chloride or the bromate ion. While it is true that, in the case of the acids, ionization is the greater the more electronegative the ion, this is not true generally for salts in solvents of lower dielectric constant, where ion association is appreciable.

V. Summary

The conductances of solutions of the sodium salts of triphenyltin, triphenylgermanium and triphenylmethyl in liquid ammonia have been measured.

All three salts are very strong electrolytes. The dissociation constant of sodium triphenylstannide is approximately four times that of sodium bromate.

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Properties of Electrolytic Solutions. VII. Conductance of Sodium Trimethylstannide and of the Sodium Salts of Certain Phenols and Thiols in Liquid Ammonia

BY CHARLES A. KRAUS AND EDMUND G. JOHNSON

I. Introduction

In the two preceding papers of this series, conductance values were given for electrolytes in which the charge of the negative ion was localized on nitrogen,[1] tin, germanium or carbon,[2] the remaining valences of these elements being satisfied by organic groups. The purpose of these investigations has been to study the influence of ion size and constitution on the properties of the electrolyte, particularly its dissociation constant. The results already presented lend support to the view that the dissociation of an electrolyte is primarily determined by the size of its ions and, to a lesser degree, by their configuration. Electrolytes with large ions, which cannot approach each other very closely, have a lower energy of dissociation and, consequently, a higher dissociation constant. Where the ions are unsymmetrical, constitutional factors have a marked influence and it may be expected that the salts of such ions will be the more highly ionized the more the charge is screened by neutral atoms of the ion complex.

It seemed of interest to determine the dissociation constants of salts of simple oxygen and sulfur acids of the type RAH, which give ions of the type RA^-. The salts of the ordinary alcohols are not sufficiently soluble in liquid ammonia to permit of conductance measurements, but the salts of the aromatic alcohols are readily soluble and are well suited to the purpose

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(1) Kraus and Hawes, THIS JOURNAL, **55**, 2776 (1933).

(2) Kraus and Kahler, *ibid.*, **55**, 3537 (1933).

of the present investigation. In the case of sulfur, both the alkyl and the aryl substituted thiols yield readily soluble salts. It was to be expected that, owing to the larger diameter of the sulfur atom, the salts of thio alcohols would prove to be markedly better electrolytes than their oxygen analogs. In the salts of alpha and beta naphthol, we have the interesting case where the oxygen atom, which presumably carries the charge electron, is located in different positions on the naphthalene nucleus, and we should expect a somewhat higher dissociation constant in the case of the α-naphtholate because of the somewhat greater screening due to the remainder of the molecule.

Sodium trimethylstannide was measured for the purpose of comparison with sodium triphenylstannide.[2] Unfortunately, this salt, like the corresponding phenyl derivative, yields solutions that are not entirely stable at low concentrations. Nevertheless, it was possible to carry out measurements to concentrations sufficiently low to show that, as was to be expected, this salt is a markedly weaker electrolyte than sodium triphenylstannide.

II. Experimental

Apparatus and Procedure.—The apparatus employed in the present investigation was very similar to that of Kraus and Kahler and need not be described, except for a few minor variations. Instead of stirring the solution by means of vapor withdrawn from the cell with a Toepler pump, the electrode system was moved up and down in the slip-joint through which the stem of the electrode system passed. An improved three-way stopcock was employed for withdrawing the ammonia, which made it possible to equalize the pressure between the cell and the withdrawal capillary without use of an additional stopcock. The electrical measuring apparatus was the same as that used by Kraus and Kahler.

Excepting sodium phenolate, all solutions were prepared by the action of sodium or sodium amide on the proper compounds in the cell itself. Sodium phenolate was prepared by the action of metallic sodium on phenol in liquid ammonia. It was washed with ether to remove traces of phenol and was sealed in weighed glass bulbs, the bulbs being broken in the cell as described by Kraus and Kahler. The naphtholates were prepared in the cell by the action of sodium amide on the corresponding naphthols. The naphtholates cannot be prepared by the action of metallic sodium on the naphthols because of the reducing action of the resulting hydrogen.[3] The thiophenolate and ethyl mercaptide were prepared by the action of sodium on the corresponding thiols. Ethyl mercaptan was introduced into the cell with a stream of ammonia vapor, a weighed bulb of sodium having been crushed under ammonia previous to introducing the mercaptan. In this case, the cell was exhausted after preparation of the salt in order to remove traces of excess mercaptan. Sodium trimethylstannide was prepared by the direct action of metallic sodium on an equivalent amount of trimethyltin in the cell.

In measuring the conductance of sodium trimethylstannide, the cell electrodes had a constant of 0.1299 and were lightly platinized. For the remaining salts, the electrodes had a constant of 4.682 and were heavily platinized.

All the solutions excepting those of sodium trimethylstannide were stable down to the lowest concentrations measured. The solutions of the sodium naphtholates were strongly fluorescent, the color being yellow by transmitted light and a deep violet by reflected light.

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(3) White and Anderson, THIS JOURNAL, **46**, 965 (1924).

III. Results

The conductance values for sodium phenolate, sodium α-naphtholate, sodium β-naphtholate, sodium ethyl mercaptide, sodium thiophenolate and sodium trimethylstannide are given in Table I. The conductance values have been corrected for the conductance of the pure solvent, which was determined just prior to preparation of the solution in the case of each salt. This value l is given at the head of each table of values. Check measurements, made in the case of the phenolate, the α-naphtholate and trimethylstannide, were in agreement with previous values and are not tabulated.

TABLE I

CONDUCTANCE OF PHENOLATES, THIOLATES AND SODIUM TRIMETHYLSTANNIDE

V	Λ	V	Λ	V	Λ
Sodium Phenolate ($l = 1 \times 10^{-7}$)		Sodium β-Naphtholate ($l = 1.1 \times 10^{-7}$)		Sodium α-Naphtholate ($l = 9.2 \times 10^{-8}$)	
27.41	41.22	28.23	52.71	19.19	54.20
55.03	52.19	56.74	65.07	36.93	63.46
107.8	66.05	115.8	83.19	73.11	74.41
210.9	83.48	230.3	101.1	145.6	95.16
409.3	104.2	465.1	124.8	289.8	116.2
810.0	129.1	924.3	150.3	578.0	140.5
1641	158.0	1830	177.5	1169	166.4
3280	186.7	3709	205.4	2279	192.0
6589	214.6	7419	232.3	4552	217.5
13190	239.7	Sodium Ethyl Mercaptide ($l = 8.6 \times 10^{-8}$)		Sodium Thiophenolate ($l = 9.8 \times 10^{-8}$)	
26590	257.0				
Sodium Trimethylstannide		10.67	85.08	12.11	104.8
112.1	179.5	21.46	94.84	24.31	114.9
219.2	195.7	42.75	108.5	48.98	129.1
434.0	215.9	84.57	125.9	97.20	146.2
859.1	237.7	167.3	146.9	193.1	166.0
1719	257.4	334.6	170.9	389.2	186.9
3451	274.1	667.1	195.3	767.9	207.9
		1331	218.2	1552	227.2
		2655	238.2	3118	243.3
		5320	255.4	6240	255.9

IV. Discussion

The values of Λ_0 and K for the different salts have been evaluated by the method of Fuoss and Kraus.[4] In the figure, values of the ratio Λ/Λ_0 are plotted as ordinates against the square root of concentrations as abscissas. This plot is more convenient than a plot of the conductance in comparing different salts with one another. The straight line as drawn in the figure is the limiting Debye–Hückel–Onsager slope averaged for the different salts. Actually, this slope varies slightly with Λ_0, but the variation is so small that it seemed unnecessary to introduce the limiting tangent for each electrolyte.

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(4) Fuoss and Kraus, THIS JOURNAL, **55**, 476 (1933).

The curves as drawn are the calculated curves based upon the values of the constants Λ_0 and K as computed. In evaluating these constants, the following values of constants were assumed for the solvent medium: dielectric constant 22, viscosity 0.00256, temperature 240°. From the figure, it is evident that the measured values of the conductance are satisfactorily accounted for by a combination of ionic dissociation and the usual interionic effects. The deviations from the limiting Debye–Hückel slope, due to the mass action effect, is marked in all cases and is the greater, the lower the dissociation constant of the electrolyte. None of the salts are sufficiently strong to approximate the limiting curve closely.

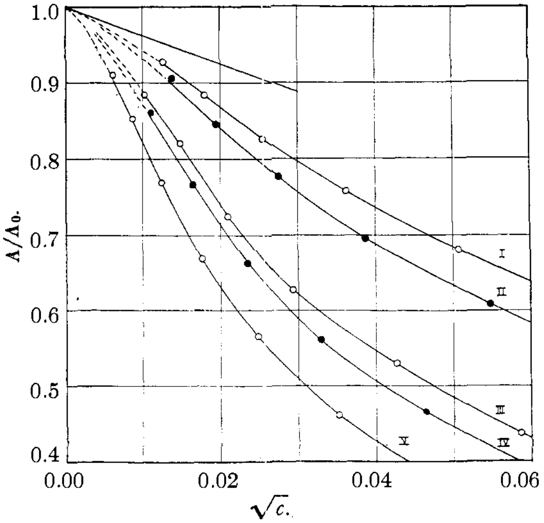

Fig. 1.—Conductance of sodium phenolates and thiolates in liquid ammonia: I, C_6H_5SNa; II, C_2H_5SNa; III, α-$C_{10}H_7ONa$; IV, β-$C_{10}H_7ONa$; V, C_6H_5ONa.

In Table II are given values of Λ_0, the limiting conductance, K, the dissociation constant, and a, which may be looked upon as the minimum distance between ion centers in the ion pairs. The quantity a was computed from the data according to the method of Fuoss and Kraus.[5]

TABLE II

CONSTANTS OF ELECTROLYTES IN LIQUID AMMONIA

Electrolyte	Λ_0	$K \times 10^4$	$a \times 10^8$
Sodium phenolate	279.4	3.82	2.70
Sodium β-naphtholate	268.1	6.50	2.94
Sodium α-naphtholate	265.3	8.08	3.08
Sodium ethylsulfide	281.4	22.5	4.04
Sodium thiophenolate	275.1	36.0	4.95
Sodium triphenylstannide	(307)	(36)	(4.95)

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(5) Fuoss and Kraus, THIS JOURNAL, **55**, 1019 (1933).

The table illustrates in striking fashion the influence of the substituent groups on the dissociation of electrolytes. Thus, the dissociation constant of sodium phenolate is 3.82×10^{-4}, while that of the β- and α-naphtholates is 6.50 and 8.08×10^{-4}, respectively. The greater size of the naphthyl group, in comparison with that of the phenyl group, has a very marked influence on the dissociation constant. It is particularly interesting to note that the dissociation constant of sodium α-naphtholate is nearly one-third greater than that of sodium β-naphtholate. This shows clearly that it is not only the size of the substituent group, but also the relation of the substituent group to the central charged atom, that determines the dissociation constant.

Sulfur, being a larger atom than oxygen, the dissociation constant of its monosubstituted ions is much greater than that of similar oxygen derivatives. Thus, sodium ethyl sulfide has a dissociation constant of 22.5, which is about three times that of the naphtholates and six times that of the phenolate. The replacement of the ethyl group by a phenyl group raises the dissociation constant from 22.4 to 36.0×10^{-4}. Sodium thiophenolate is an electrolyte as strong as the strongest of the common inorganic salts. The dissociation constant of sodium bromate, for example, is 35.0×10^{-4}.

The data for sodium trimethylstannide do not permit of an accurate determination of constants. It is believed that the values given are not substantially in error. The conductance curve of the stannide closely parallels that of the thiophenolate. The much lower value of K for the methyl derivative as compared with that of the phenyl derivative ($K = 0.013$, Kraus and Kahler) illustrates the influence of ion size on dissociation.

The a-values vary in accordance with the values of K. As to order of magnitude, they are in reasonable agreement with atomic dimensions. In the case of unsymmetrical ions, the a-values cannot be interpreted simply as the distance between ions; rather they represent an average distance or, perhaps better, they correspond to average energies, depending upon the relative position of the ions in the ion pair.

The results of the present investigation bring out clearly the fact that the strength of electrolytes, in solution in solvents of lower dielectric constant, varies markedly with the constitution of the ions of these electrolytes and that both the dimensions and the configuration of these ions have a marked influence upon dissociation. In general, those electrolytes will be the most highly ionized which have the largest ions and whose configuration is such that their charges are most completely screened by surrounding atoms or groups.

V. Summary

The conductance of the sodium salts of phenol, α- and β-naphthol, ethyl mercaptan, thiophenol and of trimethyltin have been measured in liquid ammonia at −33°.

Values of Λ_0 and of K have been computed and the influence of constitution upon dissociation is discussed.

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The Action of Sodium upon Trimethylgallium and Dimethylgallium Chloride in Liquid Ammonia

BY CHARLES A. KRAUS AND FRANK E. TOONDER[1]

I. Introduction

The present paper is concerned with the action of metallic sodium upon trimethylgallium and dimethylgallium chloride. In the light of our knowledge of reactions of similar derivatives of the elements of the fourth group, it might be expected that dimethylgallium chloride would be reduced to the free group $(CH_3)_2Ga$ and that this, in turn, might be further reduced to the negative ion, $(CH_3)_2Ga^-$. On the other hand, no reaction is to be expected in the case of trimethylgallium or, otherwise, a reaction in which one methyl group is substituted by the reducing metal as in the case of tetramethyltin.[2]

Excepting that free dimethylgallium $(CH_3)_2Ga$ is obtained by reduction of the corresponding chloride, there is little resemblance between reactions of organic derivatives of the elements of the third and those of the fourth group of the periodic system. Perhaps the most characteristic reaction of third group elements is that of addition of neutral molecules or negative ions, with formation of coördination compounds. Thus, in the case of boron, we have such coördinate linkage in the BF_4^- ion. Similarly, boron trifluoride combines with neutral molecules, such as ammonia or the amines, to form compounds of the type $BF_3{\cdot}NH_3$.[3] There are similar compounds of the organic boron derivatives. Thus, we have $(C_6H_5)_3B{\cdot}NH_3$,[4] $(C_6H_5)_3B{\cdot}NH_2^-$,[5] and $(C_6H_5)_3B{\cdot}OH^-$.[6] The coördinate linkage in these compounds has a striking influence on their stability. For example, triphenylboron oxidizes in air with extreme ease, while potassium amide, under similar conditions, oxidizes explosively; yet the coördinated compound of the two is relatively stable in air.

Gallium shows much the same properties as boron in respect to the formation of coördinate linkages. Thus, trimethylgallium forms an

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[1] Du Pont Fellow in Chemistry at Brown University.

[2] Kraus and Sessions, THIS JOURNAL, **47**, 2361 (1925).

[3] Kraus and E. Brown, *ibid.*, **51**, 2690 (1929).

[4] Krause, *Ber.*, **57**, 813 (1924).

[5] Hawes, Thesis, Brown University, 1927.

[6] Frankland, *Ann.*, **124**, 130 (1862); Fowler, unpublished observations, Brown University (1933).