melting points of the rest are surprisingly low.

An inspection of Fig. 1 shows which one, or two, of these reagents to use to differentiate between any two alcohols.

Experimental

Preparation of Isocyanates.—The compound *p*-xenyl isocyanate was prepared by treating *p*-xenylamine hydrochloride with phosgene following the method of Hardy.[8] The compounds, 2-fluorenyl isocyanate and *p*-triphenylmethylphenyl isocyanate were prepared similarly from the appropriate amine hydrochloride.

Into a 1-liter, 3-necked flask equipped with a mechanical agitator, a gas inlet tube, a thermometer and a reflux condenser, was introduced 10 g. of the appropriate amine dissolved in 200 ml. of toluene. The solution was agitated, heated to 50° and dry hydrogen chloride passed in until the solution was saturated. The solid hydrochloride precipitated from solution. The solution was heated to reflux and dry phosgene was passed in until nearly all of the solid had dissolved (about two hours). The mixture was filtered, and the filtrate, which contained the isocyanate, was evaporated to dryness. The residue was recrystallized from ligroin. The results are summarized in Table II.

Preparation of Carbamates.—A solution of 0.5 g. of *p*-triphenylmethylphenyl, 2-fluorenyl, or *p*-xenyl isocyanate dissolved in 5 ml. of toluene reacted with 50% excess of the *n*-alcohol by heating in a boiling water-bath for three hours. With methyl and ethyl alcohols a larger excess was used (5 moles per mole of isocyanate). With methyl alcohol the solution was heated to reflux for three hours. The solution was evaporated to dryness under reduced pressure and the residue was recrystallized twice from alcohol. There was always present some substituted urea which formed as a result of the action of water on the isocyanate, but this compound was insoluble in the alcohol from which the carbamate was crystallized. The carbamates are colorless crystalline solids and the yields are 60–70%.

The carbamates from phenyl and α-naphthyl isocyanates were prepared in similar manner except that the compounds were recrystallized twice from 90–120° ligroin.

Each compound gave an analysis for nitrogen in good accord with that required by theory.

Acknowledgment.—The authors wish to thank Mr. Cecil A. Rush for the microanalyses of the compounds reported in this paper.

Summary

p-Triphenylmethylphenyl isocyanate and 2-fluorenyl isocyanate have been synthesized and two series of carbamates obtained by the reaction of these reagents with the normal alcohols, from methyl to *n*-octadecyl alcohol, inclusive, have been prepared. The missing members of the carbamates from phenyl, α-naphthyl, *p*-xenyl isocyanates have been synthesized.

Comparisons of the melting points indicate that no one reagent is suitable for the identification of all of the alcohols; the reagent has to be selected for the particular alcohol suspected of being present.

EDGEWOOD ARSENAL, MD. RECEIVED APRIL 23, 1947

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[8] Hardy, *J. Chem. Soc.*, 2011 (1934).

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXIX. The Conductance of Some Electrolytes in Nitrobenzene at 25°[1]

BY CHARLES R. WITSCHONKE[2] AND CHARLES A. KRAUS

I. Introduction

In the preceding paper of this series,[3] results were presented which go to show how the properties of electrolytes in nitrobenzene solution are dependent on various constitutional factors. The substances studied were found to fall into three main classes: (1) strong electrolytes whose dissociation constants are in accord with the dielectric constant of the solvent and the dimensions of the constituent ions of the salt; (2) weak electrolytes in which non-coulombic interactions must be considered along with the usual interaction due to coulombic forces; and (3) weak electrolytes in which dissociation into free acid and base takes place to a measurable extent.

In the present paper are presented results of a more detailed study of the phenomena mentioned above, along with some further studies relating to factors not previously considered. This investigation relates to: (A) solutions of stable electrolytes, both inorganic and organic (salts of the alkali metals and of the partially or completely substituted ammonium ions); (B) solutions of salts of weak bases, such as aniline and pyridine, which undergo dissociation into free acid and base; (C) the effect of added bases, such as amines, on the dissociation constant of weak electrolytes, such as partially substituted ammonium salts and trimethylhydroxyammonium salts; and (D) the conductance of solutions of triphenylmethyl halides and of triphenylmethylborofluoride.

The conductance of typical salts of various anions was measured and the influence of the anion on the properties of the electrolyte was studied.

II. Experimental

Apparatus and Procedure.—For the most part, these have been described in earlier papers of this series.[3] Small quantities of the added bases were introduced into the solvent reservoir by

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[1] This paper is based on a portion of a thesis presented by Charles R. Witschonke in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1941.

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[3] Taylor and Kraus, THIS JOURNAL, **69**, 1731 (1947).

means of a small weight pipet or by adding a known weight of the base in a small, fragile bulb.

The solubilities of sodium, potassium and ammonium picrates in nitrobenzene are so low (approximately $2 \times 10^{-4} M$) that it was found necessary to modify the method of making up known solutions. Small quantities of these salts, weighed on a microbalance, were shaken mechanically with a known weight of nitrobenzene until complete solution was effected. The conductance cell was rinsed several times with the solution in order to eliminate adsorption effects. When consecutive resistance readings were identical, a series of dilutions was made in the usual manner.

Resistances above one hundred thousand ohms were measured with a special Leeds and Northrup alternating current parallel bridge which permitted of precision conductance measurements to as low as 10^{-9} mho when necessary.[3a]

Since triphenylmethyl compounds are extremely sensitive to moisture, stringent precautions were taken to eliminate traces of water. The glassware used was thoroughly cleaned, baked and pumped at low pressures. The conductance cell was fitted with a side arm by means of which a pressure of pure dry nitrogen could be maintained in the cell during additions or withdrawals. In spite of these precautions, some hydrolysis proved to be unavoidable.

Materials.—Nitrobenzene of technical grade[4] was washed successively with 1 N sulfuric acid, saturated sodium carbonate solution and water. Most of the water was then removed by shaking with powdered calcium chloride. The dried solvent was then fractionated under low pressure. The temperature of the stillhead was maintained as low as 30° since it was found that the conductance of the distillate was very dependent upon the temperature at which the liquid came over. A slow rate of distillation (about ten drops per minute) also improved the quality of the product.

Several fractionations yielded nitrobenzene having a specific conductance of 5×10^{-10}. The conductance was reduced further to 1×10^{-10} by shaking with activated alumina for at least twenty-four hours. The solvent was freed from fine particles of alumina by means of a fine grade sintered glass filter.

Pyridine of conductance grade was kindly furnished by Dr. D. S. Burgess. The specific conductance of a 0.038 M solution of pyridine in nitrobenzene was approximately 1×10^{-9} while that of a 0.01 M solution was as low as 3×10^{-10}.

Piperidine was purified by Dr. G. W. Moessen; the specific conductance of a 0.001 M solution in nitrobenzene was approximately 3×10^{-9}.

Triethylamine was dried with calcium chloride and fractionated. A 0.001 M solution in nitrobenzene had a specific conductance of 1×10^{-9}. A 0.01 M solution of water in nitrobenzene had a specific conductance of 3×10^{-10}.

Picric acid was recrystallized successively from water, methyl alcohol and benzene, m. p. 122°. The specific conductance of a 0.001 M solution of picric acid in nitrobenzene could not be reduced below 1×10^{-8}.

The partially substituted butylammonium salts were prepared by interaction of the amine with the acid. Butylammonium picrate was recrystallized from water and from ethyl acetate, m. p. 145.2°. Butylammonium perchlorate was recrystallized from nitrobenzene and washed free from the latter with benzene. The salt was further purified by precipitation from ethyl acetate solution by addition of benzene, m. p. 195.4°. Dibutylammonium picrate was recrystallized from ether at the temperature of Dry Ice, m. p. 63.8°. Tributylammonium picrate was recrystallized from alcohol, m. p. 106.6°. The iodide was recrystallized from ethyl acetate, m. p. 103°.

Phenylammonium picrate, dec. 160–165°; phenyldimethylammonium picrate, m. p. 160°; piperidonium picrate, m. p. 152°; and pyridonium picrate, m. p. 162°, were prepared by the interaction of equivalent amounts of the corresponding amine and picric acid. They were purified by recrystallization from water, alcohol or mixtures of the two.

Ammonium lithium, sodium and potassium picrates were kindly furnished by Dr. D. S. Burgess.

Phenyldimethylhydroxyammonium picrate (dec. 137°) and trimethylhydroxyammonium picrate, m. p. 204°, were obtained by oxidation of aqueous solutions of dimethylaniline and trimethylamine, respectively, with hydrogen peroxide and neutralization of the resulting solutions with picric acid. The salts were recrystallized from water and from alcohol.

Tetra-*n*-butylammonium nitrate was prepared by metathesis of the iodide with silver nitrate. The salt was recrystallized from benzene, m. p. 120°. The insoluble form of this salt, reported earlier[4a] was not encountered.

Tetra-*n*-butylammonium bromide was recrystallized from ethylacetate, m. p., 118°.

Tetra-*n*-butylammonium borofluoride was obtained by the interaction of ammonium borofluoride with tetra-*n*-butylammonium hydroxide solution. The salt was recrystallized from water, water–alcohol mixtures and from ethyl acetate by cooling with Dry Ice, m. p., 161.8°.

Tetra-*n*-butylammonium acetate was furnished by Dr. W. E. Thompson. It was recrystallized from dry butyl chloride, m. p., 118 ± 2°.

Tetraethylammonium chloride was recrystallized from ethylene chloride and from acetone–alcohol mixture by cooling with Dry Ice.

Triphenylmethyl chloride was prepared by Dr. E. C. Evers by the reaction of benzene and carbon tetrachloride in the presence of aluminum chloride.[5] To prevent hydrolysis, the salt and its solutions were kept in an atmosphere of dry nitrogen. Recrystallization from pentane–ethyl acetate mixtures at Dry Ice temperatures yielded a pure product, m. p., 111.0–111.3°.

Triphenylmethyl fluoride was obtained by the addition of liquid hydrogen fluoride to triphenylmethyl chloride in a platinum crucible until complete solution had occurred. The excess hydrogen fluoride was allowed to evaporate and the last traces were removed by heating. The salt was recrystallized from ether at Dry Ice temperatures, m. p. 100°. The pure compound is white, although, if it is pumped too long or allowed to stand for several days, it becomes yellow and hydrogen fluoride can be detected.

Triphenylmethyl bromide was prepared by dropping bromine into molten triphenylmethane until no further reaction occurred.[6] The product was pumped to remove hydrogen bromide and excess bromine, and the salt was recrystallized from benzene, m. p. 153.6–154.0°. The bromide had a light yellow color and appeared to be more reactive toward moisture than is the chloride.

Triphenylmethyl borofluoride was prepared by saturating a benzene solution of triphenylmethyl fluoride with boron trifluoride. The red precipitate was filtered off, washed with benzene and ether and pumped to dryness. The salt was purified by precipitation from ethylene chloride–acetone solution with pentane. It was then washed with benzene, ether and pentane, m. p. 195–196°. The salt was of a pale yellow color and turned brown on standing in the light; it darkened slightly when pumped. The compound reacts almost instantaneously with water.

[3a] Laurence E. Strong, Thesis, Brown University, May, 1940.

[4] This material was kindly donated by the Calco Chemical Division, American Cyanamid Company.

[4a] Cox, Kraus and Fuoss, *Trans. Faraday Soc.*, **31**, 749 (1935).

[5] Gomberg, *Ber.*, **33**, 3144 (1900).

[6] Allen and Kölliker, *Ann.*, **227**, 107 (1885).

TABLE I

CONDUCTANCE OF VARIOUS STABLE ELECTROLYTES IN NITROBENZENE AT 25°

$C \times 10^4$	Λ
Potassium picrate	
0.9102	29.85
.7159	30.49
.4790	31.37
.3346	31.98
.2475	32.37
.1900	32.67
Lithium picrate	
107.4	0.0994
93.62	.1080
77.82	.1132
57.54	.1237
26.71	.1367
10.91	.1574
Tetra-*n*-butylammonium bromide	
55.15	25.12
21.42	28.24
8.184	30.39
3.268	31.67
1.284	32.44
0.5260	32.88
Tetra-*n*-butylammonium acetate	
28.81	27.77
9.382	31.16
4.628	32.56
2.372	33.45
1.156	34.13
0.6103	34.58
.3048	34.91
Tetraethylammonium chloride	
26.27	31.28
9.832	34.36
3.544	36.27
2.303	36.82
1.651	37.15
1.207	37.39
0.7061	37.81
Trimethylhydroxyammonium picrate	
16.62	3.328
5.621	5.430
2.105	8.314
0.9193	11.653
.7402	12.64
.5645	13.93
.4099	15.78
.2916	17.57
n-Butylammonium picrate	
24.37	7.469
8.846	11.23
3.157	16.27
1.967	18.87
0.9468	22.82
.4231	26.66
.2017	29.25
.1060	30.76
Di-*n*-butylammonium picrate	
19.79	7.646
8.164	10.874
4.050	14.01
1.903	17.79
0.8459	21.81
.4018	25.02
Tri-*n*-butylammonium iodide	
17.66	7.098
6.513	10.72
2.285	15.78
0.9411	20.71
.3170	26.30
.1031	30.15
Sodium picrate	
2.901	7.912
2.151	9.062
1.441	10.96
0.8580	13.77
.4708	17.34
.2940	20.06
.1657	23.10
Lithium picrate +0.032*M* water	
116.1	0.4346
43.55	.6131
17.88	.8486
7.387	1.229
2.896	1.950
Tetra-*n*-butylammonium nitrate	
44.33	27.74
14.00	30.79
5.070	32.40
2.159	33.24
1.643	33.42
1.210	33.59
0.8968	33.72
0.5835	33.90
Tetra-*n*-butylammonium borofluoride	
25.32	29.66
10.47	31.24
7.119	31.75
4.849	32.16
3.218	32.52
2.214	32.79
1.212	33.12
0.6286	33.38
Phenyldimethylhydroxyammonium picrate	
30.58	2.475
10.28	3.921
5.029	5.341
1.834	8.029
0.8378	10.88
.4296	13.72
.2219	17.08
.1001	20.68
Ammonium picrate	
1.433	21.37
1.163	22.65
0.9120	23.96
.5984	26.11
.2664	29.62
n-Butylammonium perchlorate	
10.22	28.52
4.734	32.01
2.671	33.85
1.085	35.81
0.4525	36.85
0.2221	37.41
Tri-*n*-butylammonium picrate	
13.238	9.193
6.543	12.01
3.544	14.80
2.067	17.39
0.7343	22.07
.3451	24.74
.1682	26.51
Piperidonium picrate	
16.42	8.989
5.856	13.37
1.926	19.29
0.9403	23.23
.4370	26.88
.1448	30.39

In view of the reactivity of the above triphenylmethyl compounds with water, all solvents used in their purification were carefully dried and distilled.

III. Results

The results of conductance measurements are given in Tables I to IV, inclusive. All measurements were carried out at 25 ± 0.01°. Concentrations are expressed in moles per liter of pure nitrobenzene, the density being taken to be 1.1986.[7] The conductance of nitrobenzene containing added picric acid or bases was much above that of the pure solvent and at times was greater than one-tenth of one per cent. of the measured conductance of the most dilute solutions. In such cases, the specific conductance of the solvent medium is recorded in the tables.

A. Stable Electrolytes. Values of the equivalent conductance, Λ, at concentration C, are given in Table I for strong electrolytes as well as for weaker electrolytes that do not undergo dissociation into free acid and base.

B. Salts that Undergo Acid–Base Dissociation.—Pyridonium, phenylammonium and phenyldimethylammonium picrates undergo dissociation into free acid and base when dissolved in nitrobenzene. Such dissociation may be repressed by addition of either acid or base. Conductance values are given in Table II for pyridonium picrate in pure nitrobenzene and in the presence of added picric acid or pyridine. Conductance values are also given for the two aniline derivatives in the pure solvent as well as for solutions of each salt at a fixed concentration with varying amounts of added base.

C. Effect of Bases on Conductance of Electrolytes with Cations Containing Active Hydrogen Atoms.—In Table III are presented data that show the effect of bases on the conductance

[7] Walden and Birr, *Z. physik. Chem.*, **163A**, 281 (1932).

of solutions of unsubstituted and partially substituted ammonium salts and of solutions of two quaternary ammonium salts having an OH

TABLE II

EFFECT OF ADDED ACID OR BASE ON CONDUCTANCE OF SALTS THAT UNDERGO ACID-BASE DISSOCIATION

$C \times 10^4$	Λ
Pyridonium picrate	
18.63	5.415
6.482	8.271
1.826	12.73
1.029	14.89
0.4845	17.47
.2767	19.04
.1415	20.44
Pyridonium picrate +0.0101 M pyridine	
23.72	6.137
12.60	8.082
6.707	10.49
3.939	12.92
2.293	15.70
1.270	19.03
0.7804	21.81
.4057	25.38
.2186	28.19
Pyridonium picrate +0.0528 M pyridine	
13.26	11.50
4.287	17.18
2.228	20.85
1.027	25.01
0.5766	27.09
.4029	29.01
Pyridonium picrate +0.00200 M picric acid ($\kappa = 1.1 \times 10^{-8}$)	
28.41	4.640
9.133	7.671
6.844	8.678
4.967	9.909
3.601	11.28
2.359	13.29
1.684	15.03
1.138	17.20
Phenylammonium picrate C, Salt = 2.99×10^{-4} N C, aniline	
0.000	1.49
.0105	6.46
.0218	7.63
.0372	8.14
.0585	9.14
Phenyldimethylammonium picrate C, Salt = 1.58×10^{-4} N C, dimethylaniline	
0.000	7.21
.0028	12.3
.0065	12.6
.0106	12.7
.0210	12.8
Pyridonium picrate +0.00095 M pyridine	
15.80	6.205
7.617	8.522
3.146	12.20
1.482	16.08
0.5508	21.80
.2700	25.78
Pyridonium picrate +0.0272 M pyridine	
19.22	8.228
5.193	13.81
1.897	19.29
0.9091	23.42
.4440	26.98
.2590	29.16
Pyridonium picrate +0.000994 M picric acid ($\kappa = 1.5 \times 10^{-8}$)	
20.50	5.344
11.16	6.995
6.508	8.818
3.989	10.78
2.077	13.88
1.341	16.22
0.6812	20.16
.3873	23.51
.1172	30.09
Phenylammonium picrate	
81.80	1.207
28.73	1.314
13.98	1.384
8.676	1.370
4.846	1.466
2.989	1.492
Phenyldimethyl-ammonium picrate	
66.53	2.263
29.01	3.151
12.69	4.250
6.770	5.171
3.556	6.109
1.581	7.209

TABLE III

EFFECT OF BASES ON AMMONIUM SALTS CONTAINING ACTIVE HYDROGEN ATOMS IN CATIONS

$C \times 10^4$	Λ
Ammonium picrate +0.039 M pyridine ($\kappa = 3 \times 10^{-9}$)	
0.9917	25.06
.8332	25.78
.5908	27.16
.3534	28.98
.2216	30.27
.1345	31.37
Dibutylammonium picrate +0.035 M pyridine	
13.77	9.778
6.843	12.72
4.367	14.85
2.237	18.21
1.386	20.60
0.5958	24.36
.3886	25.90
Phenyldimethylhydroxy-ammonium picrate +0.0353 M pyridine	
25.29	13.19
9.856	16.88
3.936	20.73
1.794	23.87
1.102	25.61
0.5822	27.47
Trimethylhydroxy-ammonium picrate +0.00104 M pyridine	
24.62	3.939
7.743	6.517
2.614	10.21
1.330	13.24
0.8992	15.19
.5188	18.19
.3382	20.55
.2324	22.58
Trimethylhydroxy-ammonium picrate +0.037 M pyridine	
23.11	11.02
9.547	14.78
3.710	19.43
1.603	23.56
0.9217	25.99
.6309	27.39
.4780	28.29
.3799	29.03
Trimethylhydroxy-ammonium picrate +0.00101 M triethylamine ($\kappa = 2 \times 10^{-9}$)	
41.00	8.279
14.95	17.18
5.120	20.87
2.615	23.30
1.545	25.14
0.8895	26.89
.5663	28.10
.3379	29.20
Trimethylhydroxy-ammonium picrate +0.000993 M piperidine ($\kappa = 2 \times 10^{-9}$)	
3.101	22.45
2.087	23.90
1.156	25.89
0.7046	27.35
.4921	28.23
.3008	29.21
Trimethylhydroxy-ammonium picrate +0.0101 M piperidine ($\kappa = 4\text{–}12 \times 10^{-9}$)	
25.18	16.72
14.01	18.87
4.501	23.09
1.758	26.13
0.9795	27.60
.5740	28.69
Piperidonium picrate +0.036 M pyridine ($\kappa = 5\text{–}11 \times 10^{-10}$)	
14.13	10.69
6.887	13.98
4.120	16.62
2.263	19.89
1.141	23.48
0.5172	27.02
.2445	29.38
Tributylammonium picrate +0.036 M pyridine ($\kappa = 2 \times 10^{-9}$)	
32.02	7.047
13.32	10.02
7.389	12.46
4.420	14.81
1.937	18.78
0.9322	22.07
.4547	24.73
Trimethylhydroxy-ammonium picrate +0.0100 M water	
21.20	3.332
5.887	5.929
2.886	8.079
1.116	11.87
0.4903	16.01
.2272	20.36

TABLE III (*Concluded*)

$C \times 10^4$	Λ	$C \times 10^4$	Λ
Trimethylhydroxyammonium picrate +0.0101 *M* pyridine		Trimethylhydroxyammonium picrate +0.0385 *M* triethylamine ($\kappa = 2–6 \times 10^{-9}$)	
21.26	7.477	23.24	18.24
7.857	10.90	10.23	20.52
2.406	16.28	4.567	23.00
1.095	20.38	2.749	24.60
0.7651	22.22	1.816	25.83
.4768	24.53	1.227	26.91
.3000	26.49	0.7211	28.21
.1910	28.08		
Trimethylhydroxyammonium picrate +0.00089 *M* triethylamine ($\kappa = 1.6 \times 10^{-9}$)		Trimethylhydroxyammonium picrate +0.00100 *M* piperidine ($\kappa = 3–4 \times 10^{-9}$)	
		20.62	14.99
27.14	11.18	6.772	19.56
8.316	19.16	2.970	22.60
2.587	23.32	1.762	24.48
1.362	25.54	1.177	25.84
1.013	26.49	0.7429	27.19
0.7466	27.37	.4253	28.54
.5523	28.15	.2831	29.34
.3843	28.97	.1176	30.54

group attached to the nitrogen of the ammonium ion (phenyldimethylhydroxyammonium picrate and trimethylhydroxyammonium picrate).

D. Conductance of Triphenylmethyl Compounds.—The conductance of solutions of triphenylmethyl bromide, chloride, fluoride and borofluoride was measured at 25°, and the results are presented in Table IV. Only the borofluoride is a fairly good electrolyte.

TABLE IV

CONDUCTANCE OF SOME TRIPHENYLMETHYL COMPOUNDS IN NITROBENZENE AT 25°

$C \times 10^4$	Λ	$C \times 10^4$	Λ
Triphenylmethyl borofluoride		Triphenylmethyl-bromide	
124.4	23.99	647.7	0.00888
50.21	25.93	346.4	.01175
38.12	26.12	167.3	.01604
14.07	26.39	107.3	.01947
		36.43	.03824
		6.095	.1300
Triphenylmethyl-chloride		Triphenylmethyl-fluoride	
C	Λ	C	Λ
0.02	0.015	0.05	0.02

IV. Discussion

A. Stable Electrolytes.—The characteristic constants, Λ_0 and K, of the electrolytes listed in Table I have been evaluated by the method of Fuoss[8] and the results are given in Table V. In the computations, the viscosity has been taken as 0.01811[7] and the dielectric constant as 34.5.[9]

On plotting values of F/Λ against those of $C\Lambda f^2/F$, the experimental values were found to conform to a linear relation within the limit of experimental error. These plots are not reproduced but similar plots will be found in an earlier paper.[3]

TABLE V

CONSTANTS FOR ELECTROLYTES IN NITROBENZENE AT 25°

Salt	Λ_0	Λ_0^+	Λ_0^-	$K \times 10^4$
$(C_4H_9)_4NBF_4$	33.96	(11.9)[a]	22.1	510
$(C_4H_9)_4NNO_3$	34.51	..	22.6	250
$(C_4H_9)_4NBr$	33.48	..	21.6	162
$(C_4H_9)_4NAc$	35.5	..	23.6	67
$(C_2H_5)_4NCl$	38.55	(16.4)[a]	22.2	125
$(C_4H_9)_3NHPi$	28.85	12.9	(16.0)[a]	1.90
$(C_4H_9)_3NHI$	33.33	..	20.4	0.95
$(C_4H_9)_2NH_2Pi$	30.41	14.4	..	1.56
$(C_4H_9)NH_3Pi$	32.97	17.0	..	1.49
$(C_4H_9)NH_3ClO_4$	37.92	..	20.9	25.3
$C_5H_{10}NH_2Pi$	33.26	17.3	..	1.53
$(C_6H_5)(CH_3)_2(HO)$-NPi	28.50	12.5	..	0.20
$(CH_3)_3(HO)NPi$	33.26	17.3	..	0.17
NH_4Pi	34.4	18.4	..	1.46
LiPi	...	..	..	0.0006
NaPi	32.30	16.3	..	0.28
KPi	33.81	17.8	..	6.86

[a] Taylor and Kraus, ref. 3.

By halving the conductance of tetrabutylammonium triphenylborofluoride, Taylor[3] obtained 11.7 for the conductance of the tetrabutylammonium ion. A careful redetermination of the conductance of this salt leads to a Λ_0 value of 23.78 for the salt and 11.9 for the tetrabutylammonium ion. This value has been employed in deriving the ion conductances of Table V.

The conductance of the negative ions of Table V lie within narrow limits, 20.4 for the iodide ion and 23.6 for the acetate ion. The conductance of the chloride, bromide and iodide ions decreases regularly in that order; it will be recalled that the conductance of the picrate ion is 16.0.

Taylor[3] found the conductance of the tetramethylammonium ion to be 17.3 (cor.); the conductance of the ammonium ion, the highest for any normal cation thus far measured, is 18.4, while that of the potassium ion is 17.8. It is a remarkable fact that the conductance values for the simpler cations lie within a narrow range.

As hydrogen atoms of the ammonium group are substituted by butyl groups, ion conductances diminish regularly; the greatest change occurs in going from the monobutyl to the dibutyl derivative.

Very striking is the fact that the conductance of positive ions is uniformly much lower than that of comparable negative ions. Thus, the conductance of the tetramethylammonium ion is 17.3[3] while that of the borofluoride ion is 22.1 and that of the perchlorate ion 20.9.

A comparison of ion conductances in nitro-

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

(9) Lattey and Gattey, *Phil. Mag.*, Series 7, 7, 985 (1929).

benzene with those in other solvents, such as ethylene chloride and pyridine, would be of much interest. However, it seems best to defer any such intercomparisons until the results in all solvents have been presented.

The dissociation constants of salts in nitrobenzene are large, as was to have been expected from the relatively high value of its dielectric constant. For salts of very large ions, the constant cannot be evaluated if, indeed, it has physical meaning. From Taylor's[3] earlier work, it follows that the constant for tetrabutylammonium picrate is greater than 2000×10^{-4}; for the corresponding tetraethylammonium salt, it is 1400×10^{-4}. The constant decreases greatly with decreasing size of the negative ion. The constant of tetrabutylammonium borofluoride is not more than one-fourth that of the picrate while that of the acetate is one-thirtieth.

On replacing one of the butyl groups of the tetrabutylammonium ion by a hydrogen atom, the constant of the picrate is decreased a thousandfold. Further substitution of hydrogen for butyl groups causes only a slight further diminution of the dissociation constant; indeed, the constant for ammonium picrate is little smaller than that of monobutylammonium picrate. It seems clear that the low value of the dissociation constant of the salts of the partially substituted ammonium ions is due to interaction between the negative ion and a proton of the ammonium group.

The interaction between a negative ion and an active proton in the positive ion is strikingly illustrated by phenyldimethylhydroxyammonium picrate and trimethylhydroxyammonium picrate. Here, the active proton is attached to an oxygen atom which, in turn, is attached to the central nitrogen atom of the ammonium ion. The constants for these two salts are 0.2×10^{-4} and 0.17×10^{-4}, respectively. Comparing the dissociation constants of tetramethylammonium picrate (380×10^{-4}) and trimethylhydroxyammonium picrate (0.17×10^{-4}), the bonding energy due to the proton-ion interaction must amount to several thousand calories.

The low values found for the dissociation constant of the alkali metal picrates indicate that interactions may be involved other than those due to Coulombic forces. This is particularly apparent in the case of lithium picrate whose dissociation constant is of the order of 6×10^{-8}. If we compute the shortest distance between charges by the method of Fuoss[10] we obtain the "a" value, 0.62 Å. On the basis of accepted atomic dimensions, this distance could hardly be less than several ångstrom units. In this connection, it may be noted that "a" values, as computed from conductance data, are generally uniformly larger than distances between charges as computed from the polar moments of ion-pairs.[11] It is of interest to note that the constant for lithium picrate (6×10^{-8}) is increased 25-fold on addition of 0.03 M water ($K = 1.5 \times 10^{-6}$).

B. Salts that Undergo Acid–Base Dissociation.—The picrates of weak aromatic bases, such as dimethylaniline, aniline and pyridine, follow the Fuoss linear relationship but yield limiting conductance values which are abnormally low. This result is due to the dissociation of the salt into free acid and base as has been shown by Elliott and Fuoss[12] and Taylor.[3]

We have to consider two coexistent equilibria; the ordinary ionic dissociation—$BHA \rightleftarrows BH^+ + A^-$ (a)—and the dissociation of the electrolyte into free acid and base, represented by—$BHA \rightleftarrows B + HA$ (b). The mass action expressions for equilibria (a) and (b) may be written

$$\frac{(BH^+)(A^-)}{(BHA)} = \frac{C\gamma^2 f^2}{1 - \gamma - x} = K \tag{1}$$

and

$$\frac{(B)(HA)}{(BHA)} = \frac{Cx^2}{1 - \gamma - x} = k \tag{2}$$

where K and k are the dissociation constants of the equilibria represented in (a) and (b), respectively. C is the stoichiometric concentration of the salt; x is the fraction of salt which is dissociated into free acid and base; and γ is the fraction dissociated into ions. The activity coefficients of the uncharged molecules have been taken as unity while f represents the activity coefficient of the ions.

Dividing (2) by (1) and rearranging, we obtain

$$x = f\gamma\sqrt{\frac{k}{K}}$$

and substituting for x in (1), we arrive at the expression

$$K = \frac{C\gamma^2 f^2}{1 - \gamma - \gamma f\sqrt{\frac{k}{K}}} \tag{3}$$

According to Fuoss[8]

$$\gamma = \frac{\Lambda}{\Lambda_0 F}$$

where the symbols have their usual significance. Substituting this value of γ in (3) and rearranging, we obtain

$$\frac{1}{f}\left(\frac{F}{\Lambda} - \frac{1}{\Lambda_0}\right) = \frac{C\Lambda f}{F} \cdot \frac{1}{K\Lambda_0^2} + \frac{1}{\Lambda_0}\sqrt{\frac{k}{K}} \tag{4}$$

Thus, when acid–base dissociation is taken into account in addition to ordinary electrolytic dissociation, a plot of $\frac{1}{f}\left(\frac{F}{\Lambda} - \frac{1}{\Lambda_0}\right)$ against $C\Lambda f/F$ should result in a straight line with intercept equal to $\frac{1}{\Lambda_0}\sqrt{\frac{k}{K}}$ and slope equal to $1/K\Lambda_0^2$. In this way K and k may be evaluated.

It is, of course, necessary to know the limiting conductance of the electrolyte before k and K can be determined by means of equation (4). For

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

[11] J. A. Geddes, *Trans. Faraday Soc.*, **32**, 595 (1936).

[12] Elliott and Fuoss, THIS JOURNAL, **61**, 294 (1939).

salts of very weak bases, the limiting conductance may be approximated only by reference to the limiting conductance of electrolytes of similar structure. For salts of stronger bases, Λ_0 may be determined experimentally by means of conductance measurements with solutions in which the acid–base dissociation has been repressed by the addition of free acid or base.

With dilute solutions in solvents of high dielectric constant, such as nitrobenzene, the value of the activity coefficient f approaches close to unity. Under this condition, a plot of F/Λ against $C\Lambda f^2/F$ closely approximates a straight line and the intercept $(1/\Lambda_0')$ on the F/Λ axis closely approximates the true value of $\frac{1}{\Lambda_0} + \frac{1}{\Lambda_0}\sqrt{\frac{k}{K}}$. Such a plot is shown for pyridonium picrate in curve 1 of Fig. 1. The intercept corresponds to a false Λ_0 value of 22.5 as against a true value of 32.8. The difference between the reciprocals of these two numbers closely approximates the true value of $1/\Lambda_0 \sqrt{k/K}$.

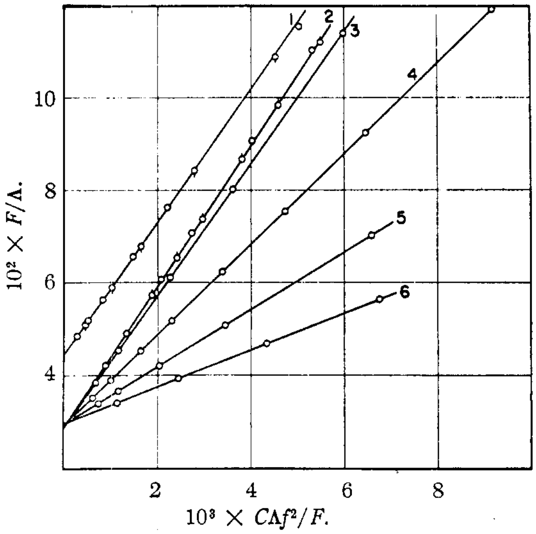

Fig. 1.—Pyridonium picrate in pure nitrobenzene and in the presence of picric acid and pyridine: 1, pyridonium picrate in nitrobenzene; 2, pyridonium picrate + 0.001 M picric acid (circles); 2, pyridonium picrate + 0.002 M picric acid (tailed circles); 3, pyridonium picrate + 0.001 M pyridine; 4, pyridonium picrate + 0.01 M pyridine; 5, pyridonium picrate + 0.027 M pyridine; 6, pyridonium picrate + 0.053 M pyridine.

True values of Λ_0 and K were obtained for pyridonium picrate by plotting F/Λ against $C\Lambda f^2/F$ for solutions in which the acid–base dissociation was repressed. The primary data are those given in Table II. Constants for the various solutions are collected in Table VI and plots are shown in Fig. 1, curves 2, 3, 4, 5 and 6.

Examination of Fig. 1 (curve 2) shows that the acid–base dissociation of pyridonium picrate is completely repressed on addition of 0.001 molar picric acid. On doubling the concentration of picric acid, conductance values remain practically unchanged. There may be a very slight decrease in Λ_0 and increase of K on further additions of picric acid as will appear on inspection of Table VI. These constants, however, cannot be fixed with the highest precision because the correction for solvent conductance may amount to as much as 1% for the most dilute solution.

TABLE VI

CONSTANTS FOR PYRIDONIUM PICRATE IN NITROBENZENE IN THE PRESENCE OF PICRIC ACID AND PYRIDINE

Concn. of added acid or base	Λ_0	$K \times 10^5$
0.00	22.5 (Λ_0')	...
.00100 picric acid	34.7	5.42
.00200 picric acid	34.5	5.54
.00095 pyridine	34.60	5.85
.0101 pyridine	34.19	8.76
.0272 pyridine	33.90	14.15
.0529 pyridine	33.84	22.0

As may be seen from Fig. 1 (curves 3, 4, 5 and 6), the acid–base dissociation of pyridonium picrate is completely repressed by as little as 0.00095 M pyridine. As appears from Table VI, this addition causes a small, although well-defined, decrease in Λ_0 and a marked increase of the dissociation constant. The addition of 0.053 M pyridine increases the dissociation constant approximately four-fold. The constant varies as a linear function of the pyridine concentration and on extrapolation to zero pyridine concentration, a value of 5.54×10^{-5} is found for the dissociation constant of pyridonium picrate in pure nitrobenzene. This value is in excellent agreement with that obtained on addition of picric acid.

The limiting conductance for pyridonium picrate on the addition of pyridine changes markedly on initial additions but the change diminishes rapidly with increasing pyridine concentration. A rough extrapolation to zero pyridine concentration yields the value 34.8 for the limiting conductance of the salt in pure nitrobenzene. This value is in good agreement with that obtained in the presence of added picric acid. Subtracting the conductance of the picrate ion, a value of 18.8 is obtained for the conductance of the pyridonium ion, the highest for any positive ion measured.

Using the value of 34.8 for the limiting conductance of pyridonium picrate, values of $\frac{1}{f}\left(\frac{F}{\Lambda} - \frac{1}{\Lambda_0}\right)$ have been plotted against those of $C\Lambda f/F$ and therefrom the ionic and the acid–base dissociation constants have been evaluated for this salt from the intercept and slope of the straight line (plot not shown). The value of K derived from the plot is 5.54×10^{-5} in excellent agreement with values derived from data for solutions in which the acid–base dissociation was repressed.

As appears from data presented in Table II, the acid–base dissociation of phenylammonium (aniline) picrate and phenyldimethylammonium (dimethylaniline) picrate cannot be completely repressed by addition of base at permissible concentrations. Accordingly, the value of Λ_0 has been approximated at 32 on the basis of 31.65[3] for the conductance of phenyltrimethylammonium picrate. Using these values of Λ_0, plots were constructed for the two picrates and the ionic dissociation constant, K, and the acid–base dissociation constant, k, were evaluated. The results for these picrates are given in Table VII.

TABLE VII

IONIC AND ACID–BASE DISSOCIATION CONSTANTS FOR SOME PICRATES IN NITROBENZENE

Salt	Apparent Λ_0	True Λ_0	$K \times 10^6$	$k \times 10^4$
$(C_6H_5)NH_3Pi$	2	32	2.0	80
$(C_6H_5)(CH_3)_2NHPi$[a]	9.6	32	4.1	2.5
C_5H_5NHPi	22.5	34.8	5.54	0.163

[a] See also Taylor, ref. 3.

The evaluation of k provides a quantitative measure of the relative strength of acids or bases in non-aqueous neutral solvents. The values of k in Table VII show that, in nitrobenzene, aniline is a much weaker base than dimethylaniline and this, in turn, is weaker than pyridine. Values of the dissociation constants of aniline, dimethylaniline and pyridine in water, as given in the literature, vary rather widely; the values 5×10^{-10}, 1×10^{-9} and 2.3×10^{-9}, respectively, for these bases are, perhaps, as reliable as any. It is evident from the k values of Table VII that the acid–base dissociation constants of these picrates in nitrobenzene differ greatly; that of dimethylaniline is 15 times that of pyridine and that of aniline is 32 times that of dimethylaniline.

In view of the above results and the fact that even pyridine is a very weak base, it is safe to assume that salts of strong acids with bases, having constants in the neighborhood of 1×10^{-4} in water, will not be appreciably dissociated into free acid and base in nitrobenzene. This is borne out by the results obtained with various partially and unsubstituted ammonium salts.

Elliott and Fuoss[12] have suggested that in solutions of picrates of aromatic amines in tricresyl phosphate, a non-ionic molecular species occurs which, while in direct equilibrium with free acid and base, is not in direct equilibrium with free ions. The occurrence of such a non-ionic species in solutions of pyridonium picrate in nitrobenzene is not excluded but the fraction of total solute occurring in such form must be very small. This is indicated by the fact that the conductance of the pyridonium ion is 18.8, the highest for any positive ion as yet measured. The existence of a portion of the salt in non-ionic form would necessarily lower the limiting conductance of the pyridonium ion proportionately, since the proportion of solute existing in the non-ionic form would not be affected by addition of small amounts of acid or base.

C. Effect of Bases on the Ionic Dissociation Constant of Salts having Active Hydrogen Atoms in Their Cations.—The ionic dissociation constant of pyridonium picrate increases markedly with increasing concentration of added pyridine. It appears that this effect is due to the interaction of the basic pyridine molecule with the hydrogen atom in the cation, which interaction tends to exclude the interaction of the proton with the negative ion. Salts whose cations lack an active hydrogen atom exhibit little change of conductance on addition of bases; for example, the addition of 0.15 M pyridine to a dilute solution of tetramethylammonium picrate in nitrobenzene (8×10^{-4} M) caused a conductance increase of only 0.36%. This increase can be accounted for by the viscosity change alone. With a few exceptions, conductance changes due to the addition of other neutral molecules are due to change of the dissociation constant.

Table VIII summarizes the results obtained in measuring the conductance of solutions of unsubstituted and partially substituted ammonium picrates in nitrobenzene containing small, known, approximately equal concentrations of pyridine. None of these salts shows an acid–base dissociation in nitrobenzene solution.

TABLE VIII

EFFECT OF PYRIDINE ON THE CONSTANTS OF AMMONIUM AND PARTIALLY SUBSTITUTED AMMONIUM PICRATES IN NITROBENZENE

Salt	Concn. C_5H_5N	Λ_0	$K \times 10^4$	K/K_0
NH_4Pi	0.000	34.4	1.46 (K_0)	1.61
NH_4Pi	.039	33.1	2.35	
$C_5H_{10}NH_2Pi$	.000	33.3	1.53 (K_0)	1.39
$C_5H_{10}NH_2Pi$	.036	32.7	2.12	
$(C_4H_9)_2NH_2Pi$	.000	30.4	1.56 (K_0)	1.28
$(C_4H_9)_2NH_2Pi$	.035	30.4	1.99	
$(C_4H_9)_3NHPi$	.000	28.9	1.90 (K_0)	1.22
$(C_4H_9)_3NHPi$	.036	29.0	2.32	

The increase in the value of the dissociation constant (K/K_0) on the addition of a given quantity of pyridine becomes greater as the number of unsubstituted hydrogen atoms in the cation increases. This is further evidence in support of our hypothesis that the added base interacts largely with these hydrogen atoms.

For phenyldimethylhydroxyammonium and trimethylhydroxyammonium picrates, the effect of added bases is even greater than it is for the salts just discussed. The conductance of these salts in nitrobenzene containing various known concentrations of water, pyridine, triethylamine and piperidine has been measured. The results are presented in Table IX. Values of Λ_0 are given in the second column and of K in the third column. The ratio of the dissociation constant in the presence of base, K, and in the pure solvent, K_0, is given in the fourth column, and the dissociation constant of the added base in water is given in the last column. The plots for trimethylhydroxyammonium picrate (based on data of Table III) are shown in Fig. 2.

TABLE IX

EFFECT OF BASES ON CONSTANTS OF PHENYLDIMETHYLHYDROXYAMMONIUM PICRATE AND TRIMETHYLHYDROXYAMMONIUM PICRATE IN NITROBENZENE

Molarity of base added	Λ_0	$K \times 10^5$	K/K_0	K_b (water)
Phenyldimethylhydroxyammonium Picrate				
0.00	28.5	2.0 (K_0)	..	2.3×10^{-9}
.0353 C_5H_5N	30.8	49	25	
Trimethylhydroxyammonium Picrate				
.00	33.26	1.69 (K_0)	..	
.0100 H_2O	32.93	2.23	1.3	
.00104 C_5H_5N	32.84	3.53	2.1	
.0101 C_5H_5N	32.26	11.9	7.0	2.3×10^{-9}
.0370 C_5H_5N	32.07	33.4	20.0	
.00089 $(C_2H_5)_3N$	31.4	47	28	
.00101 $(C_2H_5)_3N$	31.3	50	30	6.4×10^{-4}
.0380 $(C_2H_5)_3N$	30.7	88	52	
.00100 $C_5H_{10}NH$	31.0	52	31	
.0100 $C_5H_{10}NH$	30.4	108	64	1.6×10^{-3}

It will be noted on examining Fig. 2, that all curves are linear below 2×10^{-4} N. While the conductance of nitrobenzene on introduction of triethylamine and piperidine becomes appreciable in this region, extrapolation errors are small for such strong electrolytes as those here considered.

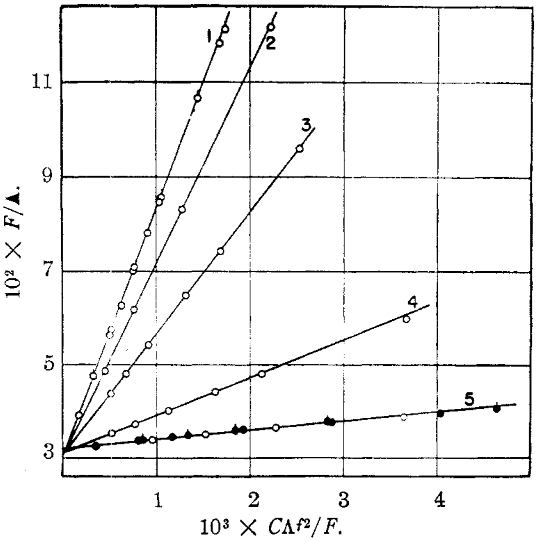

Fig. 2.—Trimethylhydroxyammonium picrate in pure nitrobenzene and in the presence of various bases: 1, trimethylhydroxyammonium picrate in pyridine; 2, trimethylhydroxyammonium picrate + 0.01 M H_2O; 3, trimethylhydroxyammonium picrate + 0.001 M C_5H_5N; 4, trimethylhydroxyammonium picrate + 0.01 M C_5H_5N; 5, trimethylhydroxyammonium picrate + 0.001 M $(C_2H_5)_3N$ (open circles); 5, trimethylhydroxyammonium picrate + 0.001 M $C_5H_{10}NH$ (shaded circles).

While the limiting conductance of phenyldimethylhydroxyammonium picrate is increased appreciably by the addition of pyridine, the conductance of trimethylhydroxyammonium picrate is decreased only slightly in all cases. In this connection, it may be recalled that the conductance of the phenyldimethylhydroxyammonium picrate is abnormally low in pure nitrobenzene.[3] The addition of pyridine appears to restore, partially, at least, a normal conductance to this ion.

The increase in the dissociation constant on addition of strong bases is, indeed, very great. The differences in the inclination of the curves of Fig. 2 illustrate this; the lower the constant, the steeper the inclination. In column 5 of Table IX, are given the dissociation constants of the added bases in water. It is seen that for a given concentration of added base, the ratio (K/K_0) increases greatly as the dissociation constant (strength) of the base increases. Triethylamine and piperidine have practically the same effect as may be seen from curve 5 of Fig. 2. The effect of bases on the dissociation constant of salts of partially substituted ammonium ions and of quaternary ammonium ions that have a hydroxyl group attached to the nitrogen atom are understandable if it is assumed that the active hydrogen atom in the ammonium ion interacts with the negative ion through non-coulombic forces. As a result of such interaction, which is additional to coulombic interaction, the energy of the ion pairs is greatly increased with a corresponding decrease in the value of the dissociation constant over what it would be due to coulombic forces alone. Different added bases interact in a similar manner with the hydrogen atom, the interaction being the greater, the stronger the base; this tends to minimize the non-coulombic interaction between the negative ion and the hydrogen atom of the cation.

D. Triphenylmethyl Compounds.—While the conductance values found for the triphenylmethyl compounds are not as precise as might be desired, approximate values of the dissociation constants have been computed on the basis of the Ostwald dilution law. Values are given in Table X.

TABLE X

DISSOCIATION CONSTANTS OF SOME TRIPHENYLMETHYL COMPOUNDS IN NITROBENZENE AT 25°

Negative ion	Br^-	Cl^-	F^-	BF_4^-
Constant, $K \times 10^9$	5.0	5.0	22	1×10^7

The bromide, chloride and fluoride are all very weak electrolytes, with the fluoride somewhat the stronger. All three compounds are so weak, however, that the K-values, as given, must be taken as rough approximations. The borofluoride is a fairly strong electrolyte with a constant in the neighborhood of 0.01. The borofluoride ion is, in many respects, similar to the perchlorate ion. It will be recalled that triphenylmethyl perchlorate is a good electrolyte in many solvents.[13]

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[13] P. Walden, "Chemie der freien Radikalen," S. Hirzel, Leipzig, 1924, p. 137.

V. Summary

1. The conductance of solutions of a number of quaternary ammonium salts having different anions has been measured in nitrobenzene at 25° and values of Λ_0 and K determined.

2. The conductance of solutions of an ammonium salt, as well as of some partially substituted ammonium salts, has been measured and values of Λ_0 and K determined; all are weak electrolytes.

3. The conductance of solutions of lithium, sodium and potassium picrates has been measured and Λ_0 and K values computed. All three salts are weak, with the lithium salt much the weakest ($K = 6 \times 10^{-8}$).

4. The constants for phenyldimethylhydroxyammonium picrate and trimethylhydroxyammonium picrate have been derived from conductance measurements. Both salts are very weak electrolytes.

5. Ion conductances have been evaluated for all but the weakest electrolytes by the method of Fowler.

6. The acid–base dissociation of phenylammonium, phenyldimethylammonium and pyridonium picrates has been studied by the conductance method, the pyridonium salt in detail. Constants of the ionic and the acid–base equilibria have been evaluated for the three salts.

7. The effect of bases on the dissociation constant of partially substituted ammonium salts and of quaternary salts containing a hydroxyl group attached to the nitrogen of the cation has been investigated. The effect is often large, depending on the constitution of the cation and the strength of the added base.

8. The conductance of triphenylmethyl chloride, bromide, fluoride and borofluoride has been measured. The halogen derivatives are very weak electrolytes; the borofluoride is a fairly strong electrolyte.

PROVIDENCE, R. I. RECEIVED MAY 14, 1947

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXX. Conductance of Some Inorganic and Organic Electrolytes in Pyridine at 25°[1]

By William F. Luder[2] and Charles A. Kraus

I. Introduction

In view of the fact that pyridine exhibits a strong basic function, accurate conductance measurements with solutions of electrolytes in this solvent should yield valuable and new information as to the interaction of solvent molecules with ions, particularly with certain inorganic cations. The dielectric constant of pyridine, 12.01,[3] is such that accurate Λ_0 and K values readily can be obtained for all but very weak salts. These constants often serve to throw light on the nature of the ions and their interactions in solution. It is possible, moreover, to carry out measurements with several inorganic salts which are readily soluble in pyridine although practically insoluble in ethylene chloride.

Previous conductance measurements in pyridine are uncertain because of the high conductance of the solvent—usually greater than 2×10^{-8}. In the present investigation, it has been found possible to obtain pyridine, the specific conductance of which was less than 1×10^{-9}. Solvent corrections were unnecessary even in the most dilute solutions.

The salts measured were: silver nitrate and perchlorate, tetra-*n*-butylammonium bromide, iodide and picrate and ethyltriphenylarsonium picrate. Several other salts were investigated, but difficulty was experienced in obtaining reproducible results. The underlying source of the difficulty will be elucidated in a following communication.

II. Experimental

Materials.—For initial purification of pyridine, a modification of the method of Heap, Jones and Speakman[4] was adopted. Zinc chloride forms a molecular compound containing two molecules of pyridine per molecule of zinc chloride. This compound was precipitated by the interaction of the appropriate quantities of anhydrous zinc chloride and pyridine in alcohol solution. The precipitate was filtered off, washed with alcohol and then recrystallized from alcohol containing 20% of water. The crystallized product was washed with alcohol; m. p. 207°. The pyridine was regenerated by the addition of an aqueous solution of sodium hydroxide. The mixture was filtered, solid sodium hydroxide was added to the filtrate and the water layer removed in a separatory funnel. Most of the water remaining in the pyridine was removed by several treatments with sodium hydroxide. After storing over barium oxide for several days, the pyridine was shaken with activated alumina for a further period and finally distilled from activated aluminum oxide in an all-glass apparatus which was protected against the entrance of carbon dioxide and moisture.

Tetra-*n*-butylammonium picrate and ethyltriphenylarsonium picrate had been previously prepared and employed by other workers in this laboratory.

Tetra-*n*-butylammonium iodide (m. p. 145°) and tetra-

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[1] This paper is based on a portion of a thesis presented by William F. Luder in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1937.

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[3] Le Fèvre, *J. Chem. Soc.*, Part I, 776 (1935).

[4] Heap, Jones and Speakman, THIS JOURNAL, **43**, 1936 (1921).