[CONTRIBUTION FROM METCALF RESEARCH LABORATORY, BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XLII. Conductance of Aluminum Bromide in Nitrobenzene on Addition of Dimethyl Ether at 25°[1]

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I. Introduction

In the preceding number of this series, Jacober and Kraus presented data on the conductance of aluminum bromide in methyl bromide on addition of dimethylether.[3] They found that on such addition the conductance of aluminum bromide fell to a minimum when the ratio of ether to bromide was slightly under unity; thereafter the conductance rose sharply with increasing ether and then increased approximately linearly with increasing ether content. This phenomenon appeared somewhat extraordinary and it seemed worth while to study it in another solvent in which the concentration of free ether in the liquid phase could be determined.

For this purpose, nitrobenzene was selected as solvent; its vapor pressure at 25° is only 0.045 cm. and the solubility of dimethyl ether in this solvent is such that its concentration in the liquid phase may readily be determined by the partial pressure of the ether. In addition to dimethyl ether, the effect of ammonia and trimethylamine were studied as complexing agents. Finally, the effect of hydrogen bromide on the conductance of aluminum bromide in nitrobenzene was investigated.

II. Materials, Apparatus and Procedure

1. **Materials.**—Nitrobenzene was initially purified according to the method of Witschonke and Kraus.[4] It was found, however, that, although the specific conductance was as low as 1×10^{-10}, impurities were still present and these could not be eliminated by the purification method used. Accordingly, the solvent was purified by fractional crystallization. After several recrystallizations, which raised the melting point 0.1°, a solvent was obtained in which no evidence of impurities could be detected. The melting point of this solvent was 5.72°, in good agreement with the best values in the literature.[5,6] The solvent was stored in a 3-liter flask over activated alumina from which it was withdrawn through a fine, fritted filter as needed.

Dimethyl ether was treated according to the method of Jacober and Kraus.[3] Its vapor density at 25° was determined to be 1.915 g./l., in reasonably good agreement with 1.9185, the value given in the literature.[7]

Trimethylamine,[8] stated to consist of 95% trimethylamine and 4-5% dimethylamine, gave a vapor density corresponding to 95% trimethylamine, assuming that the contaminant was dimethylamine. Determinations were referred to the values of Arthur and Felsing.[9] Ammonia, from a stock cylinder, was dried over sodium amide. Vapor densities employed were those of Dietrichson, Bircher and O'Brien.[10]

Hydrogen bromide was prepared by the action of 98% sulfuric acid on sodium bromide and by the action of water on phosphorus tribromide. It was condensed on aluminum bromide.

Nitrogen was dried by passing over phosphorus pentoxide.

Aluminum bromide was prepared and filled into fragile bulbs as described by Jacober and Kraus.[3]

2. **Apparatus and Procedure.**—Conductance measurements were carried out as described in earlier papers.[3] The conductance cell was of the customary Erlenmeyer type except that the bottom was rounded to withstand the pressure of the atmosphere when evacuated. The cell was baked out at 120° and transferred to a vacuum desiccator which was filled with dry air before removal. The ampule of aluminum bromide was introduced, the cell was exhausted and filled with nitrogen and the ampule was broken by cautiously shaking the cell. The cell was provided with a small ground cap on removal of which nitrobenzene was introduced from the stock flask while a stream of nitrogen was kept passing out of the cell. The cell was then exhausted and shaken at intervals for about an hour to remove dissolved gases. The loss of solvent in this process was well under 0.1%.

Ether vapor was introduced from a graduated cylindrical tube; the amount introduced was found from the volume change. The ether in the cylinder was kept over mercury the level of which was adjustable. The ether in the cell was equilibrated with the solution; the pressure was read on a mercury manometer by means of a cathetometer.

The cell was detachable from the system for the purpose of measuring the resistance of the solution. For this purpose, it was placed in an oil-bath at 25 ± 0.01°.

3. **Solubility of Dimethyl Ether and Hydrogen Bromide.**—The solubility of these two compounds in nitrobenzene was determined as a function of pressure at 25°. The results are presented in Table I, A and B, where the pressure of the solution is given in the first column and the concentration of the solute in moles per 1000 grams of solvent in the second column. The pressures were read by means of a cathetometer. The vapor pressure of nitrobenzene is 0.45 mm.

TABLE I

SOLUBILITY OF $(CH_3)_2O$ AND HBr IN NITROBENZENE AT 25°

A. Dimethyl Ether		B. Hydrogen Bromide	
p. cm.	Molality	p. cm.	Molality
0.05	0.0	0.08	0.0
5.76	.0955	2.42	.0258
14.07	.2362	5.52	.0583
27.00	.4720	8.64	.0928
42.23	.7565		

The results of these measurements are shown graphically in Fig. 1. By interpolation from the curve, the concentration of free ether in the nitrobenzene solutions of aluminum bromide could be determined with considerable precision.

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

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

[5] Sidgwick and Ewbank, *J. Chem. Soc.*, **125**, 2268 (1924).

[6] Massy, Warren and Wolfenden, *ibid.*, PTI, 91 (1932).

[7] Kennedy, Sagenkahn and Aston, THIS JOURNAL, **63**, 2267 (1941).

[8] Kindly furnished by the Rohm and Haas Company.

[9] Arthur and Felsing, THIS JOURNAL, **68**, 1883 (1946).

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

III. Results

1. Dimethyl Ether.—The conductance of aluminum bromide in unrecrystallized nitrobenzene was measured at two concentrations of salt, *m* (molality) = 0.0234 and 0.3073. Numerical data for the latter solution are given in Table II, A, and are shown graphically in Fig. 2. In the tables, the specific conductance is given in the first column, the partial pressure of ether above this solution in the second column, the uncombined ether in the third column, the combined ether in the fourth column and the moles of combined ether to moles of aluminum bromide in the last column.

TABLE II

CONDUCTANCE OF ALUMINUM BROMIDE IN NITROBENZENE AT 25° ON ADDITION OF DIMETHYL ETHER

A. Unrecrystallized Solvent, mm. $AlBr_3$ = 14.481; *m* = 0.3073

$\kappa \times 10^4$	V. p., cm.	Mm. ether uncombined	Mm. ether combined	Ratio of moles ether to salt
12.58	0.035	0.0	0.0	0.0
9.729	.315	0.217	3.527	0.2436
6.694	.555	.405	7.047	.4866
3.445	.755	.565	10.733	.7412
1.865	.810	.613	12.602	.8702
1.172	.830	.631	13.558	.9363
1.069	.855	.646	13.805	.9533
1.077	1.061	.810	13.974	.9650
1.179	1.75	1.366	14.088	.9729
1.354	2.93	2.266	14.289	.9867
1.644	5.00	3.920	14.518	1.003
2.483	10.86	8.576	15.329	1.059
B. Recrystallized Solvent, mm. $AlBr_3$ = 1.972; *m* = 0.0298				
1.237	0.045	0.0	0.0	0.0
0.9490	.045	.0	0.514	0.2606
.6668	.040	.0	1.036	.5254
.4198	.045	.0	1.525	.7733
.3390	.045	.0	1.793	.9092
.3190	.045	.0	1.900	.9635
.3189	.080	.040	1.906	.9665
.3261	.150	.119	1.936	.9817
.3657	.700	.735	2.007	1.018
.4050	2.46	2.687	2.066	1.048
.5098	11.36	12.609	2.099	1.064
.6643	24.76	28.376	2.200	1.116
C. Recrystallized Solvent, mm. $AlBr_3$ = 14.407; *m* = 0.3013				
12.46	0.040	0.0	0.0	0.0
9.415	.040	.0	3.942	0.2736
6.127	.040	.0	7.907	.5488
2.848	.040	.0	11.804	.8193
1.153	.040	.0	13.968	.9695
0.9302	.200	.124	14.403	.9997
1.169	1.70	1.348	14.588	1.013
1.652	5.20	4.136	14.875	1.032
2.596	11.60	9.299	15.610	1.084
3.426	17.90	14.582	16.174	1.123
4.180	24.02	19.865	16.754	1.163
D. Recrystallized Solvent, mm. $AlBr_3$ = 28.584; *m* = 0.8190				
22.51	0.035	0.0	0.0	0.0
19.21	.035	.0	7.672	0.2684
13.99	.035	.0	15.330	.5363
7.082	.035	.0	22.984	.8041
1.738	.045	.0	28.368	.9924
1.663	.180	.077	28.571	.9995
2.363	1.84	1.064	29.101	1.018
4.130	6.43	3.738	30.279	1.059
7.743	18.06	10.714	32.972	1.154
10.88	29.74	18.113	35.285	1.234
7.069[a]	15.50[a]	9.144[a]	32.487[a]	1.137[a]
E. Recrystallized Solvent, mm. $AlBr_3$ = 38.692; *m* = 1.095				
22.91	0.040	0.0	0.0	0.0
21.52	.035	.0	9.130	.2360
17.81	.035	.0	18.250	.4717
11.13	.040	.0	28.228	.7296
2.179	.040	.0	38.208	.9875
1.937	.040	.0	38.661	.9992
2.067	.590	.353	38.866	1.004
3.168	2.68	1.569	39.659	1.025
5.972	9.02	5.317	41.824	1.081
9.410	17.51	10.507	44.614	1.153
12.41	26.03	15.969	47.046	1.216

[a] These results were obtained by removing a weighed quantity of dimethyl ether to show reversibility of the equilibrium.

The conductance of aluminum bromide in recrystallized nitrobenzene on addition of ether was measured at the following molal concentrations: 0.0298, 0.0862, 0.2431, 0.2814, 0.3013, 0.7106, 0.8190, 1.095, 1.337 and 0.1555. Numerical data are presented for four of these concentrations of salt in Table II, B, C, D and E. Experimental values for two of them and for other concentrations are shown graphically in Fig. 3. At the head of the table for each salt are given the amount of solvent and salt used, in millimoles, and the concentration, *m*, of the solution in moles per 1000 g. of solvent.

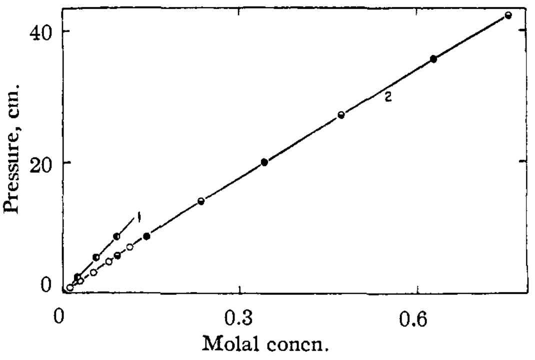

Fig. 1.—The solubility of complexing agents in nitrobenzene at 25°: (1) hydrogen bromide; (2) dimethyl ether.

2. Ammonia and Trimethylamine.—The conductance of aluminum bromide in recrystallized

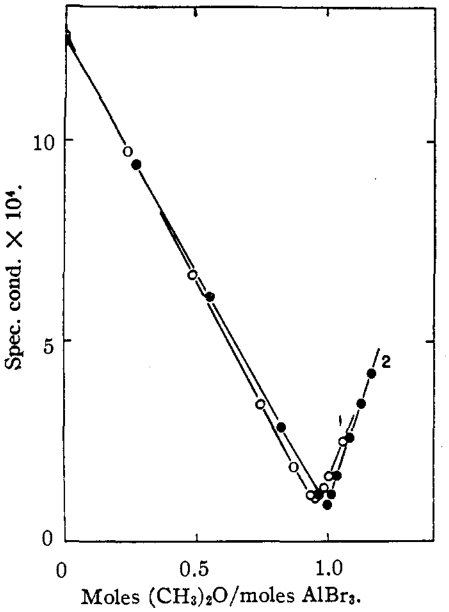

Fig. 2.—Conductance of aluminum bromide in nitrobenzene at 25° in the presence of dimethyl ether: (1) 0.3073 molal $AlBr_3$ in uncrystallized nitrobenzene; (2) 0.3013 molal $AlBr_3$ in recrystallized nitrobenzene.

nitrobenzene on addition of ammonia was measured at three different concentrations of solute: 0.1037, 0.0310 and 0.0106 molal. Numerical data are presented in Table III, A. The specific conductance of the solution is given in the first column, the total ammonia added in the second column and the molar ratio of ammonia to aluminum bromide in the last column. The amount of solvent and of aluminum bromide, in millimoles, is given at the head of each table as is, also, the molal concentration of salt initially. In Table III, B, are given data for trimethylamine.

Table III

Conductance of Aluminum Bromide in Nitrobenzene in the Presence of Ammonia and Trimethylamine

A. Ammonia

40.85 g. solvent; 4.236 mm. $AlBr_3$; ammonia, m = 0.1037 — 63.46 g. solvent; 0.671 mm. $AlBr_3$; ammonia, m = 0.0106

$\kappa \times 10^4$	Mm. base	Ratio base/ $AlBr_3$	$\kappa \times 10^4$	Mm. base	Ratio base/ $AlBr_3$
4.482	0.0	0.0	0.4512	0.0	0.0
5.042	0.843	0.1990	.6312	0.078	0.116
5.100	1.795	.4238	.7066	.181	.270
5.065	2.069	.4883	.7203	.263	.392
4.784	2.848	.6724	.7328	.358	.534
4.088	3.755	.8864	.7218	.463	.690
3.994	3.840	.9067	.7066	.561	.836
3.808	3.980	.9396	.7166	.604	.900
4.310	4.405	1.040	.7149	.648	.966
6.317	4.839	1.142	.8753	.706	1.05
6.621	5.693	1.344	1.076	.781	1.16
			1.100	.863	1.29

B. Trimethylamine

83.47 g. solvent; 2.586 mm. $AlBr_3$; ammonia, m = 0.0310 — 32.81 g. solvent; 3.301 mm. $AlBr_3$; trimethylamine, m = 0.1006

1.270	0.0	0.0	4.340	0.0	0.0
1.403	0.286	0.1106	4.223	0.338	0.1024
1.451	.555	.2146	3.744	.885	.2681
1.472	.808	.3125	3.241	1.402	.4247
1.469	1.084	.4192	2.742	1.953	.5916
1.449	1.375	.5317	2.415	2.519	.7631
1.304	2.019	.7807	2.265	3.079	.9327
1.223	2.316	.8956	3.320	3.530	1.069
1.174	2.410	.9319			
1.128	2.568	.9930			
1.281	2.641	1.021			
2.051	2.943	1.138			
2.450	3.165	1.224			

3. **Hydrogen Bromide.**—The conductance of aluminum bromide was measured on addition of hydrogen bromide for two salt concentrations, 0.3070 and 0.0782 molal. Results are given for

Table IV

Conductance of Aluminum Bromide in Nitrobenzene on Addition of Hydrogen Bromide

49.05 g. solvent; 15.067 mm. $AlBr_3$ m = 0.3076

$\kappa \times 10^4$	V. p. (cm.)	Mm. HBr uncombined	Mm. HBr combined	Ratio HBr/ $AlBr_3$
12.58	0.040	0.0	0.0	0.0
13.16	6.24	3.252	.196	.013
13.66	12.57	6.553	.418	.028
14.13	18.73	9.766	.523	.035
14.59	24.08	12.557	.750	.050

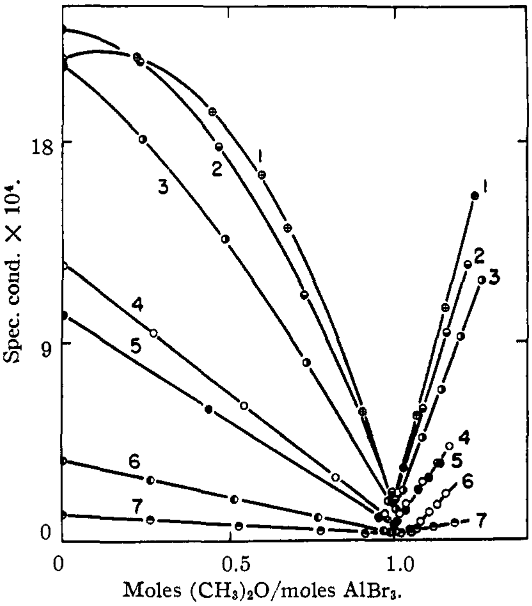

Fig. 3.—Conductance of aluminum bromide in recrystallized nitrobenzene at 25° in the presence of dimethyl ether: initial molal concentration of $AlBr_3$: (1) 1.337; (2) 1.095; (3) 0.7106; (4) 0.3013; (5) 0.2431; (6) 0.0862; (7) 0.0298.

the higher concentration in Table IV, which is arranged after the manner of Table II.

IV. Discussion

The results of Table II, A and C, are shown graphically in Fig. 2. The course of the conductance curves on addition of ether closely resembles that of solutions of aluminum bromide in methyl bromide as determined by Jacober[3] and Kraus. On addition of ether, the conductance decreases to a minimum after which it increases sharply. In the unrecrystallized nitrobenzene as in methyl bromide, the minimum comes at a ratio of ether to bromide which is somewhat under unity. Thus, as shown in Fig. 2, the conductance in the unrecrystallized solvent falls to 8.5% of its value in the pure solvent and the ether solvent ratio at the minimum is 0.95; with recrystallized solvent the conductance falls to 7.5% of its original value and the ether solute ratio is 1.0. In the unrecrystallized solvent, the breakpoint ratio decreases with decreasing concentration of aluminum bromide; for $m = 0.0234$, the minimum lies at a ratio of 0.90.

It seems clear that in the unrecrystallized solvent, a basic substance is present which competes with dimethyl ether in reaction with aluminum bromide. This is most conclusively shown by the partial pressure of ether above the solution for ratios below the minimum point. Thus, in Table II, A, with 14.48 mmoles. of aluminum bromide, on addition of 7.45 mmoles. of ether, the partial pressure of ether was 0.555 cm., corresponding to 0.405 mmoles. of uncombined and 7.047 mmoles. of combined ether. For a ratio of 0.965, the pressure was 1.061 cm. and there were 0.81 mmoles. of uncombined and 13.97 mmoles. of combined ether. In contrast to this, with recrystallized solvent, we find in Table II, C, that for a ratio of 0.97, the partial pressure of ether was not measurable. For a ratio of unity the partial pressure of ether was 0.2 cm., corresponding to 0.120 mm. of free ether in the solution. As shown in Table II, E, the partial pressure of ether for a solution 1.095 molal was not measurable at an ether–aluminum bromide ratio of unity. These results illustrate the influence of traces of impurities on observed values of physical properties and they show the need for caution in interpreting the results of physical measurements with such systems.

As appears from Fig. 3, addition of ether beyond a molar ratio of unity causes a marked increase in conductance, approximately as a linear function of the added ether. The maximum which occurs in the case of the most concentrated solution of aluminum bromide indicates that the bromide in the pure solvent exists as a dimer and that an etherate of this dimer is formed. It is probable that the monoetherate is monomeric. On further addition of ether, a reaction probably occurs somewhat as follows

$$AlBr_3 \cdot (CH_3)_2O + (CH_3)_2O \rightleftharpoons AlBr_2^+ \cdot (CH_3)_2O + Br^-$$

The ionic dissociation of the dietherate is probably not large and the compound exists mainly as ion pairs. If, for the moment, we neglect ionic dissociation, we should expect to find an equilibrium constant

$$\frac{AlBr_3 \cdot 2(CH_3)_2O}{AlBr_3 \cdot (CH_3)_2O \times (CH_3)_2O} = \frac{A}{B \cdot C} = K$$

From the data of Table II, the value of the constant K may be obtained. Several examples are given in Table V.

TABLE V

EQUILIBRIUM CONSTANTS

$AlBr_3$ molal	$\frac{A}{B}$	C molal	$K_C = A/B \cdot C$
0.3013	0.033	0.086	0.384
	.092	.195	.472
	.140	.305	.459
	.195	.416	.469
0.8190	.018	.030	.600
	.063	.107	.589
	.182	.307	.593
	.305	.519	.588
	.159[a]	.262[a]	.607[a]
1.095	.026	.044	.591
	.088	.151	.583
	.181	.297	.609
	.276	.452	.611

[a] Results obtained by removing known weight of ether from system.

As may be seen from the table, the constant at a given concentration of bromide varies only with what may be expected to be the limit of error of these experiments. The consistency of the results may be judged from Fig. 4 in which values of $B \times C$ are plotted against values of C. It will be noted that the experimental points lie on a number of different straight lines whose slopes correspond to different values of K. Values of aluminum bromide concentrations and corresponding K_C values (as determined from the slope of the plots) are given in Table VI.

TABLE VI

VALUES OF K_C FOR DIFFERENT CONCENTRATIONS OF $AlBr_3$

$AlBr_3$ (molal)	K_C	$AlBr_3$ (molal)	K_C
0.2431	0.346	0.8190	0.606
.2814	.346	1.095	.606
.3013	.469	1.337	.606
.7106	.469	0.1555	.908

The manner in which the constants fall into groups is rather puzzling. Equilibrium near the minimum point established itself rather slowly as was indicated by the conductance of the solutions. That a true equilibrium exists is shown by the last point of Table II, D, in which ether was withdrawn. The solution of 0.1555 molal was made up to an ether–bromide ratio above unity. The value of the constant is surprisingly high in view of the fact that in all other cases the constant decreased with decreasing concentration or re-

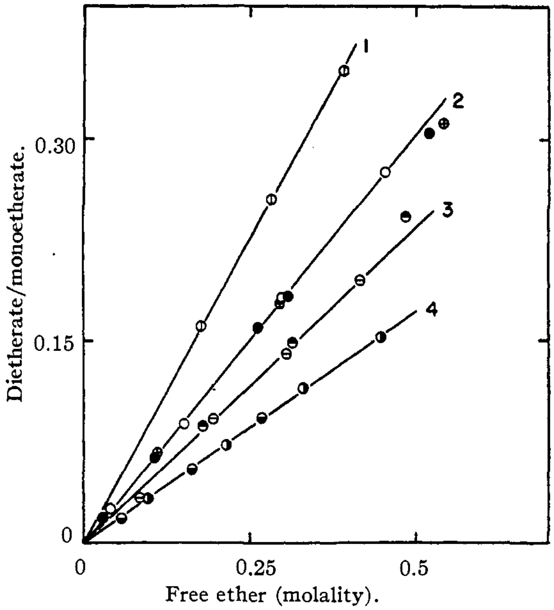

Fig. 4.—Aluminum bromide etherate equilibrium in nitrobenzene at 25°: initial molal concentration of $AlBr_3$: (1) 0.1555 ⦶; (2) 0.8190 ●, 1.337 ⊕, 1.095 ⊙; (3) 0.7106 ◓, 0.3103 ⊖; (4) 0.2814 ◒, 0.2431 ◑.

mained constant. This phase of the problem requires further study.

The monoetherate is a much poorer electrolyte than aluminum bromide as appears from Table VII and Fig. 5.

Table VII

Comparisons of Conductance for $AlBr_3$ and $AlBr_3 \cdot (CH_3)_2O$

Concn., molal	Λ $AlBr_3$ molal	Λ Ethereate molal
0.0298	4.15	1.070
.0862	4.30	0.432
.1555	4.33	...
.2431	4.21	.302
.2814	4.15	.250
.3013	4.13	.309
.3202	4.06	.256
.7106	3.01	.195
.8190	2.75	.203
1.095	2.09	.177
1.337	1.61	.152

There is some fluctuation in the conductance values for the etherate; this is due to the fact that these values were taken from the data for experiments in which ether was added progressively to the solution of the bromide. The minimum conductance value could not be precisely determined in this manner. It is clear, however, that the etherate is a much weaker electrolyte than the pure bromide.

The conductance curve of aluminum bromide has a maximum. It will be recalled that, as Jacober and Kraus have shown,[3] the curve has a minimum at lower concentrations.

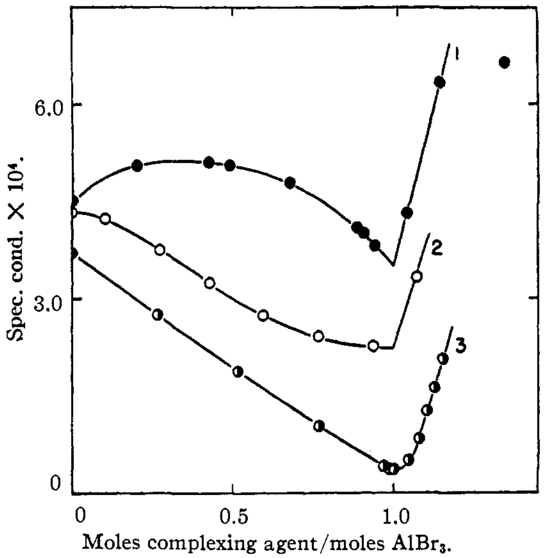

Fig. 5.—Conductance of aluminum bromide in recrystallized nitrobenzene at 25° in the presence of various complexing agents: (1) 0.1037 molal $AlBr_3$ in presence of ammonia; (2) 0.1006 molal $AlBr_3$ in presence of trimethylamine; (3) 0.0862 molal $AlBr_3$ in presence of dimethyl ether.

2. **Ammonia.**—On addition of ammonia, the conductance of aluminum bromide passes through a maximum for all salt concentrations measured, as may be seen from curve 1, Fig. 5. The presence of a maximum would seem to indicate a complex of the dimer of aluminum bromide with one molecule of ammonia. The conductance change due to addition of ammonia is not great until a molar ratio of unity is reached when the conductance increases markedly.

3. **Trimethylamine.**—On addition of trimethylamine to solutions of aluminum bromide, the conductance curve lies intermediate between that of ammonia and dimethyl ether. While the ammonia curve exhibits a maximum and that of the ether is nearly linear, the curve for the amine exhibits a pronounced inflection point. The conductance values for the amine are intermediate, approaching those of ammonia more nearly than those of the ether.

4. **Hydrogen Bromide.**—The acids frequently seem to act as promoters for Friedel–Crafts catalysts. It seemed worth while to determine if complexes were formed between hydrogen bromide and aluminum bromide in nitrobenzene. As may be seen from Table IV, on addition of 13.3 mmoles. of HBr to 15.08 mmoles. of $AlBr_3$ ($m = 0.3072$), the molar ratio of combined HBr to $AlBr_3$ is only 0.05. With 3.155 mmoles. of salt ($m = 0.0782$), the ratio is 0.05 on addition of 4.07 mmoles. of HBr. Thus, with an excess of hydrogen bromide, the fraction of salt that complexes with it amounts to only 5%. However, it is doubtful that complexes are formed at all. The presence of aluminum bromide may affect

the solubility of HBr to the extent here observed.

It is of interest to note that with addition of HBr, the conductance of the solution increases. For a ratio 0.05 for combined HBr to $AlBr_3$, the extreme conductance increase for the higher concentration of salt is 16% and for the lower concentration 20%.

Hydrogen bromide was condensed on aluminum bromide and thereafter was evaporated at −78°. The amount of hydrogen bromide that was evaporated was measured and the pressure was measured as a function of the $HBr/AlBr_3$ ratio. The pressure varied continuously until no HBr was left behind; no breakpoint could be observed. Under the conditions of this experiment a compound was not formed.

V. Summary

1. The conductance of aluminum bromide in nitrobenzene on addition of dimethyl ether has been measured at 25°. In pure nitrobenzene the conductance decreases continuously and markedly up to a molar ratio of unity; thereafter the conductance increases sharply and approximately linearly with increasing molar ratio of ether to salt. With an impure solvent, the minimum comes at a molar ratio slightly less than unity.

2. With ammonia, the conductance passes through a not very pronounced maximum and then decreases to a value differing little from that of the pure salt at a molar ratio of unity. Thereafter, the conductance increases linearly with increasing molar ratio.

3. On addition of trimethylamine, the conductance decreases continuously along a rather complex curve to a minimum value at a molar ratio of unity. Thereafter the conductance increases linearly with increasing ratio of amine to salt.

4. On addition of hydrogen bromide, the conductance increases slightly with increasing hydrogen bromide concentration.

5. The solubility of dimethyl ether and of hydrogen bromide in nitrobenzene have been determined at 25°. From these data, it is possible to determine the concentration of the free additions in solution.

6. In pure nitrobenzene, dimethyl ether is completely combined with aluminum bromide up to a molar ratio of unity. In less pure solvent, there is a measurable concentration of ether beginning with the first additions at molar ratios much below unity.

7. Assuming an equilibrium between aluminum bromide monoetherate, dietherate and ether, an equilibrium constant may be obtained that is constant as a function of the free ether concentration. However, this constant, while holding for certain aluminum bromide concentrations, differs from that at other concentrations.

8. The maximum in the conductance curves of aluminum bromide on addition of ammonia would seem to indicate the existence of a dimeric compound.

9. On condensing hydrogen bromide on aluminum bromide, and thereafter evaporating the hydrogen bromide at −78°, no evidence was found of the formation of a compound between the two components.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CATHOLIC UNIVERSITY OF AMERICA]

The Molecular Kinetics of the Urea–Urease System. I. The Kinetic Laws

BY K. J. LAIDLER AND J. P. HOARE

Introduction

The urease-catalyzed hydrolysis of urea, which follows the stoichiometric equation

$$CO(NH_2)_2 + 2H_2O = 2NH_3 + CO_2$$

has a number of unusual kinetic features. One of these relates to the influence of the urea concentration upon the rate of reaction: as the concentration is increased from zero the rate first increases linearly, and later shows a falling-off from linearity, reaching a maximum, and then decreasing.[1] A second characteristic is that the energy of activation is sensitive to the oxidation–reduction potential of the reaction system, and under certain circumstances depends upon the temperature.[2] The present work was undertaken with the primary object of investigating the concentration effect, and of obtaining some information as to the molecular kinetics and energetics of the reaction. The results have also shed some light on the variation of energy of activation with the temperature and on the nature of the intermediate complex which is formed; this will be presented in a later paper (Part II).

Experimental

The Enzyme Preparation.—Urease was prepared from finely ground jack-bean meal and crystallized according to Sumner's method.[3] The enzyme was stored in concentrated solution at 2° under which conditions its activity showed no significant change over a period of ten days. In all of the work the water employed was laboratory distilled water which had been redistilled using an all-glass apparatus.

The urease solution used in the kinetic runs was prepared by diluting 5 cc. of the concentrated solution to 100

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(1) S. F. Howell and J. B. Sumner, *J. Biol. Chem.*, **104**, 619 (1934).

(2) I. W. Sizer, *J. Gen. Physiol.*, **22**, 719 (1939); *J. Biol. Chem.*, **132**, 209 (1940); Sizer and A. A. Tytell, *ibid.*, **138**, 631 (1941).

(3) J. B. Sumner, *ibid.*, **69**, 435 (1926).