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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE JOHNS HOPKINS UNIVERSITY]

The Conductance of Gallium Trichloride and Tribromide in Nitrobenzene on Addition of Complexing Agents at 25°

BY ROSS E. VAN DYKE

I. Introduction

In recent communications Kraus and co-workers[1a] have reported studies of the conductivities of solutions of aluminum bromide on addition of dimethyl ether and other electron-donor molecules. In the latter of these studies[1b] nitrobenzene was found to be a quite convenient solvent because the concentration of free ether in the liquid phase could be determined by measuring the partial pressure of ether in the system. The conductance of aluminum bromide decreased approximately linearly to a minimum when the molar ratio of ether to salt was 1.0; with further addition of ether the conductance increased linearly with an equilibrium operating among the dietherate and monoetherate of aluminum bromide and one mole of free ether.

The results of similar studies with the gallium halides using dimethyl ether, trimethylamine and ammonia as complexing agents are reported in this paper.

II. Experimental

Materials.—Nitrobenzene[2] was purified according to the procedure of Jacober and Kraus[3] followed by several recrystallizations.[2] The solvent was finally dried over finely divided activated aluminum oxide in a large flask from which it was withdrawn through a fritted filter as needed. The solvent had a specific conductance of 1×10^{-10} reciprocal ohms and melted at 5.72°.

Gallium trichloride was prepared by allowing liquid chlorine to condense on the metal in an evacuated reaction vessel. The reaction was controlled by regulating the rate of condensation of the halogen. Gallium tribromide was prepared by a similar procedure. The resultant halide was sublimed several times *in vacuo* and finally filled into fragile bulbs as described previously.[3] *Anal.* $GaBr_3$, % Br, required, 77.47; found, 77.42; % Ga, required, 22.53; found, 22.47.

Dimethyl ether was dried initially over activated aluminum oxide and finally by passing over freshly prepared barium oxide. The vapor density at 25° was found to be 1.9175 g./liter.

Trimethylamine was dried by passing the vapor over barium oxide. Analysis of a sample gave a vapor density corresponding to 98% trimethylamine, assuming dimethylamine to be the chief impurity. The determination was based on the values of Arthur and Felsing.[4]

Ammonia was dried by passing the vapor over freshly prepared barium oxide. The vapor density data reported by Dietrichson, Bircher and O'Brien[5] were used.

Nitrogen was dried by passing over silica gel and phosphorus pentoxide.

Apparatus and Procedure.—Conductance measurements were made with a Leeds and Northrup bridge of the Jones type. The bridge was connected by shielded leads to a thermostated oil-bath maintained at 25 ± 0.01°. The cells used were of the Erlenmeyer type with rounded bottom and bright platinum electrodes adjoined as previously described.[6] The technique of preparation of the solutions and of addition of complexing agents to the solutions was carried out as described by Van Dyke and Kraus.[1b] A ground glass joint attached to the conductance cell permitted transfer of the cell from the ether addition system to the thermostat for resistance measurements. The concentration of free ether was determined by interpolation from the solubility curve for dimethyl ether in nitrobenzene.[1b]

The molecular weight of gallium tribromide in nitrobenzene was determined by the Beckmann method. The solution cell was arranged with two side arms conveniently placed to maintain an atmosphere of dry nitrogen above the solution throughout the determination. Solvent melting points were reproducible on the Beckmann thermometer with a precision of ±0.001°.

The solubility curve for trimethylamine in nitrobenzene at 25° was determined as a function of total pressure. These results are presented in Table I where the values of the constant $m/(p - p_0)$ are calculated on the basis

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[1] (a) Jacober and Kraus, THIS JOURNAL, **71**, 2409 (1949); (b) Van Dyke and Kraus, *ibid.*, **71**, 2694 (1949).

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

[3] Jacober and Kraus, THIS JOURNAL, **71**, 2405 (1949).

[4] Arthur and Felsing, *ibid.*, **68**, 1883 (1946).

[5] Dietrichson, Bircher and O'Brien, *ibid.*, **55**, 1 (1933).

[6] Hnizda and Kraus, *ibid.*, **71**, 1565 (1949).

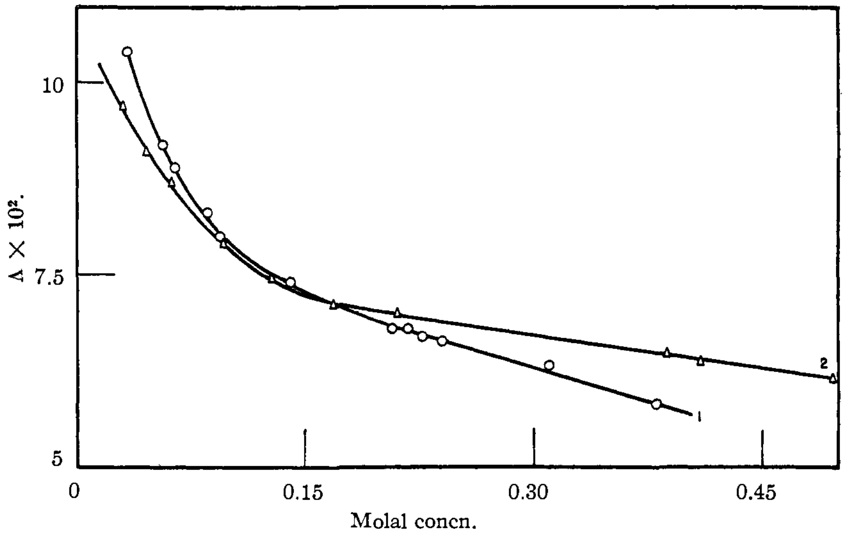

Fig. 1.—Conductance of gallium trichloride and tribromide in nitrobenzene at 25°: (1) $GaBr_3$, (2) $GaCl_3$.

of molality. The pressures were read by means of a cathetometer.

TABLE I

SOLUBILITY OF TRIMETHYLAMINE IN NITROBENZENE AT 25°

P, cm.	$m/(p - p_0)$	P, cm.	$m/(p - p_0)$
0.04	0.0260	6.91	0.0279
1.96	.0265	7.47	.0279
2.45	.0266	9.23	.0282
3.85	.0270	13.61	.0288

By interpolation from a plot of these data, the concentration of free amine in the nitrobenzene solutions could be determined.

III. Results

Dimethyl Ether.—The conductance of gallium trichloride in nitrobenzene on addition of carefully dried dimethyl ether was studied at four concentrations of salt m (molality) = 0.3868, 0.1677, 0.1159 and 0.0601. Data for three of these solutions are plotted in Fig. 2 and numerical data for two of them are shown in Table II. The fourth is a preliminary series which may be somewhat less accurate and therefore is not presented. The conductance of gallium trichloride in nitrobenzene on addition of dimethyl ether which contained 0.12% water by weight was studied at several concentrations. Data for one of these solutions molality = 0.2102 are presented graphically in Fig. 2, Curve 2.

The conductance of gallium tribromide in nitrobenzene on addition of carefully dried dimethyl ether was studied at several concentrations of salt. Numerical results are tabulated for two of these solutions molality = 0.3100, 0.2067 in Table II. The conductance of gallium tribromide in nitrobenzene on addition of ether which contained 0.12% water by weight was also studied. Data for one such solution are given in Table II and are presented graphically in Fig. 3, Curve 2. At the head of each table is given the concentration M of the solution in moles per 1000 g. of solvent.

Trimethylamine.—The conductance of gallium trichloride in nitrobenzene on addition of varying amounts of trimethylamine was measured at two different concentrations of salt: 0.4091 and 0.0963 molal. The conductance of gallium tribromide in nitrobenzene on addition of trimethylamine was measured at two different concentrations of salt: 0.2264 and 0.0988 molal. These data are presented in Table III.

Ammonia.—The conductance of gallium trichloride and tribromide in nitrobenzene on addition of ammonia was measured at several concentrations for each salt. Data for two solutions of each salt are presented in Table IV. Vapor pressures of these solutions indicate that the ammonia is all combined.

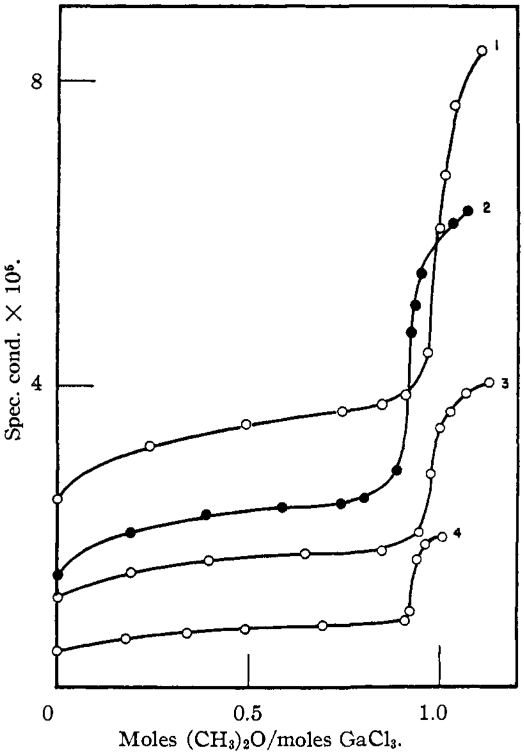

Fig. 2.—Conductance of nitrobenzene solutions of gallium trichloride in presence of dimethyl ether: (1) 0.3868 molal; (2) 0.2102 molal (ether containing 0.12% water); (3) 0.1677 molal; (4) 0.0601 molal.

TABLE II

THE CONDUCTANCE OF GALLIUM TRICHLORIDE AND TRIBROMIDE IN NITROBENZENE ON ADDITION OF DIMETHYL ETHER AT 25°

$\kappa \times 10^5$ 1/ohms	V. p., cm.	Ether/salt, M	$\kappa \times 10^5$ 1/ohms	V. p., cm.	Ether/salt M
0.3868 M $GaCl_3$			0.1677 M $GaCl_3$		
2.506	0.035	0.0	1.191	0.035	0.0
3.188	.165	.2418	1.528	.140	.1926
3.515	.235	.4900	1.682	.175	.3949
3.676	.290	.7428	1.774	.230	.6460
3.762	.320	.8495	1.819	.250	.8488
3.871	.350	.9110	2.059	.505	.9426
4.439	.430	.9679	2.837	1.030	.9707
6.067	.950	.9963	3.449	2.740	.9994
6.773	1.583	1.012	3.644	4.085	1.025
7.680	2.965	1.037	3.907	7.775	1.065
8.427	7.015	1.104	4.040	10.795	1.124
0.3100 M $GaBr_3$			0.2067 M $GaBr_3$		
1.961	0.035	0.0	1.408	0.035	0.0
2.285	.150	.1895	1.759	.160	.2152
2.497	.250	.3881	2.079	.310	.6360
2.633	.345	.5802	2.226	.395	.8550
2.750	.415	.7775	2.494	.480	.9305
2.840	.470	.8603	2.874	.595	.9525
2.959	.500	.9071	3.430	.815	.9698
3.417	.640	.9579	3.796	1.170	.9735
4.511	.995	.9832	4.060	1.560	.9772
5.294	1.745	.9942	4.563	2.600	.9779
5.670	2.455	1.003	5.020	5.100	.9979
6.384	5.615	1.031			
6.933	12.035	1.079			
0.2398 M $GaBr_3$ (+H_2O)			0.2398 M $GaBr_3$ (+H_2O)		
1.595	0.035	0.0	2.939	1.930	0.7995
2.098	0.243	.1955	3.277	1.985	.8451
2.359	0.650	.3697	5.865	4.275	.8732
2.550	1.210	.5372	6.594	7.255	.8754
2.731	1.702	.7113	7.441	13.160	.9006
2.828	1.825	.7613			

IV. Discussion

Jacober and Kraus[3] have pointed out that in general the strength of an electrolyte such as aluminum bromide depends to a great extent upon the complexing power of the solvent. Molecular weight determinations for gallium tribromide in nitrobenzene indicate a monomeric structure. Experimental values ranging from 309.25–309.62 (theoretical for $GaBr_3$ = 309.47) were obtained for solutions in the concentration range of from 0.0381–0.2230 molal. These results indicate that the complexing power of nitrobenzene in this case is great enough to rupture the bridge structure of the salt which involves at least 20 kcal.[7]

However, the gallium salts appear to be very weak electrolytes in nitrobenzene even when compared with aluminum bromide which yields molal conductances of approximately 4.0[1b] in the concentration range considered here. Molal conductances for several concentrations of the gallium salts are listed in Table V and are shown graphically in Fig. 1.

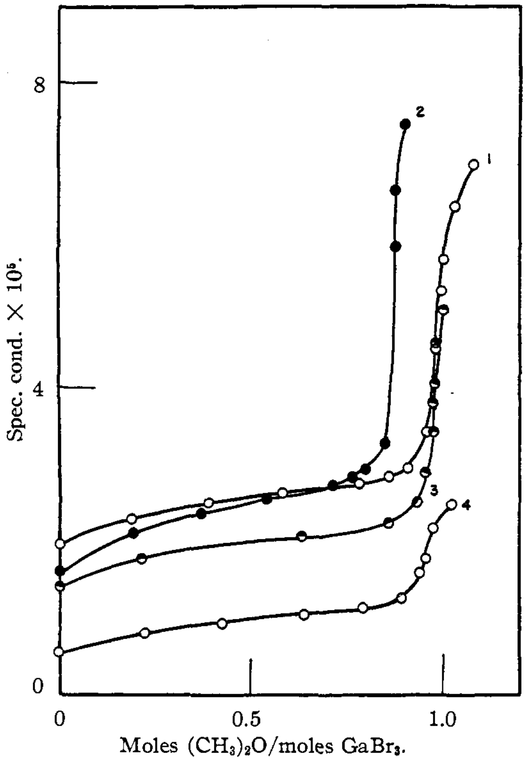

Fig. 3.—Conductance of nitrobenzene solutions of gallium tribromide in presence of dimethyl ether: (1) 0.3100 molal; (2) 0.2398 (ether containing 0.12% water); (3) 0.2067 molal; (4) 0.0647 molal.

The deviation from linearity of the conductance curves for the gallium salts occurs at a concentration of about 0.15 molal which corresponds to the position of the maximum in the conductance curve for aluminum bromide in nitrobenzene.[1b] The conductance of chloride and bromide ion in nitrobenzene[8] is 22.2 and 21.6, respectively; therefore, the degree of dissociation of these salts must be extremely small in nitrobenzene. It seems reasonable that if a complex does exist between the gallium halides and nitrobenzene, it is comparatively unstable. Attempts to isolate such a complex in this laboratory have been unsuccessful. If a complex of constant composition does not exist, it is clear that the monomeric halide must be stabilized by a solvation energy approximating 20 kcal.

Dimethyl Ether.—The results of Table II for dimethyl ether as a complexing agent are shown graphically in Figs. 2 and 3. The conductance of the gallium salts increases slightly with addition of ether until the molar ratio of ether to salt is about 0.90; thereafter, the conductance increases rapidly and almost linearly with added

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[7] Laubengayer and Schirmer, THIS JOURNAL, 62, 1578 (1940).

[8] Witschonke and Kraus, *ibid.*, 69, 2472 (1947).

TABLE III

THE CONDUCTANCE OF GALLIUM TRICHLORIDE AND TRIBROMIDE IN NITROBENZENE ON ADDITION OF TRIMETHYLAMINE AT 25°

$\kappa \times 10^5$ 1/ohms	V. p., cm.	Amine/salt, M	$\kappa \times 10^5$ 1/ohms	V. p., cm.	Amine/salt, M
0.4091 M $GaCl_3$			0.0963 M $GaCl_3$		
2.606	0.035	0.0	0.7594	0.035	0.0
20.27	.035	.1540	9.837	.035	.2331
22.66	.035	.3861	12.83	.035	.4662
25.16	.035	.6186	13.62	.035	.6939
27.75	.035	.8558	14.25	.035	.8917
29.15	.035	.9877	14.62	.035	.9836
29.58	.532	1.064	14.87	.485	1.053
30.15	1.843	1.130	15.16	1.160	1.105
32.13	4.705	1.238	15.76	2.420	1.134
34.04	7.305	1.323	16.53	3.610	1.178
35.15	8.765	1.373	17.31	4.822	1.211
0.2264 M $GaBr_3$			0.0988 M $GaBr_3$		
1.514	0.035	0.0	0.7874	0.035	0.0
18.85	.035	.2461	14.51	.035	.2642
21.82	.035	.4947	16.40	.035	.4452
23.07	.035	.7451	17.23	.035	.6431
24.48	.035	.9834	17.93	.035	.8369
23.71	1.310	1.066	18.47	.035	.9754
24.39	3.160	1.098	18.27	.255	1.039
25.38	5.120	1.111	17.80	.750	1.060
27.40	8.885	1.139	17.79	1.310	1.074
28.49	10.575	1.188	17.99	2.525	1.079
			18.45	3.875	1.081
			19.49	6.640	1.080

TABLE IV

THE CONDUCTANCE OF GALLIUM TRICHLORIDE AND TRIBROMIDE IN NITROBENZENE ON ADDITION OF AMMONIA AT 25°

$\kappa \times 10^5$ 1/ohms	NH_3/salt, M	$\kappa \times 10^5$ 1/ohms	NH_3/salt, M
0.1271 M $GaCl_3$		0.0624 M $GaCl_3$	
0.9469	0.0	0.5422	0.0
28.22	.1744	19.30	.1936
36.88	.3628	22.35	.3781
43.51	.5470	24.82	.5503
49.11	.7394	28.30	.7772
50.82	.9375	28.53	.9219
50.34	1.016	28.60	.9817
49.98	1.119	28.54	1.077
		27.11	1.164
0.1397 M $GaBr_3$		0.0635 M $GaBr_3$	
1.034	0.0	0.5652	0.0
29.48	.1780	18.46	.1872
45.06	.3739	27.00	.3599
54.97	.5875	32.78	.5241
60.58	.7780	34.71	.6812
61.27	.9675	35.35	.8674
54.40	1.025	35.47	.9754
		33.99	1.080
		33.53	1.206

TABLE V

CONDUCTANCE VALUES FOR GALLIUM CHLORIDE AND BROMIDE IN NITROBENZENE AT 25°

$GaCl_3$ Concn., molal	$GaCl_3$ Λ, 1/ohms	$GaBr_3$ Concn., molal	$GaBr_3$ Λ, 1/ohms
0.4965	0.0615	0.3799	0.0582
.4091	.0637	.3100	.0633
.3868	.0648	.2398	.0665
.2102	.0700	.2264	.0669
.1677	.0710	.2182	.0679
.1271	.0745	.2067	.0681
.0963	.0789	.1397	.0740
.0624	.0869	.0988	.0797
.0454	.0910	.0856	.0829
.0306	.0969	.0635	.0890
		.0568	.0919
		.0329	.1040

ether. According to the vapor pressure data of Table II there is a small concentration of free ether appearing along the flat region of the conductance curves. In the case of aluminum bromide in unrecrystallized solvent a measurable concentration of free ether was observed from the first addition. However, this was shown to be due to solvent impurities.[1b] The gallium salts have been studied in recrystallized nitrobenzene in which these impurities presumably have been eliminated. Additional recrystallization of solvent had no noticeable effect upon the results.

In coördination of a polar molecule such as dimethyl ether by the electrophilic halides there appear to be two possibilities: first, stabilization of the monomeric halide by the ether to form the complex $(CH_3)_2O:GaX_3$[9]; and secondly, coördination involving replacement of a halogen ion by a mole of ether with resultant formation of an ionic bond between halogen and the coördinated metallic ion, $(C_6H_5NO_2)_xGaX_2:O(CH_3)_2^+ + X^-$.[10] Dimethyl ether and aluminum bromide react in nitrobenzene to give the monoetherate $(CH_3)_2O:AlBr_3$ which is a much weaker electrolyte in this solvent than is aluminum bromide. The reaction of the gallium halides with dimethyl ether in this solvent appears somewhat more complex. If one assumes that the monoetherate $(CH_3)_2O:GaX_3$ does not differ appreciably or is weaker in electrolytic strength than the halide itself in nitrobenzene, then the increase in conductance upon first addition of ether may be explained by formation of a small amount of the better conducting complex $(C_6H_5NO_2)_xGaX_2:O(CH_3)_2^+ + X$ while most of the ether combines to form the monoetherate $(CH_3)_2O:GaX_3$.[11] In solution then we have an equilibrium among the following species: $(C_6H_5NO_2)_xGaX_3$, $(CH_3)_2O:GaX_3$, $(C_6H_5NO_2)_xGaX_2:O(CH_3)_2^+ + X$, and $(CH_3)_2O$. As

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[9] This type of coördination usually does not increase the conductance of the solution 1b, 1a.

[10] This type of coördination usually increases the conductance of the solution and is less stable, provided that the monomeric halide is stabilized by the solvent or some other polar molecule.[1b]

[11] An alternative explanation for this region of the curve might be to assume that the monoetherate is a better electrolyte than the uncoördinated halide. In this case the conductance should increase more uniformly as the molar ratio increases.

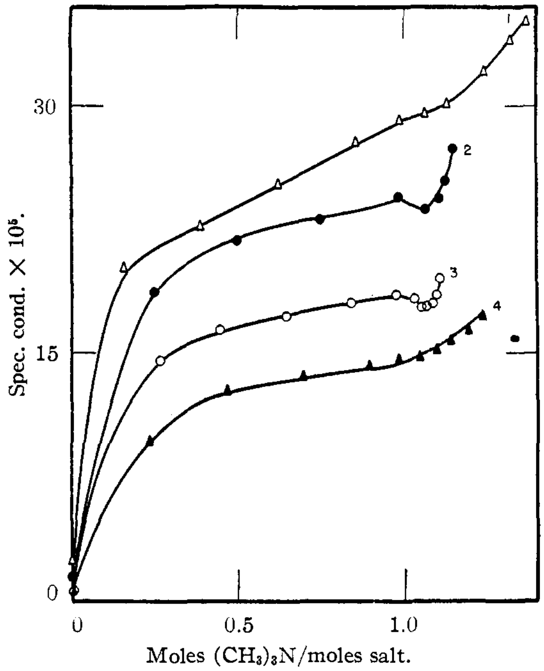

Fig. 4.—Conductance of nitrobenzene solutions of gallium trichloride and tribromide in presence of trimethylamine: (1) $GaCl_3$, 0.4091 molal; (2) $GaBr_3$, 0.2264 molal; (3) $GaBr_3$, 0.0988 molal; (4) $GaCl_3$, 0.0963 molal.

the conductance and concentration of free ether increase more rapidly for molar ratios above 0.90 the formation of the complex $(C_6H_5NO_2)_xGaX_2$: $O(CH_3)_2^+ + X^-$ is probably the principal reaction. For molar ratios of 1.0 and beyond when the conductance begins to level off somewhat the principal reaction probably involves conversion of some of the latter complex to the dietherate (assuming that at this point the concentration of $(C_6H_5NO_2)_xGaX_3$ is negligibly small). Molar ratios as high as 1.124 for gallium chloride solutions in Table II indicate appreciable concentrations of the dietherate, assuming ideal behavior of the ether except for compound formation. The apparent formation to some extent of a dietherate in nitrobenzene solution, while only the monoetherate seems to form in dimethyl ether itself,[12] indicates that one of the bromines of the monoetherate is more labile in nitrobenzene than is the case in ether solution.

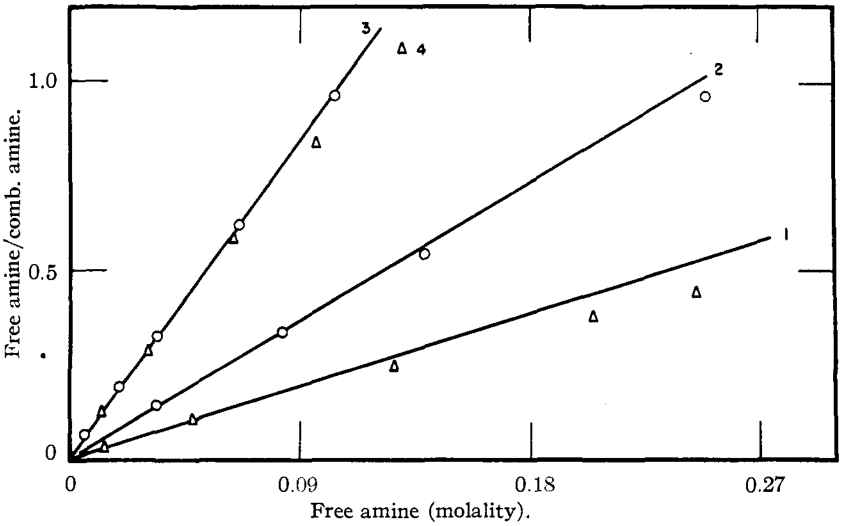

Fig. 5.—Equilibrium between free amine and combined amine in nitrobenzene solutions of the gallium halides: (1) $GaCl_3$, 0.4091 molal; (2) $GaBr_3$, 0.2264 molal; (3) $GaBr_3$, 0.0988 molal; (4) $GaCl_3$, 0.0963 molal.

In curves 2 of Figs. 2 and 3 are plotted data in which the ether contained 0.12% water by weight. The concentration of free ether along the flat region of the conductance curves was considerably greater than in the case of dry ether. For example in Table II with 8.868 millimoles of gallium bromide on addition of 5.840 millimoles of dried ether the vapor pressure was 0.310 cm. corresponding to 0.197 millimole of free ether. With 8.960 millimoles of gallium bromide on addition of 5.45 millimoles of wet ether, the vapor pressure of the solution was 1.21 cm. corresponding to 0.732 millimole uncombined. It seems clear from this comparison that a small amount of water in the system involves a reaction which is somewhat more complicated than a simple displacement of an equimolar quantity of ether by the water. With wet ether the marked rise in conductance takes place at lower molar ratios of combined ether to salt, particularly in the gallium bromide solutions. It seems difficult to interpret these results by assuming the conductance of the hydrate to be greater than the etherate because the extent of interaction of the hydrate, if any, with dimethyl ether is unknown. Furthermore, the addition of small amounts of water to dilute solutions of aluminum bromide in nitrobenzene produced a marked decrease in the conductance.[8]

Trimethylamine.—The amine apparently forms more stable complexes with the gallium salts in nitrobenzene than is the case with dimethyl ether. This is shown by the fact that free amine appears only for molar ratios of 1.0 and beyond. However, the conductance curves do not break sharply at a molar ratio of unity. In Fig. 5 are plotted the ratios of free to combined amine *versus* the molal concentration of free amine for the four solutions reported. For the

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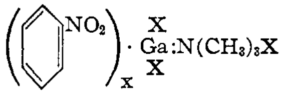
[12] Unpublished observations in the author's laboratory.

gallium bromide solutions (curves 2 and 3) the plots appear to be linear, indicating an equilibrium involving one mole of free amine. The deviations from linearity in the case of the chloride solutions indicate that the equilibrium may involve more than one mole of amine. Reversibility is shown by removal of a weighed quantity of amine. For example in Table III with 13.368 mmoles of amine added, upon removal of 8.16 mmoles by pumping the vapor pressure was 0.04 cm. and the specific conductance was 14.81 × 10^{-5} in good agreement with the data for a molar ratio of unity. Loss of nitrobenzene in such pumpings is of the order of 0.10% and therefore neglected.

The conductance data in Table III for trimethylamine as complexing agent are presented in Fig. 4. The tremendous increase in conductance of these solutions upon addition of amine is very striking. With the first addition of complexing agent the conductance increases continuously and rapidly for a period of twenty-four to thirty-six hours before equilibrium is achieved. With further additions the system equilibrates in thirty minutes or less. Obviously, the reaction taking place is a very complicated one. However, it appears reasonable that the curves might be explained qualitatively on the basis of formation of several complexes. If one assumes that the solvated complex  $\left(C_6H_5NO_2\right)_x \cdot \overset{X}{\underset{X}{Ga}}{:}N(CH_3)_3X$ is a stronger electrolyte than the 1:1 addition compound $(CH_3)_3N{:}GaX_3$, then the curves may be explained by formation of the solvated complex at first, followed by formation of increasing quantities of the 1:1 addition compound as the conductance levels off. The decrease in conductance for molar ratios in the neighborhood of unity in the case of gallium bromide solutions indicates an extremely complicated interaction. The increase in conductance with increasing molar ratios beyond unity may be explained by the coördination to some extent of a second mole of amine by either or both of these complexes. Comparison of curves 3 and 4, Fig. 4, for solutions of approximately the same salt concentration shows that the bromide–amine complexes are considerably better electrolytes than are the chloride complexes in this solvent. The conductance of bromide and chloride in nitrobenzene are nearly the same.[8] Apparently, ion pairing is greater in the gallium chloride solutions.

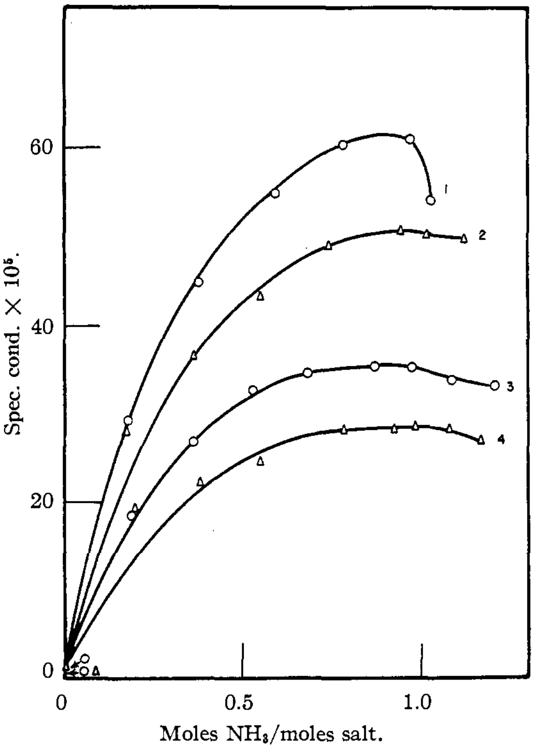


Fig. 6.—Conductance of nitrobenzene solutions of gallium trichloride and tribromide in presence of ammonia: (1) $GaBr_3$, 0.1397 molal; (2) $GaCl_3$, 0.1271 molal; (3) $GaBr_3$, 0.0635 molal; (4) $GaCl_3$, 0.0624 molal.

Ammonia.—The data in Table IV for ammonia as complexing agent are shown graphically in Fig. 6. The conductance increases markedly and gradually levels off, becoming almost constant as the molar ratio of ammonia to salt approaches 1.0. Upon first addition of ammonia a small amount of gelatinous precipitate appears, but quickly dissolves on shaking. However, twenty-four to forty-eight hours are required for equilibrium. As the conductance curve levels off, equilibrium takes place more rapidly. When the molar ratio exceeds unity, the conductance decreases slowly and precipitation occurs. In contrast, for solutions of aluminum bromide the conductance does not change greatly for additions of ammonia up to a molar ratio of unity. The reactions of the gallium salts with ammonia in nitrobenzene appear to be similar to those with trimethylamine. The gallium bromide solutions yield considerably greater conductance increases than are observed with the chloride solutions. Comparison of the conductance curves for ammonia with those for trimethylamine shows that the ammonia complexes are better electrolytes in nitrobenzene.

V. Summary

1. The conductance of gallium chloride and bromide in nitrobenzene on addition of dimethyl ether has been measured at 25°. The conductance increases very little for molar ratios up to approximately 0.90; thereafter, the conductance increases more rapidly and almost linearly. A small amount of water vapor contained in the ether has a pronounced effect upon the conductance of these salts in nitrobenzene.

2. The gallium halides and their ether complexes are very weak electrolytes in nitrobenzene.

The ether complexes are less stable than the corresponding aluminum bromide complexes in this solvent.

3. With trimethylamine, the conductance increases appreciably at first and then levels off somewhat as the molar ratio approaches unity. For molar ratios beyond 1.0 the curves for the bromide solutions are particularly complex.
4. On addition of ammonia the conductance increases tremendously at first and slowly levels off at a molar ratio of 1.0.
5. The conductance curves are explained qualitatively by assuming the formation of several coördination complexes.
6. Trimethylamine and ammonia are completely combined with the gallium halides up to a molar ratio of unity. For molar ratios beyond unity, there is a measurable concentration of free amine. With dimethyl ether there is a measurable concentration of free ether from the first addition.
7. The molecular weight of gallium bromide in nitrobenzene has been determined. The results indicate a monomeric structure in this solvent.
8. The solubility of trimethylamine in nitrobenzene has been determined at 25°.

Baltimore, Maryland Received August 22, 1949

[Contribution from the Chemical Laboratories of The Johns Hopkins University]

Some Coördination Compounds of Aluminum and Gallium Halides

By Ross E. Van Dyke and Harry E. Crawford

I. Introduction

During the course of some recent investigations of the electrolytic properties of solutions of aluminum and gallium halides, it was decided to examine some properties of various complexes of these compounds which have not been reported heretofore. In particular, the complexes of these halides with dimethyl ether and trimethylamine were considered.

Menzel[1] reports the preparation of the compound $AlCl_3 \cdot 2(CH_3)_2O$ as well as similar ethyl ether complexes of aluminum chloride and bromide. Jacober and Kraus[2] report a very stable monoetherate of aluminum bromide $AlBr_3 \cdot (CH_3)_2O$. In this paper are reported vapor pressure–composition studies for the chlorides and bromides of aluminum and gallium with dimethyl ether and trimethylamine as well as investigations of the stability of some of the resultant complexes.

II. Experimental

Materials.—Anhydrous aluminum chloride was prepared by reaction of a very pure sample of metallic aluminum[3] with chlorine at 300°. The salt was then sublimed several times in a closed system and finally collected in a long manifold to which numerous fragile ampules were attached. The product was sublimed into these ampules which were then sealed off. *Anal.* % Al, calcd. 20.22; found 20.10; % Cl, calcd. 79.78; found 80.03. Anhydrous aluminum bromide[4] and the gallium halides[5] were prepared and handled as previously described. Trimethylamine and dimethyl ether were dried as reported previously.[5]

Apparatus and Procedure.—The apparatus consisted of a large test-tube equipped with a large ground glass cap which was arranged with appropriate stopcocks and another ground joint to connect with the vacuum system. A fragile ampule filled with salt was introduced through the large ground cap; the system was then exhausted and the bulb was carefully broken. The complexing agent now was condensed on the salt by means of a Dry Ice–acetone-bath. The weight of complexing agent withdrawn from the system was determined by adsorption on activated silica gel[6] which was contained in a large evacuated tube. The tube was provided with a stopcock and ground joint connection to the solution vessel.

Pressures were measured on a closed end manometer with the aid of a cathetometer. Temperatures were read by means of a seven-junction copper–constantan thermocouple which was calibrated using the freezing points of water and mercury and the sublimation point of carbon dioxide.

III. Results

Vapor pressure–composition diagrams were determined for solutions of the chlorides and bromides of aluminum and gallium in dimethyl ether and in trimethylamine. These data are presented graphically in Figs. 1 and 2.

Variation of Vapor Pressure with Temperature.—The vapor pressures of the solid gallium halide monoetherates as a function of temperature were determined. The dissociation pressure of the solid, 2:1 addition compounds of the aluminum halides as a function of temperature have been determined. These data are presented in Table I.

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[1] Menzel and Froehlich, *Ber.*, **75B**, 1055 (1942).

[2] Jacober and Kraus, This Journal, **71**, 2409 (1949).

[3] Kindly donated by The Aluminum Company of America.

[4] Jacober and Kraus, This Journal, **71**, 2405 (1949).

[5] Van Dyke, *ibid.*, **72**, 2823 (1950).

[6] Kindly donated by the Davison Chemical Company.