[CONTRIBUTION FROM THE HAYDEN LABORATORIES OF NORTHEASTERN UNIVERSITY]

The Conductance of Some Salts in Ethylenediamine[1]

BY WILLIAM H. BROMLEY, JR.,[2] AND W. F. LUDER

I. Introduction

In considering various solvents for use in an investigation of the ionization of metallic salts as acids according to the Lewis theory of acids and bases,[3,4] ethylenediamine seemed to offer interesting possibilities. However, due to the present emergency the work had to be abandoned after securing conductance measurements on three salts: silver nitrate, silver iodide and potassium iodide. The data obtained are presented herewith.

Ethylenediamine is a stronger base than ammonia, having a dissociation constant of 8.5×10^{-5} in water.[5] One would expect then that acidic metallic salts would be soluble in it. However, its high basicity makes it extremely difficult to work with because of its rapid absorption of carbon dioxide and water.

Some conductivity measurements have been made in ethylenediamine,[6] but at concentrations much too high to permit evaluation of Λ_0 or K. Apparently none of these have been made below 0.2 molar; our measurements go down to 1×10^{-4} molar or below.

Because of the reactivity of the ethylenediamine the solvent conductance becomes an appreciable factor in the conductance of solutions at such low concentrations. This introduces considerable uncertainty in the extrapolated values of Λ_0, as compared with the very precise results which may be obtained with such relatively inert solvents as ethylene chloride.[7] In such solvents it is possible to reduce the solvent conductance to a value entirely negligible in comparison with the conductance of the lowest concentration of solution measured. This is impractical in ethylenediamine. The best previously reported solvent conductance[6] is 1.4×10^{-6} mho. With the most drastic drying methods carried out in the absence of air in an all-glass sytem, we were only able to reduce this value to 9×10^{-8} mho.

This is not surprising since from the structure of ethylenediamine one would expect a rather high conductivity even if carbon dioxide and water could be completely removed. But such a value of solvent conductance means that its value may be as much as 5% of the total conductance of a solution at 1×10^{-4} molar. Since there is considerable uncertainty as to how the solvent correction should be made this will affect the reliability of Λ_0 values. In our data the solvent conductance was subtracted from the conductance of the solution at each concentration.

II. Apparatus, Materials and Method

The bridge[8,9] and procedure of conductance runs[7] have been described previously. The temperature of the oil thermostat was held at 25 ± 0.01° by an electronic relay.

Salts.—C. P. potassium iodide was recrystallized from conductivity water. C. P. silver nitrate was dissolved in hot conductivity water and recrystallized by slowly adding freshly distilled ethyl alcohol. Silver iodide was prepared by mixing equivalent silver nitrate and potassium iodide solutions and washing the precipitate repeatedly with conductivity water. No further precautions were considered necessary because of the high solvent conductance.

Solvent.—95% ethylenediamine was stored over sodium hydroxide and barium oxide for several days, kept over sodium for a day, then fractionated off freshly activated alumina into a receiver containing alumina and sodium hydroxide. This receiver was provided with a ground glass cap carrying a tube through which the solvent could be discharged by dry nitrogen pressure. The solvent was kept from contact with moisture and carbon dioxide by a slow stream of dry nitrogen coming through a side arm and out the top of the receiver. About three-fourths of the ethylenediamine came over at constant temperature. This portion was used for runs.

The solvent thus obtained was placed in an all-glass system consisting of two stills, a solvent conductance cell, and a closed receiver. Each still was fitted with a fractionating column. The only opening to the atmosphere during the distillation was through a drying train consisting of phosphorus pentoxide, soda lime, and calcium chloride tubes and a concentrated sulfuric acid trap. This train was also used to dry nitrogen flowing through the system and out the filling tube of the first still while it was being loaded with solvent. The two successive distillations were carried out over alumina in an atmosphere of moisture and carbon dioxide-free nitrogen. The conductance was read from a sealed-in cell as the solvent was collected in the receiver from the second still. The best value was 9×10^{-8} mho. Solvent was forced into the cell[7] used in runs by nitrogen pressure while a slow stream of nitrogen emerged from the top of its long neck to prevent the entrance of air. The same procedure was followed when making dilutions. Solvent constants used were: d_{25} 0.891,[6] n_{25} 0.0154,[10] and D_{25} 12.9.[11]

III. Results

The experimental results are given in Tables I–III and are shown graphically in Fig. 1. It was hoped that potassium nitrate could also be measured to enable comparison of Λ_0 values, but it proved to be too insoluble. Λ_0 and K were calculated according to the method of

---

[1] Abstracted from a thesis submitted by William H. Bromley, Jr., to the faculty of Northeastern University in partial fulfillment of the requirements for the M. S. degree, April, 1943.

[2] Present address: Shawinigan Resins Corp., Springfield, Mass.

[3] G. N. Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

[4] W. F. Luder, *Chem. Rev.*, **27**, 547 (1940).

[5] Britton and Williams, *J. Chem. Soc.*, 796 (1935).

[6] Putnam and Kobe, *Trans. Electrochem. Soc.*, **74**, (preprint), (1938).

[7] Mead, Fuoss and Kraus, *Trans. Faraday Soc.*, **32**, 594 (1936).

[8] W. F. Luder, THIS JOURNAL, **62**, 89 (1940).

[9] W. F. Luder, *Rev. Scientific Inst.*, **14**, 1 (1943).

[10] Dunstan, Hilditch, and Thole, *J. Chem. Soc.*, **103**, 133 (1913).

[11] Drs. J. L. Oncley and Paul Gross of the Harvard Medical School very kindly determined the dielectric constant at 25° using a sample of ethylenediamine prepared by us.

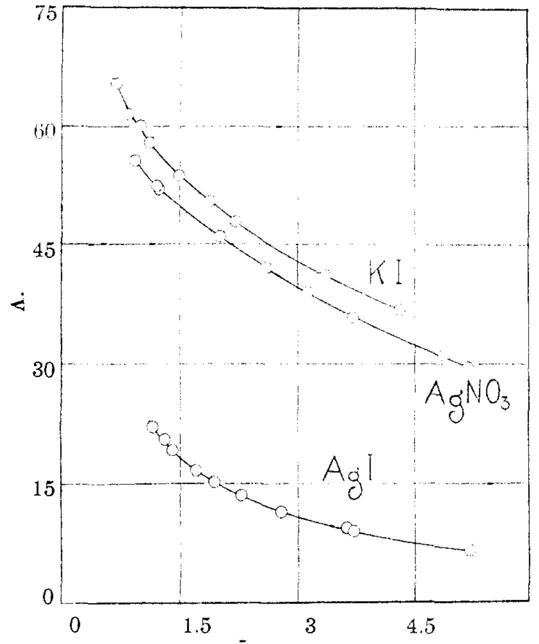


Fig. 1.

Fuoss.[12] The resulting extrapolations are shown in Fig. 2. The values obtained together with the "ion sizes" calculated from K[13] are given in Table IV. The accuracy of the measurements was probably about 0.1%, but, due to the uncertainty in the solvent conductance correction, values of Λ_0 may be off several per cent. However the values of K are apparently as good as most of those in the literature.

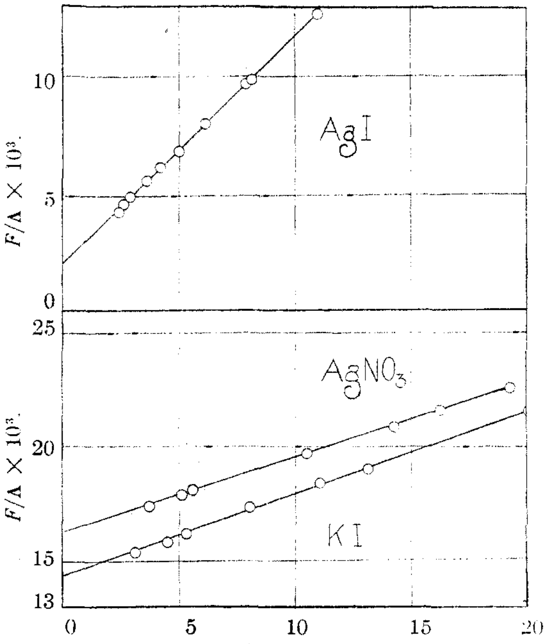


Fig. 2.

TABLE I

POTASSIUM IODIDE IN ETHYLENEDIAMINE AT 25°

$C \times 10^3$	Λ	$C \times 10^3$	Λ
4.595	27.8	3.140	31.5
1.696	37.1	0.950	41.4
0.348	50.2	.453	48.1
.122	58.1	.216	53.9
.062	62.2	.099	60.1
.049	65.5		

TABLE II

SILVER NITRATE IN ETHYLENEDIAMINE AT 25°

$C \times 10^3$	Λ	$C \times 10^3$	Λ
3.340	29.7	2.378	32.1
1.351	36.1	0.980	38.8
0.736	40.8	.586	42.8
.363	46.1	.148	52.1
.147	52.6	.087	56.0

TABLE III

SILVER IODIDE IN ETHYLENEDIAMINE AT 25°

$C \times 10^3$	Λ	$C \times 10^3$	Λ
6.615	4.79	4.490	5.36
2.748	6.91	1.355	9.30
1.420	9.11	0.525	13.51
0.794	11.51	.287	16.91
.380	15.24	.194	19.36
.167	20.48	.140	21.95

TABLE IV

Salt	Λ_0	$K \times 10^4$	$a \times 10^8$
KI	69.2	6.02	5.34
AgNO$_3$	61.4	8.07	5.98
AgI	48.8	0.431	3.84[a]

[a] This value has no meaning since other than coulomb forces are involved.

The purpose of the investigation was to secure data relevant to the electronic theory of acids and bases.[3,4] In spite of the fact that only three salts were measured, due to the premature termination of the work, some interesting conclusions may be drawn. It is not surprising that the solubility of potassium nitrate is too low for conductance measurements. The potassium ion has very little tendency to associate with bases. Silver nitrate because of the acidic silver ion, and potassium iodide because of the acidic nature of the iodide ion (in expanding its valence shell to form coördinate bonds with bases) behave about as expected. "Normal" conductance behavior is observed in that greater ion size as indicated by lower Λ_0 is associated with a larger value of K (Table IV).

At first glance, the behavior of silver iodide seems rather surprising. The low Λ_0 value indicates larger ions as would be expected since both ions should be solvated rather than only one as in the case of potassium iodide and silver nitrate. But instead of a larger value of K it

---

(12) R. M. Fuoss, THIS JOURNAL, **57**, 488 (1935).

(13) Fuoss and Kraus, *ibid.*, **55**, 1019 (1933).

is actually only about one-fifteenth the values for the other two salts. The explanation doubtless lies in the fact that the model, upon which the expectation of a high K value accompanying low mobility is based, assumes only the presence of coulomb forces between the ions.[13] In the case of silver iodide there are additional forces present which make K less than predicted when coulomb forces alone are involved. These forces are of the acid–base type.[3,4] The amphoteric nature of the iodide ion is well known[14] and is here substantiated. The results for silver nitrate and potassium iodide indicate that both silver and iodide ions are acting as acids in their association with the highly basic solvent. But toward the acidic silver ion the iodide ion acts as a base, tending to donate a pair of electrons to give partial covalent character[15] to the bond between the two ions. The presence of these additional forces decreases K to a value far below that expected from the low value of Λ_0.

IV. Summary

The conductances of three salts, potassium iodide, silver iodide, and silver nitrate in ethylenediamine have been measured, at concentrations low enough to permit calculation of Λ_0 and K. The best solvent that could be obtained had a conductance of 9×10^{-8} mho. An explanation based on the electronic theory of acids and bases is offered for the extraordinarily low value of K for silver iodide.

---

[14] R. B. Sandin, *Chem. Rev.*, **32**, 249 (1943).

[15] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

BOSTON, MASS. RECEIVED OCTOBER 8, 1943

[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL CO.]

Isomerization of Tri-alkyl Phosphites

BY GENNADY M. KOSOLAPOFF

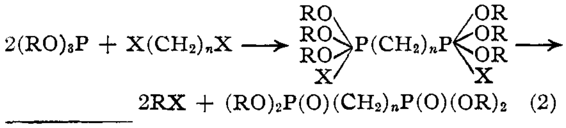
The isomerization of tri-alkyl phosphites in the course of the reaction with alkyl halides, according to the scheme

$$(RO)_3P + R'X \longrightarrow (RO)_3PR'X \longrightarrow RX + R'P(O)(OR)_2 \quad (1)$$

was first studied rather extensively by Arbuzov,[1] who utilized this reaction as an elegant method of preparation of a number of phosphonic acid esters.

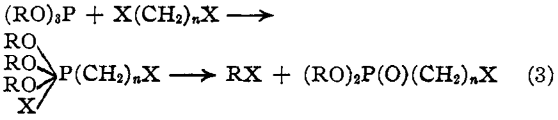
Usually the reaction is carried out by heating the reagents in a sealed tube, followed by distillation of the products. Under these conditions there are usually formed varying, and sometimes considerable, amounts of $RP(O)(OR)_2$, apparently formed through interaction of RX with either unreacted $(RO)_3P$ or the intermediate $(RO)_3PR'X$. It was felt that if the RX formed in the reaction were to be removed as rapidly as possible from the reaction mixture, not only should the course of the reaction be cleaner, but the measurement of RX evolved should offer a ready method for following the course of the reaction.

It was also felt that a technique employing the above principle could be utilized in obtaining additional information on the course of the reaction between tri-alkyl phosphites and paraffin dihalides. This reaction may be expected to follow both of the possible courses



$$2(RO)_3P + X(CH_2)_nX \longrightarrow \begin{matrix}RO\\RO\\RO\\X\end{matrix}\!>\!P(CH_2)_nP\!<\!\begin{matrix}OR\\OR\\OR\\X\end{matrix} \longrightarrow$$
$$2RX + (RO)_2P(O)(CH_2)_nP(O)(OR)_2 \quad (2)$$

and



$$(RO)_3P + X(CH_2)_nX \longrightarrow$$
$$\begin{matrix}RO\\RO\\RO\\X\end{matrix}\!>\!P(CH_2)_nX \longrightarrow RX + (RO)_2P(O)(CH_2)_nX \quad (3)$$

Actually, the literature data are rather meager as to information on the course of this reaction. Thus, Arbuzov and Kushkova[2] isolated from the reaction of methylene iodide and triethyl phosphite only the iodomethanephosphonic acid diethyl ester, *i. e.*, the product of reaction (3), among other substances. More recently, Parfent'ev and Shafiev[3] investigated the reaction of triethyl phosphite and trimethylene bromide, obtaining a product corresponding to the γ-bromopropanephosphonic acid diethyl ester, which could not be distilled without decomposition, and was apparently formed according to reaction (3). Nylen[4] studied the reaction between sodium diethylphosphite and methylene chloride, ethylene bromide and trimethylene bromide, obtaining $CH_2(PO(ONa)(OEt)_2)_2$, ethylene and tetraethyl trimethylenediphosphonate, respectively, as the identifiable reaction products.

From consideration of the available information it was evident that a further study of this reaction was desirable with variation of the proportions of the reactants as a means of influencing the predominance of either reaction (2) or (3).

---

[1] A. E. Arbuzov, "On the Structure of Phosphorous Acid," N. Alexandria, 1905.

[2] Arbuzov and Kushkova, *J. Gen. Chem.* (U. S. S. R.), **6**, 283 (1936).

[3] L. N. Parfent'ev and M. Kh. Shafiev, *Trudy Uzbesksk. Gos. Univ., Sbornik Rabot Khim.*, 87–94 (1939).

[4] P. Nylen, "Studien über organische Phosphorverbindungen," Upsala, 1930.