[CONTRIBUTION FROM METCALF RESEARCH LABORATORY, BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XLI. Conductance of Aluminum Bromides in Methyl Bromide on Addition of Dimethyl Ether

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I. Introduction

Since aluminum bromide forms stable complexes with substances having basic molecules, it seemed of interest to investigate the conductance of solutions of aluminum bromide as well as of methylaluminum dibromide and dimethylaluminum bromide in methyl bromide on addition of dimethyl ether. Such measurements might throw some light on the state of these substances in solution.

II. Experimental

1. **Materials.**—With the exception of dimethyl ether, the preparation and handling of materials has been described in an earlier paper.[1]

The ether was given an initial drying by distillation from activated alumina; and a final drying by passing over phosphorus pentoxide.

2. **Apparatus and Procedure.**—These were much the same as described earlier. With a solution having a known concentration of salt, known and increasing quantities of dimethyl ether were introduced and the conductance of the solution was measured after each introduction. The dried ether (as vapor) was contained in a graduated tube over mercury and the amount of ether introduced was found from the volume of the vapor at 25° and 760 mm. before and after introduction into the conductance cell. This cell was maintained at 0° and the ether, being readily soluble in methyl bromide, was quickly absorbed by the solvent as the vapor passed into the solution through a capillary tube. No provisions were required for removing solution or adding solvent once a series of measurements was started.

The solubility of dimethyl ether in methyl bromide is very high and the ether present in the vapor phase may be neglected. However, with this solvent, it is not possible to distinguish between ether which is combined with the solutes and that which is present, as such, in the solvent.

Aluminum bromide forms a stable monoetherate with dimethyl ether. This was established by condensing the ether on known weights of salt and thereafter removing any excess ether with a pump. The increase in weight of the aluminum bromide was found to correspond to the monoetherate as is shown in columns 3 and 4 of Table I.

TABLE I

COMPOUND OF $AlBr_3$ WITH $(CH_3)_2O$

$AlBr_3$, m. moles	$(CH_3)_2O$, m. moles	Weight increase, g. Found	Calcd.
21.55	Excess	0.985	0.992
18.68	16.21	.758	.746
36.00	12.15	.556	.560

Although both the methylaluminum bromides complex with dimethyl ether, their composition could not be determined because it was found impossible to bring them to crystallization; a highly viscous liquid was obtained in all cases.

All measurements were carried out at 0°. The density of methyl bromide at this temperature was taken to be 1.732.[2] The density of dimethyl ether vapor at 25° and 760 mm. was taken to be 1.918[3] g./liter.

(1) Jacober and Kraus, THIS JOURNAL, **71**, 2405 (1949).

(2) Beilstein, Vol. I, p. 66.

(3) Kennedy, Sagenkahn and Aston, THIS JOURNAL, **60**, 2267 (1941).

III. Results

In Tables IIA and B, are given the data for two series of measurements in which dimethyl ether was added to solutions of aluminum bromide. At the head of each table are given the concentrations of the solute in moles per liter of solvent and the millimoles of solute used. In the

TABLE II

CONDUCTANCE OF ALUMINUM BROMIDE IN METHYL BROMIDE AT 0° ON ADDITION OF DIMETHYL ETHER

A. $C = 0.3105$; mmol. $AlBr_3 = 12.38$

$\kappa \times 10^6$	Mmol. ether	$(CH_3)_2O/AlBr_3$
7.469	0	0
6.852	3.828	0.3092
5.729	7.711	.6229
3.459	11.410	.9216
2.799	11.819	.9547
14.78	12.021	.9710
32.37	13.220	1.068
60.80	18.83	1.521
70.15	20.68	1.670
81.44	22.66	1.829
91.29	24.61	1.988
99.76	25.90	2.092
106.4	27.11	2.189
136.5	32.90	2.657

B. $C = 0.9024$; mmol. $AlBr_3 = 36.00$

$\kappa \times 10^6$	Mmol. ether	$(CH_3)_2O/AlBr_3$
3.868	0	0
3.934	7.609	0.2114
3.733	15.34	.4261
3.150	23.14	.6428
2.265	30.78	.8551
1.319	34.74	.9649
1.161	35.12	.9757
6.353	35.58	.9883
12.36	37.43	1.040
39.99	46.96	1.304
66.67	56.80	1.566
90.50	67.84	1.884[a]

[a] Complex began to precipitate.

TABLE III

CONDUCTANCE OF METHYLALUMINUM DIBROMIDE IN METHYL BROMIDE AT 0° ON ADDITION OF DIMETHYL ETHER

A. $C = 0.3355$; mmol. $CH_3AlBr_2 = 6.220$

$\kappa \times 10^6$	Mmol. ether	$(CH_3)_2O/CH_3AlBr_2$
2.627	0	0
4.671	1.972	0.3170
5.691	2.969	.4773
6.316	3.893	.6259
6.567	4.911	.7895
5.789	5.780	.9292
3.214	6.245	1.004
3.176	7.794	1.253

TABLE III (*Continued*)

$\kappa \times 10^6$	Mmol. ether	$(CH_3)_2O/CH_3AlBr_2$
B. C = 0.4761; mmol. CH_3AlBr_2 = 8.608		
5.274	0	0
7.673	1.914	0.2224
10.87	3.861	.4485
12.18	5.221	.6065
12.47	5.995	.6964
11.77	6.990	.8120
9.454	7.999	.9293
7.135	8.408	.9768
6.637	8.625	1.002
6.543	10.46	1.215
6.560	13.20	1.533
C. C = 0.8016; mmol. CH_3AlBr_2 = 8.016		
1.301	0	0
1.805	1.167	0.1456
2.299	1.654	.2063
3.964	3.574	.4459
5.376	5.525	.6892
5.561	6.635	.8277
4.938	7.270	.9069
3.832	7.767	.9689
2.166	8.000	.9980
2.150	8.914	1.112
2.150	10.38	1.295

first column of the table are given values of the specific conductance corresponding to the moles of ether added as given in the second column. Values of the molar ratio $(CH_3)_2O/AlBr_3$ are given in the last column.

In Table III, results are presented similarly for solutions of methylaluminum dibromide at three different concentrations of solution.

Results for dimethylammonium bromide are presented in Table IV for four different concentrations of solute.

IV. Discussion

1. Aluminum Bromide.—As may be seen from Fig. 1, the conductance of aluminum bromide decreases with increasing methyl ether content until the molecular ratio of ether to bromide is slightly under unity. Considering the stability of the monoetherate, it was to be expected that the break in the conductance curve would come at a molecular ratio of unity. The discrepancy is not due to experimental error but, rather, to impurities that had not been eliminated from the solvent. Van Dyke[4] has found similar effects in nitrobenzene and established their nature. Traces of impurities may lead to spurious results.

Beyond the minimum point, the conductance increases greatly for a small addition of ether. Thereafter, it increases nearly linearly with increasing molar ratio of ether to solute. In the case of the more dilute solutions (Fig. 1), the conductance increases nearly 50 times as the molecular ratio increases from 0.97 to 2.66.

(4) R. E. Van Dyke, Thesis, Brown University, 1947.

TABLE IV

CONDUCTANCE OF DIMETHYLALUMINUM BROMIDE IN METHYL BROMIDE AT 0° ON ADDITION OF DIMETHYL ETHER

$\kappa \times 10^6$	Mmol. ether	$(CH_3)_2O/(CH_3)_2AlBr$
A. C = 0.3295; mmol. $(CH_3)_2AlBr$ = 12.35		
1.494	0	0
1.861	1.748	0.1415
2.701	3.644	.2951
3.927	5.580	.4518
4.724	7.573	.6132
5.280	9.513	.7703
4.061	11.390	.9923
2.339	12.14	.9832
2.178	12.42	1.006
2.127	12.87	1.042
2.048	14.75	1.195
2.057	16.58	1.343
B. C = 0.5902; mmol. $(CH_3)_2AlBr$ = 11.43		
2.200	0	0
3.424	1.754	0.1534
4.684	2.510	.2196
7.051	3.608	.3156
11.03	5.499	.4810
14.22	7.388	.6463
14.52	8.967	.7844
12.31	9.882	.8644
7.426	10.86	.9503
4.676	11.30	.9882
4.674	11.62	1.016
4.669	13.53	1.184
4.624	17.31	1.514
C. C = 0.7868; mmol. $(CH_3)_2AlBr$ = 15.96		
4.188	0	0
5.567	1.909	0.1196
9.458	3.857	.2417
15.48	5.797	.3632
21.31	7.752	.4857
26.43	9.721	.6091
28.75	11.63	.7289
25.74	13.48	.8446
11.86	15.46	.9687
7.286	15.69	.9831
7.270	16.11	1.009
7.268	17.24	1.080
7.177	21.14	1.325
D. C = 0.8610; mmol. $(CH_3)_2AlBr$ = 16.30		
5.733	0	0
7.523	1.972	0.1210
9.445	2.957	.1814
11.88	3.868	.2373
18.58	5.804	.3561
25.93	7.844	.4812
32.73	9.783	.6002
36.20	11.82	.7253
33.73	13.77	.8450
27.49	14.69	.9015
18.01	15.66	.9609
9.717	16.24	.9960
9.718	16.66	1.022
9.747	17.54	1.076
9.717	19.47	1.195

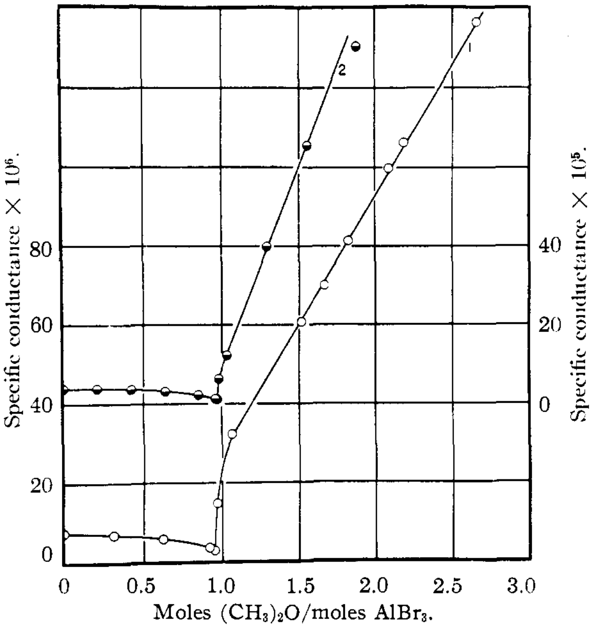

Fig. 1.—Conductance of aluminum bromide in methyl bromide in the presence of dimethyl ether: curves (1) 0.3105 molar; (2) 0.9024 molar. (Use right-hand scale for (2)).

2. **Methylaluminum Bromides.**—The conductance curves of these two salts on addition of dimethyl ether resemble each other closely and differ greatly from that of aluminum bromide. As may be seen from Figs. 2 and 3, on addition of ether, the conductance rises, passes through a maximum and then falls to a value little above that of the pure compound. Thereafter the conductance remains unchanged on addition of ether, in sharp contrast to what occurs in the case of aluminum bromide.

For convenience, characteristic conductance values for the two methyl derivatives are collected in Table V. The maximum for the two salts comes approximately at a molar ratio of 0.7 and varies little over the measured concentration range of salt.

TABLE V

CHARACTERISTIC CONDUCTANCE VALUES FOR METHYLALUMINUM BROMIDES

Curve	Concn. moles/l.	Specific conductance × 10^6 Pure salt	Maximum	Mono-etherate
		A. CH_3AlBr_2 (Fig. 2)		
1	0.3355	2.63	6.57	3.19
2	.4761	5.27	12.5	6.55
3	.8016	15.0	55.6	21.5
		B. $(CH_3)_2AlBr$ (Fig. 3)		
1	0.3295	1.49	5.28	2.05
2	.5902	2.20	14.5	4.67
3	.7868	4.19	28.8	7.20
4	.8610	5.73	36.2	9.72

The appearance of a maximum indicates that the original solute molecules exist as dimers and

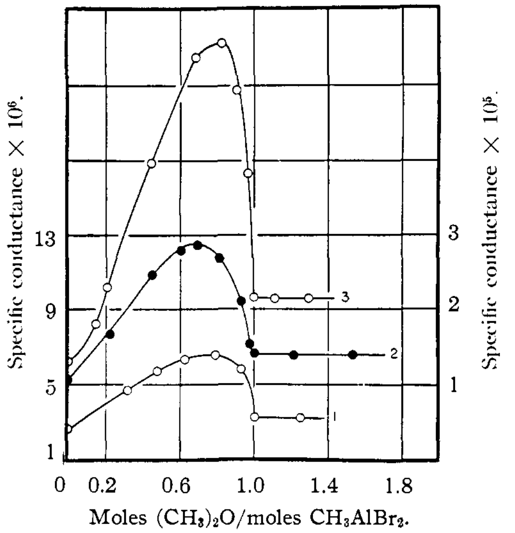

Fig. 2.—Conductance of methyl bromide solutions of methylaluminum dibromide in the presence of dimethyl ether: concn. of salt, (1) 0.3355 molar; (2) 0.4761 molar; (3) 0.8016 molar (use right-hand scale for (3)).

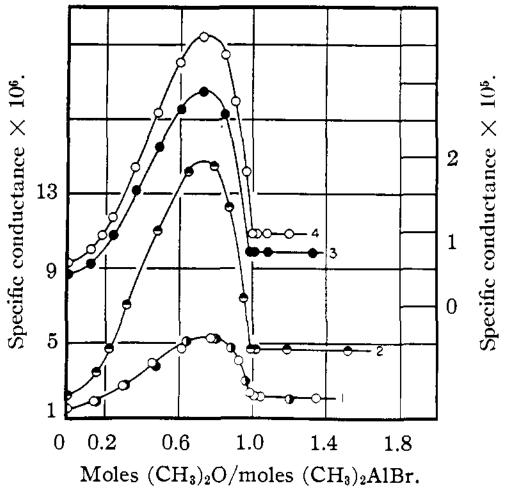

Fig. 3.—Conductance of methyl bromide solutions of dimethylaluminum bromide in the presence of dimethyl ether: concn. of salt, (1) 0.3295 molar; (2) 0.5902 molar; (3) 0.7868 molar; (4) 0.8610 molar (use right-hand scale for (3) and (4)).

that, with ether, they form a complex $(CH_3AlBr_2)_2\cdot(CH_3)_2O$ which has a much higher conductance than the original pure compound. With further addition of ether, an etherate of the monomer is formed which has a much lower conductance than the etherate of the dimer but a somewhat higher conductance than the pure compound. In solution we have an equilibrium among the following molecular species: $(CH_3AlBr_2)_2$, $(CH_3AlBr_2)_2\cdot(CH_3)_2O$, $CH_3AlBr_2\cdot(CH_3)_2O$, $(CH_3)_2O$. Since the maxima lie at molar ratios greater than 0.5, it follows that the etherate of the dimer predominates. The concentration of free ether in the solvent is doubtless extremely low; its value cannot be determined readily.

It is a striking fact that, while the conductance of aluminum bromide is greatly increased for ether additions above a molar ratio of unity, with the methyl derivatives, the conductance remains constant for ratios greater than unity. This would seem to indicate that only one of the three bromine atoms of aluminum bromide is labile and replaceable by a molecule of ether. In any case, with these compounds there seems to be no interaction between ether and the monoetherate of the monomer.

V. Summary

1. On addition of dimethyl ether, the conductance of aluminum bromide in methyl bromide decreases to a minimum value for a molar ratio of ether to salt slightly less than unity. On further addition of small quantities of ether, the conductance increases sharply and thereafter increases approximately as a linear function of the added ether.

2. The conductance of methylaluminum dibromide and of dimethylaluminum bromide passes through a maximum and thereafter decreases to a value slightly above that of the pure salts at a molecular ratio of unity. On further addition of ether, the conductance remains unchanged.

3. The presence of a maximum in the conductance curves of the methylated compounds indicates the existence of these substances in solution as dimers and that these dimers form etherates which are better conductors than the pure salts or their monoetherates.

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Ultraviolet Absorption Spectra in the Methyl Ionone Series

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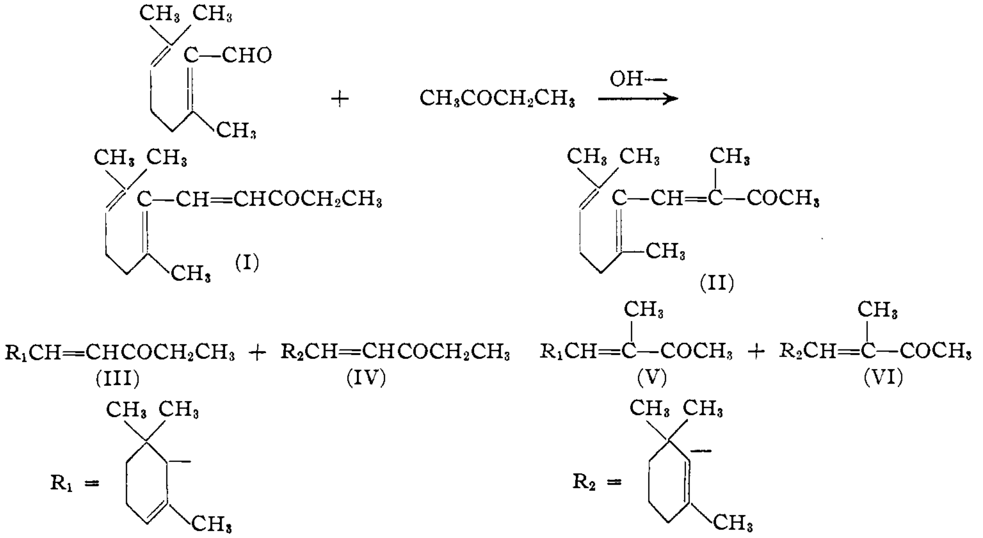
It has been demonstrated[1] that the condensation of citral and methyl ethyl ketone leads to a mixture of pseudomethylionones, (I) and (II), from which, by acid catalyzed cyclization, four methylionones, (III), (IV), (V) and (VI) are derived. Naves and Bachmann[2] have reported the absorption spectrum of α-*i*-methylionone (V), but the range in which the measurement was taken did not include the wave length of maximum absorption. Ultraviolet absorption spectra of the four methyl ionones and the two pseudo methylionones have now been determined, and the position of the maxima correlated with the structure of the chromophores.



The absorption peaks of the alpha isomers agree with Woodward's[3] generalization for the absorption of alpha-beta unsaturated ketones. α-*n*-Methylionone (III), a monosubstituted ketone, exhibits maximum absorption at 228 mμ, and α-*i*-methylionone, disubstituted, at 235 mμ.

From the values obtained in the present work and from those reported in the literature for similar compounds, it is observed that disubstituted dienones show an $\epsilon_{(max)}$ at 291 ± 1 mμ and trisubstituted at 294 ± 2 mμ (Table I).

(1) Koster, *Ber.*, **80**, 248 (1947).

(2) Naves and Bachmann, *Helv. Chim. Acta*, **26**, 2151 (1943).

(3) Woodward, THIS JOURNAL, **64**, 76 (1942).