers, ketones or alcohol are active catalysts for the alkylation of isobutane in the presence of hydrogen chloride in nitromethane solution. On the other hand, they report that if the aluminum chloride is coördinated to two moles of alcohol or if the salt is dissolved in ether, acetone, etc., the resultant solution does not catalyze the alkylation reaction. If aluminum chloride is dissolved in nitromethane the monomolecular addition complex of nitromethane and aluminum chloride is also catalytically active.

The studies to be reported in this paper have been carried out in nitrobenzene as solvent. Nitrobenzene also forms a brilliant yellow monomolecular addition compound with the aluminum halides. Nitrobenzene is readily purified for conductance studies and has a dielectric constant almost equal to that for nitromethane. It appears reasonable, therefore, to discuss the results of these studies in nitrobenzene in relation to the observations on catalytic activity of some of these complexes in nitromethane.

The conductances of aluminum bromide on addition of varying amounts of methanol, acetone, ethyl acetate, acetyl bromide and acetic anhydride in nitrobenzene at 25° have been determined and are reported here.

II. Experimental

A. Apparatus and Procedure.—Conductance measurements were carried out as described previously.[2] Sealed ampules of aluminum bromide were placed in the cells which had been baked out.[2a] The cell was evacuated and filled with dry nitrogen just before breaking the ampule. Upon introduction of solvent and the liquid complexing agents a dry nitrogen atmosphere was maintained over the solution.

Liquid complexing agents were introduced by means of a micro weight pipet which was equipped with ground glass inlet and outlet.

All additions of complexing agents were determined by weight difference on the analytical balance. This method was found to be quite reproducible and sufficiently precise for the concentration range under consideration.

B. Materials.—Nitrobenzene[4] was purified and handled as described in earlier papers.[2a,b] The purified product had a specific conductance of 1×10^{-10} mho. Anhydrous aluminum bromide was prepared, purified and filled into ampules as previously described.[2a] Methanol was purified by preliminary drying of Baker C.P. product over barium

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[1] The contents of this paper have been presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the Chicago Meeting, September, 1950.

[2] (a) Van Dyke and Kraus, THIS JOURNAL, **71**, 2694 (1949); (b) Van Dyke, *ibid.*, **72**, 2823 (1950).

[3] Ipatieff and Schmerling, "Advances in Catalysis," Vol. I, p. 51.

[4] Kindly furnished by Calco Chemicals Division, American Cyanamid Company.

oxide. This product was then refluxed and distilled successively from fresh batches of barium oxide. The material was freshly distilled as needed and had a specific conductance of 7 × 10^{-8} mho. Acetone, Baker C.P. product, was purified in a manner similar to that described for methanol. Ethyl acetate, Merck and Co., reagent grade, was purified by refluxing and distillation from freshly sublimed phosphorus pentoxide. This material distilled at 77.1° in accordance with recorded literature.[5] Acetic anhydride, Merck reagent grade, was further purified by distillation through an efficient column and was freshly distilled as needed. The distilled product came over at constant temperature in agreement with the recorded literature.[5] Acetyl bromide, Eastman Kodak Co. purified product, was further purified by careful fractionation.

III. Results

1. **Methanol.**—The conductance of aluminum bromide in nitrobenzene on addition of methanol was studied at three concentrations of salt *m* (molality) = 0.0603, 0.1497 and 0.2986. These results are shown graphically in Fig. 1. Numerical data for two of these solutions are presented in Table I.

2. **Acetone.**—The conductance of aluminum bromide in nitrobenzene on addition of varying amounts of acetone was studied at three concentrations of salt *m* = 0.0537, 0.1202, 0.2795. These results are presented graphically in Fig. 2, and numerical data for two of these solutions are listed in Table II.

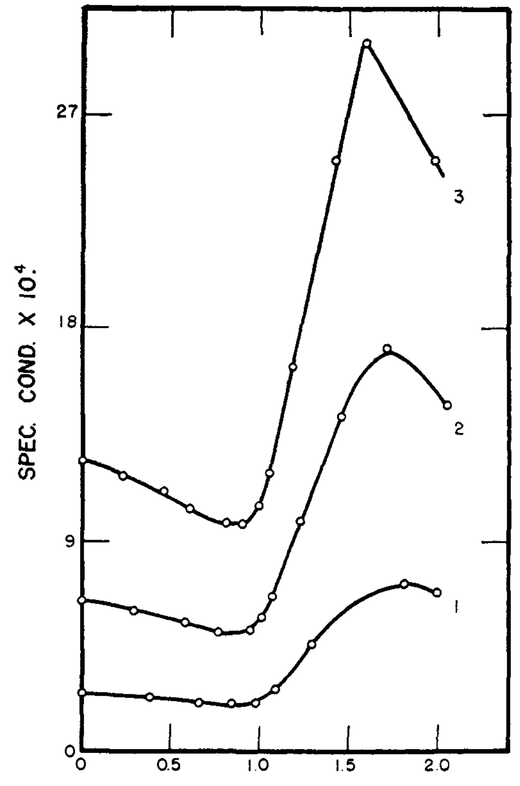
3. **Ethyl Acetate.**—This compound was studied as a complexing agent in nitrobenzene of salt concentration *m* = 0.2384. The data are listed in Table III and are shown graphically in Fig. 4, curve 3.

TABLE I

CONDUCTANCE OF ALUMINUM BROMIDE IN NITROBENZENE AT 25° ON ADDITION OF METHANOL

A. Mmoles $AlBr_3$ = 3.577, *m* = 0.0603 B. Mmoles $AlBr_3$ = 12.762, *m* = 0.2986

$\kappa \times 10^4$	Molar ratio $CH_3OH/AlBr_3$	$\kappa \times 10^4$	Molar ratio $CH_3OH/AlBr_3$
2.582	0.000	12.40	0.0000
2.327	.3839	11.78	.2282
2.110	.6570	10.98	.4598
1.985	.8429	10.37	.6009
2.127	.9781	9.722	.8078
2.716	1.089	9.685	.8980
4.590	1.290	10.42	.9851
7.182	1.808	11.87	1.049
6.772	1.989	16.33	1.180
		25.07	1.423
		29.99	1.587
		25.07	1.982



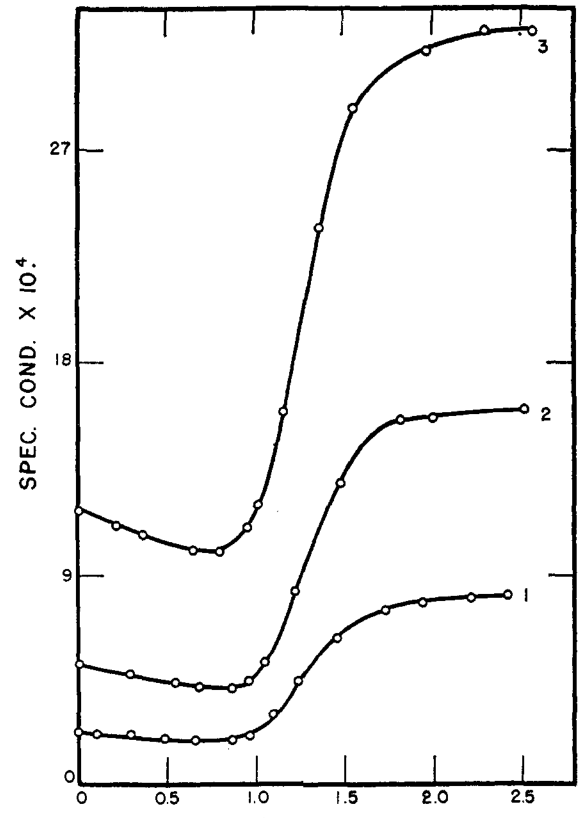
Moles CH_3OH/moles $AlBr_3$.

Fig. 1.—Conductance of aluminum bromide in nitrobenzene at 25° in presence of methanol: (1) 0.0603 molal, (2) 0.1497 molal, (3) 0.2986 molal.

4. **Acetic Anhydride.**—The conductance of aluminum bromide in nitrobenzene on addition of acetic anhydride was studied at two concentrations of salt *m* = 0.0920 and 0.2956. These data are presented graphically in Fig. 3 and are listed numerically in Table IV.

IV. Discussion

When dimethyl ether is added to solutions of alu-



Moles $(CH_3)_2CO$/moles $AlBr_3$.

Fig. 2.—Conductance of aluminum bromide in nitrobenzene at 25° in presence of acetone: (1) 0.0537 molal, (2) 0.1202 molal, (3) 0.2795 molal.

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(5) Weissberger and Proskauer, "Organic Solvents," Oxford University Press, New York, N. Y., 1935.

TABLE II

CONDUCTANCE OF ALUMINUM BROMIDE IN NITROBENZENE AT 25° ON ADDITION OF ACETONE

A. Mmoles $AlBr_3$ = 4.614, m = 0.0537 B. Mmoles $AlBr_3$ = 14.287, m = 0.2795

A. $\kappa \times 10^4$	A. Ratio acetone/$AlBr_3$	B. $\kappa \times 10^4$	B. Ratio acetone/$AlBr_3$
2.238	0.0000	11.75	0.0000
2.187	.0993	11.13	.2182
2.081	.2963	10.72	.3720
1.976	.4882	10.05	.6470
1.890	.6606	9.991	.8030
1.880	.8699	11.01	.9617
2.063	.9636	12.01	1.022
2.955	1.095	15.84	1.160
4.392	1.239	23.70	1.365
6.332	1.460	28.79	1.560
7.453	1.727	31.16	1.973
7.796	1.935	32.03	2.298
7.993	2.214	31.98	2.568
8.052	2.423		

TABLE III

THE CONDUCTANCE OF ALUMINUM BROMIDE IN NITROBENZENE AT 25° ON ADDITION OF ETHYL ACETATE

Mmoles $AlBr_3$ = 11.246, m = 0.2384

$\kappa \times 10^4$	Ratio ethyl acetate/ $AlBr_3$	$\kappa \times 10^4$	Ratio ethyl acetate/ $AlBr_3$
10.32	0.0000	4.677	1.047
9.742	.0832	7.853	1.160
8.803	.2102	11.09	1.304
7.199	.4123	13.90	1.485
5.929	.5719	17.28	1.875
4.614	.7474	18.23	2.086
3.856	.8571	18.77	2.354
3.164	.9839		

minum bromide in nitrobenzene, the conductance decreases linearly until the molar ratio of ether to salt is unity. Thereafter, the conductance increases quite rapidly and linearly with added ether. According to Fig. 1 the general form of the curves on addition of methanol is similar to that of the ether curve. More careful examination indicates that the conductance decrease on addition of methanol is not exactly linear, and percentagewise is not nearly so great as in the case of ether additions for solutions of approximately the same concentrations. This is quite clearly shown in Fig. 4. Beyond the minimum the conductance increase does not take place abruptly as is the case with ether but rather is a gradual increase similar to the curves obtained when ether was added to the gallium halides in nitrobenzene.[2b] The marked increases in conductance beyond the minimum appear to be approximately linear with added methanol for molar ratios as great as 1.5. In this region the conductance begins to level off and finally precipitation takes place. The crystalline precipitate was shown by analysis to be $AlBr_3 \cdot 2CH_3OH$. It was not feasible to determine the content of un-

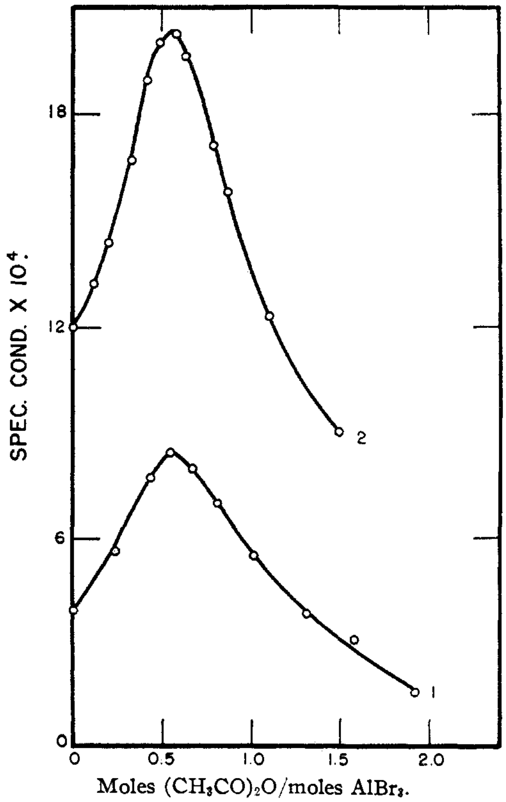


Fig. 3.—Conductance of aluminum bromide in nitrobenzene at 25° in presence of acetic anhydride: (1) 0.0920 molal, (2) 0.2956 molal.

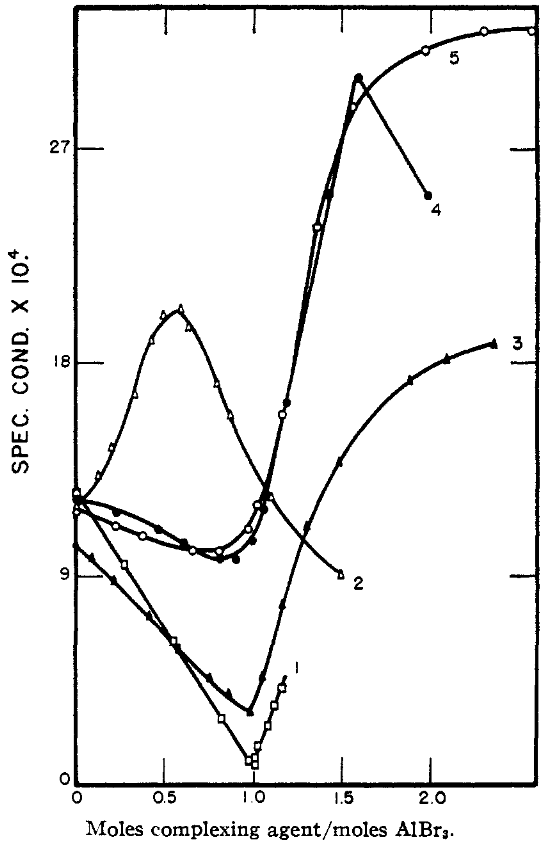


Fig. 4.—Conductance of aluminum bromide in nitrobenzene at 25° on addition of various complexing agents: (1) 0.3013 m $AlBr_3$ in presence of dimethyl ether; (2) 0.2956 m $AlBr_3$ in presence of acetic anhydride; (3) 0.2384 m $AlBr_3$ in presence of ethyl acetate; (4) 0.2986 m $AlBr_3$ in presence of methanol; (5) 0.2795 m $AlBr_3$ in presence of acetone.

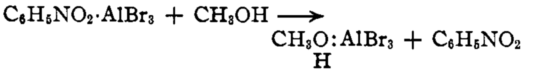
TABLE IV

THE CONDUCTANCE OF ALUMINUM BROMIDE IN NITROBENZENE AT 25° ON ADDITION OF ACETIC ANHYDRIDE

A. Mmoles $AlBr_3$ = 4.101, m = 0.0920 B. Mmoles $AlBr_3$ = 11.672, m = 0.2956

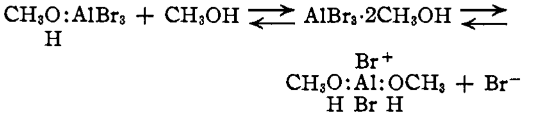
A. $\kappa \times 10^4$	A. Ratio acetic anhydride/$AlBr_3$	B. $\kappa \times 10^4$	B. Ratio acetic anhydride/$AlBr_3$
3.941	0.0000	11.99	0.0000
5.635	.2358	13.23	.1234
7.756	.4327	14.37	.2013
8.456	.5411	16.68	.3340
8.035	.6634	18.94	.4214
7.024	.8032	19.98	.4928
5.477	1.012	20.26	.5834
3.854	1.306	19.57	.6293
3.103	1.579	17.10	.7890
1.591	1.916	15.82	.8686
		12.31	1.102
		9.015	1.488

combined alcohol in these solutions. It is of interest to note that for the three solutions reported here the molar ratios of added methanol to salt for which precipitation was first observed are approximately the same. It is probable that an equilibrium among $AlBr_3\cdot 2CH_3OH$, $AlBr_3\cdot CH_3OH$ and a mole of free alcohol occurs in these solutions. The reaction corresponding to a decrease in conductance upon addition of methanol probably occurs as shown in eq. (1).



$$C_6H_5NO_2\cdot AlBr_3 + CH_3OH \longrightarrow CH_3\underset{H}{O}:AlBr_3 + C_6H_5NO_2 \quad (1)$$

In the vicinity of the conductance minimum the intense yellow color of the nitrobenzene complex of aluminum bromide appears to be dissipated. The increase in conductance on addition of alcohol beyond this point may be explained by formation of a much stronger electrolyte as indicated in eq. (2).



$$CH_3\underset{H}{O}:AlBr_3 + CH_3OH \rightleftharpoons AlBr_3\cdot 2CH_3OH \rightleftharpoons CH_3\underset{H}{O}:\overset{Br^+}{\underset{Br}{Al}}:\underset{H}{O}CH_3 + Br^- \quad (2)$$

In the neighborhood of the conductance minimum and beyond a very slight evolution of hydrogen bromide was observed. This probably resulted from a slight decomposition of the methanol complex to form methoxyaluminum dibromide. The gradual increase in conductance before a molar ratio of unity is reached is probably due to coördination of methanol to some extent by the $C_6H_5NO_2\cdot AlBr_3$ complex to form the compound $C_6H_5NO_2\cdot AlBr_3\cdot CH_3OH$ which would be a better electrolyte than the nitrobenzene complex or the monomethanolate.

Acetone.—As shown in Fig. 2 the conductance curves for acetone as complexing agent are quite similar to those obtained for methanol. The minimum point appears just below a molar ratio of 1.0 and is followed by a rapid and almost linear increase in conductance as a function of added acetone. As the molar ratio approaches a value of 2.0, the conductance levels off and thereafter becomes almost constant. No evidence of precipitation was observed, indicating that the diacetonate of aluminum bromide is quite soluble in nitrobenzene. The reactions involved with acetone as complexing agent appear to be similar to those proposed in equations (1) and (2) for methanol.

Acetyl Bromide.—Upon addition of acetyl bromide to an approximately 0.10 molal nitrobenzene solution of aluminum bromide the conductance increased only very slightly but regularly with each addition up to a value of three moles of acyl halide per mole of salt. The total conductance increase in this interval was less than 5% and the color of the yellow solvent–salt complex appeared no less intense than in the original solution. These results indicate that acetyl bromide coördinates only to a slight extent with aluminum bromide in this solvent. It has been observed in this Laboratory that methyl bromide does not interact in any way with aluminum bromide in nitrobenzene. It appears probable that the interaction with the acyl halide involves the carbonyl oxygen rather than the halogen.

Ethyl Acetate.—The conductance curve for ethyl acetate as complexing agent is shown graphically in Fig. 4, curve 3. It is of considerable interest to note that with a complexing molecule containing a carbonyl and an ethereal oxygen, the conductance curve obtained closely resembles the curves obtained with dimethyl ether as complexing agent. The decrease in conductance is rapid and linear with a minimum value appearing at a molar ratio of unity. This is followed by a sharp linear increase in conductance upon further addition of ester. Beyond a molar ratio of 1.5 the curve begins to level off somewhat as was observed in the case of acetone additions. The reactions involved appear to be similar to those reported for dimethyl ether.[2a]

Acetic Anhydride.—The conductance curves for acetic anhydride as complexing agent are shown graphically in Fig. 3. The conductance increases continuously along a rather complex curve to a maximum value at a molar ratio slightly in excess of 0.5. Beyond this point the conductance decreases to a value at a molar ratio of unity which is only slightly higher than that of the original solution. As the conductance decreases from its maximum value, fumes similar to those of acetyl bromide evolved upon opening the cell. At the conductance maximum the yellow color of the salt–solvent complex appeared to be completely dissipated. This indicates that at this point most of the aluminum bromide is coördinated to the acetic anhydride and that little or none of the nitrobenzene complex remains. The most plausible reaction up to the maximum point appears to be that of eq. 3.

$$2[C_6H_5NO_2\cdot AlBr_3] + (CH_3CO)_2O \longrightarrow (CH_3CO)_2O\cdot 2AlBr_3 + 2C_6H_5NO_2 \quad (3)$$

As the conductance decreases upon further addition of anhydride the reaction probably is that recorded in eq. 4.

$$(CH_3CO)_2O\cdot 2AlBr_3 + (CH_3CO)_2O \longrightarrow 2CH_3COO:AlBr_2 + 2CH_3COBr \quad (4)$$

When equimolar quantities of acetic anhydride and aluminum bromide react, the acyl halide is evolved. Upon removal of the acetyl bromide by prolonged pumping, the residual acetoxy-aluminum dibromide dissolves in nitrobenzene to give a solution whose conductance closely parallels that observed at a molar ratio of unity in the curves of Fig. 3. This fact provides strong evidence in support of eq. (4). A detailed explanation of the maxima in Fig. 3 will require further exploratory work.

In Fig. 4 are presented curves obtained with the various complexing agents for approximately the same concentration of aluminum bromide. When a second mole of ether, ester, ketone or alcohol is coördinated to aluminum bromide in nitrobenzene, a much better electrolyte is obtained than exists in the original solution or in the 1:1 addition compounds. When the second mole is coördinated, a strong ionic bond is formed presumably between the coördinated aluminum ion and a bromide ion. It is quite clear, however, from the order of magnitude of the conductances of these 2:1 addition compounds and the limiting value for bromide ion in nitrobenzene[6] that these compounds exist primarily as ion pairs for the concentrations considered here.

Ipatieff and Schmerling[8] report that these 2:1 addition complexes are not catalytically active for certain alkylation reactions in nitromethane. The results presented here give an interesting correlation between the catalytic activity in nitromethane and the electrolytic properties of the complexes in nitrobenzene. It is apparent from these studies that the nitrobenzene complex of aluminum bromide is much less stable than the 1:1 addition compounds with ether, alcohol, acetone, etc. These results appear to indicate that the catalytic activity of these various complexes may be more directly associated with the nature of the Al–halogen bond than with the electrophilic character of the aluminum halide molecule.

(6) Witschonke and Kraus, THIS JOURNAL, **69**, 2472 (1947).

BALTIMORE, MARYLAND RECEIVED AUGUST 24, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

The Conductance of Aluminum Bromide in Benzonitrile on Addition of Various Basic Complexing Agents at 25°[1]

BY ROSS E. VAN DYKE AND THOMAS S. HARRISON[2]

In this paper the conductivities and relative stability of a number of addition compounds of aluminum bromide in benzonitrile are compared with observations made upon similar solutions in nitrobenzene as solvent.[3,4] Conductance data are presented for benzonitrile solutions of aluminum bromide on addition of methanol, trimethylamine and pyridine. Dimethyl ether and acetone apparently do not coördinate with aluminum bromide in this solvent. Data are also presented to show the effect of addition of benzonitrile to nitrobenzene solutions of aluminum bromide and for addition of pyridine to solutions of $AlBr_3 \cdot (CH_3)_3N$ in benzonitrile. These results yield some indications as to the relative stability of $(CH_3)_3N$, C_5H_5N and C_6H_5CN complexes of aluminum bromide.

I. Introduction

The conductance of aluminum bromide on addition of a wide variety of complexing agents in nitrobenzene has been determined recently.[3,4] Nitrobenzene forms a yellow complex $C_6H_5NO_2 \cdot AlBr_3$ which appears to be less stable than the ether, acetone or alcohol, etc., addition compounds. It was of considerable interest, therefore, to determine the relative stabilities and the conductance of a number of these addition compounds in a more basic solvent in which the extent of interaction of the salt with the solvent was greater than in the case of nitrobenzene. For this purpose benzonitrile was chosen. Benzonitrile has a vapor pressure of 0.060 cm. at 25° which renders it suitable for the techniques of handling gaseous complexing agents as used in the earlier studies and it is readily purified.

The conductance curve for aluminum bromide in benzonitrile has been determined for molalities as low as 3×10^{-3} and the nature and stability of the salt–solvent complex has been clarified. The conductance of aluminum bromide in benzonitrile on addition of varying quantities of trimethylamine, methanol and pyridine has been determined. In addition, the effect of addition of pyridine to a benzonitrile solution of the 1:1 trimethylamine complex of aluminum bromide is reported.

II. Experimental

(1) **Materials.**—Benzonitrile[5] was treated with anhydrous aluminum chloride from which it was rapidly distilled *in vacuo* at 40–50°. The distillate was washed with alkali, dried over calcium chloride and subjected to several vacuum distillations at 35°. This product was then fractionally crystallized several times and was dried finally over finely divided activated aluminum oxide. The solvent was stored in this manner and withdrawn through a sintered glass filter as needed. The solvent had a specific conductance of 2×10^{-8} mho and the index of refraction was found to be $n^{25.5}_D$ 1.52568. Aluminum bromide was prepared, purified and handled as described in earlier papers.[3] Nitrobenzene was purified according to previously described procedures.[3] Trimethylamine (Matheson Product) was found by analysis to be of 98.5% purity, assuming the impurity to be dimethylamine. The gas was dried over barium oxide as used. Ammonia from the laboratory stock cylinder was dried over sodium. Acetone (Baker C.P. Product) was preliminarily dried over barium oxide, followed by distillation from a fresh batch of barium oxide through an efficient column as needed. Methanol (Baker C.P. Product) was dried and handled in a manner similar to that for acetone. Pyridine (Barrett Co. research grade) was subjected to two fractionations followed by several fractional crystallizations. The final product was stored over activated aluminum oxide. Nitrogen was dried over silica gel and phosphoric anhydride.

(2) **Apparatus and Procedure.**—Resistances were measured on a Leeds and Northrup bridge of the Jones type, the cells being thermostated in oil at 25 ± 0.01°. The conductance cells were of varying design but were similar to

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(1) This paper is based on a portion of a thesis presented by Thomas S. Harrison in partial fulfillment of the requirements for the degree of Doctor of Philosophy in The Johns Hopkins University.

(2) *Grasselli Division*, *E. I. du Pont de Nemours & Company*, Wilmington, Del.

(3) Van Dyke and Kraus, THIS JOURNAL, **71**, 2694 (1949).

(4) Van Dyke, *ibid.*, **73**, 398 (1951).

(5) Kindly donated by Socony-Vacuum Oil Company.