Details of Rate Data.—Complete experimental and calculated data for all the completed runs would consume far too much space to serve any useful purpose. To make completely clear our methods, however, Table V has been prepared summarizing the calculations for run number 16 (see also Fig. 8). The data of all completed runs were entirely consistent.

Acknowledgment.—The authors wish to acknowledge the many helpful suggestions and assistance of Prof. G. K. Rollefson, Drs. M. Kasha and R. V. Nauman, and Messrs. F. M. Huennekens and D. M. McClure. The junior author also wishes to express his appreciation for the assistance of the National Research Council.

Summary

1. The photochemical oxidation of a simple chlorin molecule to the corresponding porphin by oxygen and a number of ortho and para quinones is described.

2. From evidence based on rate experiments, a mechanism for the photochemical oxidation of tetraphenyl chlorin by β-naphthoquinone is derived involving the triplet state of the chlorin molecule as an intermediate.

3. A possible significance of the triple state of chlorophyll is indicated.

BERKELEY, CALIFORNIA RECEIVED JULY 8, 1947

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXXI. Conductance of Some Electrolytes in Pyridine at 25°[1]

BY DAVID S. BURGESS[2] AND CHARLES A. KRAUS

I. Introduction

In the last paper of this series,[3] it was shown that various quaternary onium salts are normal electrolytes in pyridine. Silver picrate and perchlorate, however, proved to have much larger dissociation constants than was to have been expected. Certain unreported results for sodium and potassium salts were erratic, indicating sources of error that had not been brought under control.

In view of these circumstances a comprehensive study of solutions in pyridine seemed worth-while.

It was suspected that inconsistencies in the results obtained with the alkali metal salts may have been due to the presence of small amounts of alcohol even though the conductance of the solvent was very low. On treating the pyridine with aluminum chloride, solvent was obtained that yielded consistent results with all salts. The marked effect of alcohol and, perhaps, other impurities that were eliminated by aluminum chloride, led to a study of the effect of the addition of small polar molecules, such as water, ammonia and methanol, on the characteristic constants of electrolytes dissolved in pyridine.

An investigation was made of several lithium, sodium and potassium salts and, in view of the unusual behavior of silver salts, silver picrate was included among the salts studied.

Certain quaternary ammonium salts which have been investigated in ethylene chloride and nitrobenzene, were measured for purposes of comparison. These salts were: tetra-*n*-butylammonium nitrate and acetate, tetramethylammonium picrate, ethyltrimethyl-, hydroxyethyltrimethyl-, bromoethyltrimethyl-, bromomethyltrimethyl-, and phenyldimethylhydroxy-ammonium picrate.

Measurements with pyridonium and piperidonium nitrates, as well as with phenylpyridonium picrate, are of obvious interest in view of the strong proton affinity of the solvent.

Measurements were also carried out with ammonium picrate, iodide and nitrate. The nitrate yielded inconsistent values for the conductance of the ammonium ion; publication of results for this salt is withheld pending further investigation.

In order to evaluate ion conductances, measurements have been made with tetrabutylammonium triphenylborofluoride and a value for the conductance of the tetrabutylammonium ion has thus been obtained according to Fowler's[4] method.

II. Experimental

Materials.—Pyridine prepared by the method of Luder[3] failed to yield consistent results; the procedure was, accordingly, modified so as to provide for elimination of residual traces of alcohol. This was accomplished by distillation from aluminum chloride. The distillate was then fractionally distilled, refluxed over aluminum oxide and finally fractionated. Pyridine obtained in this manner had a specific conductance below 1×10^{-9} and reproducible conductance values were obtained with salts which had previously yielded inconsistent results.

Methanol was refluxed over aluminum amalgam and finally distilled. Its specific conductance was 5×10^{-8}; a 0.275 *M*, solution in pyridine showed a specific conductance of 2×10^{-9}.

Ammonia was dried by distillation from sodium amide. A 0.0733 *M* solution of ammonia in pyridine had a specific conductance of 6×10^{-9}.

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(1) This paper is based on a portion of a thesis presented by David S. Burgess in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1940.

(2) University Fellow at Brown University, 1938–1939; Metcalf Fellow, 1939–1940. Present address: 1106 N. College Ave., Fayetteville, Arkansas.

(3) Luder and Kraus, THIS JOURNAL, **69**, 2481 (1947).

(4) Fowler and Kraus, *ibid.*, **62**, 2237 (1940).

Sodium and potassium iodides of reagent grade were recrystallized from water and from alcohol.

Lithium, sodium and potassium picrates were prepared from the corresponding bases and recrystallized picric acid. Potassium picrate was recrystallized from water and from ethyl alcohol. The sodium salt was recrystallized from water and from methyl alcohol. It was necessary to heat this salt to 85° in a vacuum before a constant weight was obtained. Lithium picrate was recrystallized from pure ethanol and was dried in the same manner as the sodium salt.

Tetrabutylammonium nitrate was prepared by the method described by Cox,[5] m. p. 118°.

Tetrabutylammonium acetate was prepared by the metathesis of the pure iodide with recrystallized silver acetate in aqueous solution. The solution was filtered off from the silver iodide, concentrated, and pumped to dryness. The residue was dissolved in benzene, the solution filtered and the filtrate pumped to dryness. The salt residue was kept over phosphorus pentoxide in an evacuated tube for several weeks and then used directly in a series of measurements; m. p. 118°. Another sample of the acetate which had been recrystallized from butyl chloride was furnished by Dr. W. E. Thompson.[6]

Pyridinium nitrate was recrystallized from alcohol; m. p. 117.5–118°. Piperidonium nitrate was recrystallized from ethanol–benzene mixtures and was precipitated from ethylene chloride with anhydrous ethyl acetate. It decomposed without melting at 100°.

Phenylpyridonium chloride was prepared by the method of Zincke[7]; m. p. 106°. Metathesis of this salt with silver picrate in alcohol solution yielded phenylpyridonium picrate. This salt was recrystallized from alcohol; m. p 121–122°. An analysis for nitrogen, using catalytic hydrogenation at 350°, gave nitrogen 14.3%; calculated 14.6%.

The remaining salts had been prepared and purified in this laboratory. All were subjected to a final recrystallization from alcohol before use in conductance measurements.

Apparatus and Procedure.—Except for a few details, these were the same as described in earlier papers of this series. Buoyancy corrections (of about 0.1%) were applied in calculating the concentration of solutions of heavier salts.

Ammonia was introduced into the pyridine by attaching the pyridine reservoir (by means of a flexible tube) to a four-liter flask containing air and ammonia in proper proportions at atmospheric pressure. The partial pressure of ammonia was maintained equal to that at which the pyridine was to be saturated. As the ammonia was absorbed by the pyridine, more ammonia was admitted from the tank of purified ammonia, keeping the total pressure in the system constant. The ammoniated pyridine was forced into the conductance cell each time by means of a pressure of air and ammonia over the liquid in the stock flask, thus avoiding change in the composition of the solvent medium.

In order to minimize vapor corrections when working with ammoniated pyridine, the cell used was of small capacity (about 60 ml.) and the side arm leading to the electrode chamber was wide enough to permit mixing when the liquid level in the cell was high. Only a small free volume was allowed above the solution, and diffusion losses were kept low by having a long, narrow neck fitted to the cell. Water and alcohol were added to pyridine in a 500-ml. flask from a micropipet fitted with a drawnout capillary.

III. Results

The experimental data are summarized in Tables I and II in which are given the equivalent conductance Λ and the concentration C of the solution in moles per liter of solution, whose density was taken to be 0.97792.[8] Data for solutions in pure pyridine are given in Table I, while those for solutions containing added dipolar substances are given in Table II. The result of only one series of measurements is reported for each salt although at least two concordant series were carried out. All measurements were carried out at 25±0.01°.

TABLE I

CONDUCTANCE OF SOME SALTS IN PYRIDINE AT 25°

$C \times 10^5$	Λ	$C \times 10^5$	Λ
a. Lithium picrate		b. Sodium picrate	
75.68	18.59	70.90	15.11
26.16	27.23	33.44	20.07
9.901	35.67	13.70	27.46
6.909	38.92	6.196	34.89
3.457	44.63	3.544	40.20
2.607	46.76	1.626	46.94
1.354	51.79		
c. Potassium picrate		d. Silver picrate	
39.46	28.50	145.94	49.93
16.57	36.89	69.53	54.20
6.355	46.31	32.48	58.11
3.244	52.09	14.83	61.30
1.901	56.40	6.242	63.80
		2.261	65.67
e. Sodium iodide		f. Potassium iodide	
474.7	25.05	62.25	39.79
23.25	53.71	27.38	49.39
11.144	60.45	21.26	52.36
8.656	62.40	10.79	59.96
6.481	64.45	6.564	64.68
4.219	66.99	3.328	70.08
g. Ammonium picrate		h. Ammonium iodide	
56.94	44.34	29.23	59.32
30.41	51.58	13.18	70.03
15.20	59.15	7.296	76.96
5.940	63.56	3.749	83.22
3.894	70.60	1.577	88.75
i. Tetra-*n*-butylammonium nitrate		j. Tetra-*n*-butylammonium acetate	
129.50	37.08	114.0	29.18
53.72	46.15	45.81	28.22
23.52	54.75	20.62	46.85
9.655	62.82	11.15	53.37
3.852	68.82		
k. Tetra-*n*-butylammonium triphenylborofluoride		l. Phenylpyridonium picrate	
86.73	33.13	121.94	43.32
32.95	37.94	58.16	48.80
18.92	40.34	32.18	52.86
9.774	42.62	15.10	57.08
5.161	44.33	7.042	60.35
		3.117	62.69

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[5] Cox, Kraus and Fuoss, *Trans. Faraday Soc.*, **31**, 749 (1935).

[6] Thompson and Kraus, THIS JOURNAL, **69**, 1018 (1947).

[7] Zincke, *Ann.*, **333**, 328 (1904).

[8] Walden, Audrieth and Birr, *Z. physik. Chem.*, **160A**, 337 (1932).

TABLE I (*Concluded*)

$C \times 10^5$	Λ	$C \times 10^5$	Λ
m. Tetramethylammonium picrate		n. Ethyltrimethylammonium picrate	
37.37	56.63	133.7	45.22
15.48	63.72	67.62	51.54
8.345	67.66	32.62	57.91
7.754	68.00	17.14	62.75
5.517	69.80	7.215	67.81
2.822	72.18	3.472	71.03
1.915	73.15		
o. Hydroxyethyltrimethylammonium picrate		p. Bromoethyltrimethylammonium picrate	
62.54	47.19	275.6	32.15
29.07	52.83	128.0	38.43
13.92	57.35	67.65	43.47
7.278	60.35	29.78	49.85
2.552	63.68	13.46	55.32
		6.483	59.39
		3.412	62.39
q. Bromomethyltrimethylammonium picrate		r. Phenyldimethylhydroxyammonium picrate	
37.41	49.15	133.9	40.36
19.55	54.85	64.15	45.58
8.643	60.75	27.51	50.73
3.547	65.41	11.58	55.06
1.944	67.69	6.985	57.44
		3.821	60.48
s. Pyridonium nitrate		t. Piperidonium nitrate	
21.66	42.50	16.92	27.36
10.28	53.82	7.923	36.40
4.109	68.48	4.101	45.50
2.348	76.79	1.736	58.16
1.863	79.79		

TABLE II

CONDUCTANCE OF SALTS IN PYRIDINE IN THE PRESENCE OF ADDED POLAR SUBSTANCES

$C \times 10^5$	Λ	$C \times 10^5$	Λ
a. Tetrabutylammonium picrate (0.0733 *M* ammonia)		b. Tetrabutylammonium picrate (0.146 *M* ammonia)	
59.06	42.48	72.73	41.40
32.69	46.04	55.06	43.26
16.61	49.52	33.78	46.26
8.204	52.36	15.22	50.38
5.547	53.58	8.615	52.66
c. Potassium picrate (0.275 *M* methanol)		d. Sodium picrate (0.0070 *M* water)	
116.4	22.82	65.94	16.27
64.36	27.70	25.15	23.19
24.50	36.81	10.90	30.55
9.605	46.09	6.105	36.15
4.890	52.69	4.258	39.55
e. Sodium picrate		3.164	42.28
(0.733 *M* ammonia)		1.931	46.49
157.2	19.82		
73.82	27.27		
29.80	36.50		
13.86	48.10		
8.543	52.71		

IV. Discussion

A. Solutions in Pure Pyridine.—The experimental data have been analyzed by the method of Fuoss[9] so as to obtain values for the limiting conductance and dissociation constant of the electrolytes under consideration. The dielectric constant and viscosity of pyridine were taken as 12.01[10] and 0.008824.[8] Plots were made of F/Λ against $C\Lambda f^2/F$ and values of Λ_0 and K were determined therefrom. These values are given in Table III and plots for some of the salts are shown in Fig. 1. All plots are linear at low concentrations but deviations become apparent a little below the critical concentration, 5×10^{-4}. The strongest electrolytes deviate toward too high a conductance and weaker electrolytes toward too low a conductance.

TABLE III

CONSTANTS FOR SOME SALTS IN PYRIDINE AT 25°

Salt	Λ_0	Λ_0^+	Λ_0^-	$K \times 10^4$
$(C_4H_9)_4NFB(C_6H_5)_3$	48.0	(24.0)	(24.0)	13.2
$(C_4H_9)_4NNO_3$	76.6	..	52.6	3.7
$(C_4H_9)_4NCH_3COO$	76	..	52	1.7
$(CH_3)_4NPi$	76.7	43.0	(33.7)[3]	6.7
$(C_2H_5)(CH_3)_3NPi$	75.5	41.8	..	8.2
$(HOC_2H_4)(CH_3)_3NPi$	67.0	33.3	..	1.5
$(BrC_2H_4)(CH_3)_3NPi$	67.1	33.4	..	5.8
$(BrCH_2)(CH_3)_3NPi$	71.5	37.8	..	4.8
$C_5H_5N(C_6H_5)Pi$	66.3	32.6	..	11.5
$(C_6H_5)(CH_3)_2(OH)NPi$	62.3	28.6	..	12.3
$C_5H_5NHNO_3$	102.2	49.6	..	0.51
$C_5H_{10}NH_2NO_3$	91.1	38.5	..	0.18
$AgNO_3$	86.9[3]	34.3	..	9.3
AgPi	68.0	34.3	..	30.6
LiPi	58.6	24.9	..	0.83
NaPi	60.5	26.8	..	0.43
KPi	65.7	32.0	..	1.0
NH_4Pi	80.5	46.8	..	2.8
NaI	75.2	..	48.4	3.7
KI	80.4	..	48.4	2.1
NH_4I	95.2	..	48.4	2.4

Ion Conductances.—In order to obtain the ion conductances given in columns three and four of Table III, we have assumed, as did Fowler[4] for ethylene chloride, that the conductance of the tetrabutylammonium ion is equal to that of the triphenylborofluoride ion. This gives a value of 24.0 for the conductance of the tetrabutylammonium ion. Using Luder's value for the limiting conductance of tetrabutylammonium picrate,[3] we arrive at a value of 33.7 for the conductance of the picrate ion. The remaining ion conductances are easily evaluated on the basis of these values. It may be noted here that tetrabutylammonium picrate has been reinvestigated and no appreciable error has been found in Luder's data, although traces of alcohol may have been present in his pyridine.

(9) Fuoss, THIS JOURNAL, **57**, 488 (1935).

(10) Le Fèvre, *J. Chem. Soc.*, 776 (1935).

Several salt pairs permit intercomparison of ion conductance as derived from different combinations. Thus the conductance of the silver ion, as derived from its picrate, is 34.3; from Luder's value for the conductance of silver nitrate, the same value is obtained for the silver ion. Evaluating the conductance of the sodium, potassium and ammonium ions from the conductance of their picrates, the conductance of the iodide ion may be found from the conductance of the corresponding iodides. The value found is 48.4 for the three salts. This value is not in agreement with Luder's value of 49.1 as found from the conductance of tetrabutylammonium iodide.

The conductance of the simpler negative ions is markedly greater than that of corresponding positive ions. For the perchlorate and bromide ions Luder found conductance values of 47.6 and 51.3, respectively; for the nitrate ion, we have found the value 52.6. In contrast, the conductance of the tetramethylammonium ion is only 43.0, while that of the ammonium ion is 46.8.

The conductance of the pyridonium ion is 49.6, the highest for any cation thus far measured. It seems not unlikely that this high value, considering the size of the ion, is due to proton transfer from one solvent molecule to another, as with the the hydrogen ion in water.

The conductance of the alkali metal ions decreases markedly with decreasing dimensions of the unsolvated ion. Thus, the conductance of the lithium ion is little greater than that of the tetrabutylammonium ion. Obviously, there is strong interaction between the free ion and the solvent molecules as a result of which the mobility of the ion is greatly reduced. There is evidence (to be presented in another paper) that small negative ions likewise have a low conductance. The sodium and potassium ions, also, have low conductances. It will be noted that the conductance of the silver ion is greater than that of the potassium ion.

The introduction of negative elements or groups into the cation results in a marked decrease of conductance. Thus, the conductance of the ethyltrimethylammonium ion is 41.8 while that of the bromomethyltrimethylammonium ion is 37.8 and that of the bromoethyltrimethylammonium ion is 33.4. These effects are significant and indicate increased interaction with the solvent molecules as a result of the presence of the negative atoms or groups in the cations. The conductance of the phenyldimethylhydroxyammonium ion is lower than that of the phenylpyridonium ion. There is reason for believing that the hydrogen of the hydroxyl group interacts strongly with the basic pyridine molecules.

Dissociation Constants.—The value of the dissociation constants of normal quaternary ammonium salts are such as might be expected for a solvent whose dielectric constant is 12. It is to be noted, however, that the dissociation constant does not change greatly with increasing dimension of the quaternary ammonium ion. Thus, the constant for tetrabutylammonium picrate[3] is only twice that of tetramethylammonium picrate. The constants of tetrabutylammonium salts of different negative ions follow the order of ion dimensions fairly well, the constants following the order $I^- > NO_3^- > Br^- > Ac^-$. The low value of the constant for the acetate is noteworthy.

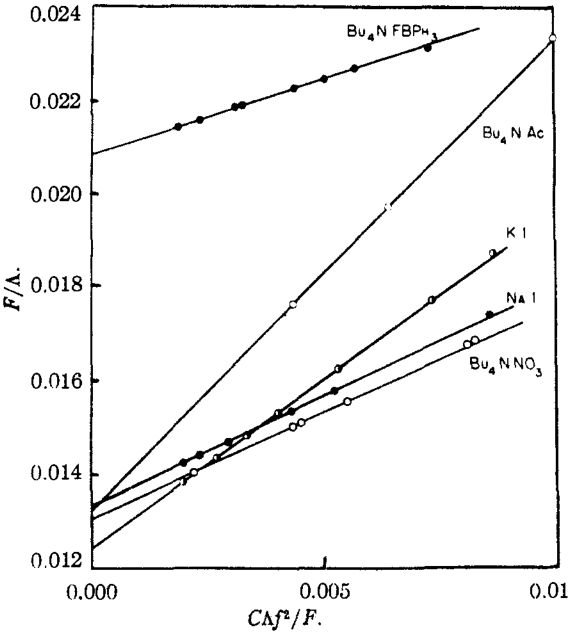

Fig. 1.—Fuoss plots for salts in pyridine at 25°.

The introduction of negative atoms or groups into the quaternary cation structure has a marked effect on the dissociation constant. Substitution of the hydroxyl group in the ethyl group of the ethyltrimethylammonium ion decreases the dissociation constant of the picrate fivefold, while introduction of a bromine atom decreases the constant 25%. Bromomethyltrimethylammonium picrate is a markedly weaker salt than tetramethylammonium picrate. Negative atoms or groups in the positive ions intensify the interaction of such ions with negative ions.

The dissociation constant of an electrolyte is determined by the distance of closest approach of the ions in the ion-pairs. We should, therefore, expect salts of larger ions to have larger dissociation constants, which ions should also have lower conductances. This simple relation usually fails in most solvents that are not of the hydroxylic type. Due to interaction with solvent molecules, ions may have a low conductance, but in their interaction with oppositely charged ions these molecules are not retained in the ion-pairs. This is well illustrated by the salts of lithium, sodium and potassium. The tetramethylammonium ion has a conductance of 43.0, and its picrate has a dissociation constant of 6.7×10^{-4}. On the other hand, lithium, sodium, and potassium ions have conductances of 24.9, 26.8 and 32.0, respectively, while their dissociation constants are, respectively, 0.83×10^{-4}, 0.43×10^{-4} and 1.0×10^{-4}. The picrate of the ammonium ion, whose conductance is 46.8, has a constant of 2.8×10^{-4}. In the case of sodium and potassium iodides, the constants increase in the order of decreasing ion conductance. It is of interest to point out that the dissociation constant of tetrabutylammonium iodide is 4.1×10^{-4}, only one-fourth that of the picrate $(12.8 \times 10^{-4})^3$. In the iodide, the sodium ion behaves like a large ion having a constant of 3.3×10^{-4}, but little smaller than that of the tetrabutylammonium salt. It will be recalled that the conductance of the two cations is 26.9 and 24.0, respectively.

An interesting case is that of the phenyldimethylhydroxyammonium ion, whose conductance is 28.6. The dissociation constant of the picrate of this ion is 12.3×10^{-4}, practically the same as that of tetrabutylammonium picrate. The hydrogen of the hydroxyl group evidently interacts strongly with the basic pyridine molecules and these molecules must be, in large measure, retained in the ion-pairs. However we may interpret the result, this ion in its interaction with other ions is effectively nearly as large as the tetrabutylammonium ion.

Pyridonium nitrate is a weak salt with a constant of 0.5×10^{-4}; piperidonium nitrate is an even weaker salt with a constant of 0.18×10^{-4}. Apparently, the additional hydrogen atom attached to nitrogen in the latter cation leads to interaction with the negative ion to yield the lower constant. It is of interest to note that phenylpyridonium picrate has a constant of 11.5×10^{-4} which is practically the same as that of tetrabutylammonium picrate. The geometrical configuration of an ion is an important factor in determining the properties of its salts.

An unexpected and exceptional result of this and the preceding investigation[3] is the high value of the dissociation constant for silver salts. For the nitrate, perchlorate and picrate, the constants are, respectively, 9.3×10^{-4}, 19.1×10^{-4} and 30.6×10^{-4}. Considering that the conductance of the silver ion is 34.4, which corresponds to that of only a moderately large ion, it is surprising to find a constant for silver picrate more than twice that of tetrabutylammonium picrate. If the distance between centers of charge in the ion-pairs is calculated according to the method of Fuoss,[11] the values "a" for the above mentioned silver salts are 6.6 Å., 10.6 Å. and 13.2 Å., respectively. The silver ion is exceptional in its interaction with other ions.

B. Solutions Containing Added Polar Molecules.—The results presented in Table II for solutions containing ammonia, water and methanol in small amount have been analyzed by the usual graphical method. Values of Λ_0 and of K for several salts are given in Table IV.

TABLE IV

EFFECT OF ADDED POLAR MOLECULES ON THE CONDUCTANCE OF SALTS IN PYRIDINE

Salt	Concn. added compound	Λ_0	$\Delta\Lambda_0$	$K \times 10^4$
$(C_4H_9)_4NPi$	0.000	57.68	..	12.2
	.073 NH_3	58.12	0.44	12.2
	.146 NH_3	58.58	.90	12.2
NaPi	0.000	60.5	..	0.44
	.007 H_2O	60.5	0.0	.49
KPi	0.000	65.27	..	1.00
	0.275 CH_3OH	64.10	−1.17	1.32
NaPi	0.000	59.98	..	0.44
	.733 NH_3	80	20	.66

As may be seen from the table, the addition of ammonia to a solution of tetrabutylammonium picrate in pyridine causes a small increase in the value of Λ_0 while the dissociation constant remains unchanged. The addition of 0.007 M of water to a solution of sodium picrate causes a 10% increase in the dissociation constant while the limiting conductance remains unchanged. The addition of 0.275 M methanol to a solution of potassium picrate increases the dissociation constant 32% while it decreases the limiting conductance 1.8%.

A striking result was obtained on the addition of ammonia to a solution of sodium picrate. For an ammonia concentration of 0.733 M, the conductance was increased approximately 20 units, or 33%. Since ammonia has but little influence on the conductance of the picrate ion, as shown by the results with tetrabutylammonium picrate, the observed conductance increase of sodium picrate must be due to an increase of approximately 50% in the conductance of the sodium ion.

While the present measurements are preliminary, there is no question as to their authenticity. Subsequent investigations, the results of which will be reported later, have confirmed the present results and have disclosed similar effects for other salts.[12] A comparison of conductance values in Table I, b, and Table II, e, will show that the conductance of sodium picrate in the presence of ammonia is much higher than it is in pure pyridine at all concentrations. This is due to the fact that while the dissociation constant of sodium picrate is not increased greatly (50%) on addition of ammonia, the conductance of the sodium ion is greatly increased. The low conductance of the sodium ion in pyridine is due to its interaction with pyridine molecules; more than one pyridine molecule must be associated with the sodium ion in order to account for its low conductance. The replacement of pyridine by smaller ammonia molecules results in a smaller ion of higher conductance. In the ion-pair equilibrium, however, the ammoniated ion is effectively somewhat larger than is the normal sodium ion in pure pyridine.

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[11] Fuoss and Kraus, THIS JOURNAL, **55**, 1019 (1933).

[12] C. J. Carignan, unpublished observations in this Laboratory.

V. Summary

1. The conductance of the following salts has been measured in pyridine at 25°: tetrabutylammonium nitrate, acetate and triphenylborofluoride; tetramethylammonium, ethyltrimethylammonium, hydroxyethyltrimethylammonium, bromoethyltrimethylammonium, bromomethyltrimethylammonium, phenyldimethylhydroxyammonium, ammonium, lithium, sodium, potassium and silver picrate; ammonium, sodium and potassium iodide; and pyridonium and piperidonium nitrate.

2. The conductance has also been determined for solutions of tetrabutylammonium picrate in the presence of ammonia; sodium picrate in the presence of ammonia and of water and potassium picrate in the presence of methanol.

3. The experimental results have been analyzed by the usual graphical methods and values of Λ_0 and of the dissociation constant K have been obtained for all the systems investigated. Ion conductances have been evaluated by the method of Fowler.

4. The effect of various interactions on ion conductances and dissociation constants are discussed.

5. It has been shown that the addition of polar molecules to the solvent medium usually causes little change in ion conductance of salts having large ions. With salts of smaller ions, the dissociation constant is often increased. In the case of sodium picrate, the addition of ammonia causes a very large change in Λ_0, up to as much as 33%, with only a small increase in the dissociation constant.

PROVIDENCE, R. I. RECEIVED JUNE 20, 1947

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Thallous Sulfoxylate Isomerism[1]

BY J. FENTRESS AND P. W. SELWOOD

The fact that thallous sulfide, Tl_2S, is easily oxidized when exposed to air was first pointed out by Lamy.[1a] At that time it was postulated that the final product of this oxidation was thallous sulfate, Tl_2SO_4. More recent investigation of the oxidation by Iskoldsky[2] has served to confirm much of Lamy's work. It is found that at 720° in air, thallous sulfide is oxidized 90% to thallous sulfate in two and a half hours. Further, the oxidation of the sulfide proceeds step-wise with the intermediate compounds, Tl_2SO_2 and Tl_2SO_3, being identified. Although one might expect to find a compound with the formula Tl_2SO, Iskoldsky was unable to prepare such a compound.

With Case's[3] discovery of the photo-sensitivity of oxidized thallous sulfide, and the more recent improvements on "Thalofide" photo-cells by Cashman[4] and several others,[5–9] new interest has developed in the actual oxidation of thallous sulfide, and the products formed.

The percentage of oxygen in various photo-sensitive cells[10] varies up to as much as a nearly 1:1 mole ratio of Tl_2:O_2, corresponding to the formula Tl_2SO_2. Thus, our interest in thallous sulfide oxidation products, from the point of view of identifying the composition of the photo-sensitive material, only extends as far as Tl_2SO_2 and is not concerned with the complete oxidation to thallous sulfate.

This present study is concerned with the two forms of thallous sulfoxylate[11] that we were able to obtain.

Preparation of Thallous Sulfide.—Thallous sulfide may be prepared either by precipitation at ordinary temperatures, or by direct reaction of thallium metal and sulfur at high temperatures. We selected the former method because early experiments indicated that oxidation proceeds more rapidly with thallous sulfide prepared by precipitation methods.

All the thallous sulfide used in our experiments was prepared by precipitation from alkaline thallous sulfate solution. The thallous sulfate starting material was originally 99% pure commercial material, which was purified by three recrystallizations from aqueous solution. This procedure yielded thallous sulfate which when analyzed by the standard chromate method gave results of satisfactorily high purity, *i. e.*, more than 99.9% of the theoretical thallium content.

A dilute solution of thallous sulfate, under nitrogen atmosphere, was made alkaline with ammonium hydroxide and the thallous sulfide precipitated at 50° with hydrogen sulfide in the pre-

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