[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. LI. Conductance of Some Salts in Ethylene Chloride and Pyridine

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In order to fill some gaps in the list of ion conductances in ethylene chloride and pyridine, the conductance of a number of quaternary ammonium salts was measured in these solvents. Thus, the conductances of the acetate, chloroacetate and thiocyanate ions have been determined in ethylene chloride; the conductance of the perchlorate ion has been redetermined.

In pyridine, the conductances of the fluoride, chloride, acetate and chloroacetate ions have been determined. The results are discussed briefly.

I. Introduction

In earlier papers of this series, conductances are recorded for a considerable number of ions—negative as well as positive—in several different solvents.[2] However, in attempting to compare the conductance of ions in different solvents, many gaps occur. The present investigation was undertaken, in the main, for the purpose of filling some of these gaps.

In ethylene chloride, the conductances of the acetate and chloroacetate ions have been determined and the conductance of the perchlorate ion has been redetermined. In pyridine, conductances of the acetate, chloroacetate, fluoride and chloride ions have been determined. The conductance of the fluoride ion in ethylene chloride could not be determined because of exchange with the chlorine atoms of the solvent molecules. Solutions of quaternary ammonium salts of dichloro- and trichloroacetate ions proved to be unstable.

II. Experimental

1. **Apparatus, Procedure and Materials.**—The apparatus and procedure employed in the present investigation have been described in earlier papers.[3]

The symmetrical quaternary ammonium salts of the acetate and the fluoride ions are very soluble and are purified with difficulty. For this reason, we have employed octadecyltrimethyl- and tributylammonium salts. These could be purified without too much difficulty. Melting points of long chain salts are often not sharp. Reproducibility of conductance values after further recrystallization was adopted as a criterion of purity.

Since octadecyltrimethylammonium acetate is a very weak salt in ethylene chloride, its limiting conductances cannot be determined with a very high degree of accuracy. Accordingly, the corresponding tributyl derivative was also measured. The latter compound has a favorable dissociation constant.

The following salts were prepared:

Octadecyltributylammonium acetate by metathesis of the nitrate with potassium acetate in absolute alcohol; recrystallized from hexane containing a small amount of acetone, m.p. 89–90°.

Octadecyltributylammonium chloroacetate by metathesis of the iodide with silver chloroacetate in methanol; recrystallized from hexane containing a small amount of alcohol, m.p. 92°.

Octadecyltrimethylammonium acetate by metathesis of the nitrate with potassium acetate in absolute alcohol; recrystallized from acetone, m.p. 188–190°.

Octadecyltrimethylammonium chloroacetate by metathesis of the iodide with silver chloroacetate in absolute alcohol; recrystallized from acetone, m.p. 185–195°.

Octadecyltrimethylammonium picrate by metathesis of the iodide with silver picrate in absolute alcohol; recrystallized from alcohol, m.p. 134–135°.

Octadecyltrimethylammonium fluoride by treating the iodide with a large excess of lead fluoride in hot absolute alcohol; recrystallized from acetone, m.p. 295–296°.

Dioctadecyldibutylammonium iodide was prepared by Mr. E. L. Swarts by reaction of dibutylamine with octadecyl iodide. It was recrystallized from ether–ethanol mixtures and from methanol, m.p. 108.5–109°.

Octadecyltributylammonium thiocyanate was prepared by Dr. H. S. Young and **octadecyltrimethylammonium chloride** was prepared by Dr. H. M. Daggett, of this Laboratory.

Tetrabutylammonium perchlorate was prepared by methathesis of the iodide with silver perchlorate in alcoholic solution. It was recrystallized from ethyl acetate; m.p. 210.5°.

Results

In Tables I and II are presented conductance values of the different salts in ethylene chloride and pyridine, respectively. Concentrations are expressed in moles of solute per liter of solution, the density of the solution being assumed equal to that of the pure solvent. The specific conductance of the solvent was in all cases negligible in comparison with that of the solution measured. Buoyancy corrections were not applied, it being assumed that the density of solution and of solvent were such that the corrections would lie within the limit of experimental error. The following values of constants were employed in computations:

Solvent	Density, g./cc.	Viscosity, poise × 10^3	Diel. const.
Ethylene chloride	1.2455	7.87	10.23
Pyridine	0.97792	8.824	12.01

Although two series of measurements were made in most instances, the results of only one series are presented here. All measurements were carried out at 25 ± 0.005°.

III. Discussion

The data of Tables I and II have been analyzed by the method of Fuoss and values of Λ_0 and K have been derived. The plots of F/Λ and $C\Lambda f^2/F$ are in all cases linear at lower concentrations and need not be reproduced.

Values of the constants for the different electrolytes are collected in Table III for ethylene chloride and Table IV for pyridine.

The values of Thompson and Kraus[2] for the conductance of the acetate and the chloroacetate ions in ethylene chloride are in error, doubtless

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(1) Graduate Fellow of the Stanolind Oil and Gas Company, Brown University, 1948–1949.

(2) Ethylene chloride: (a) D. L. Fowler and C. A. Kraus, THIS JOURNAL, **62**, 2237 (1940); (b) L. F. Gleysteen and C. A. Kraus, *ibid.*, **69**, 451 (1947); (c) L. M. Tucker and C. A. Kraus, *ibid.*, **69**, 454 (1947); (d) D. J. Mead, J. B. Ramsey, D. A. Rothrock, Jr., and C. A. Kraus, *ibid.*, **69**, 528 (1947); (e) E. R. Kline and C. A. Kraus, *ibid.*, **69**, 814 (1947); (f) W. E. Thompson and C. A. Kraus, *ibid.*, **69**, 1016 (1947). Pyridine: (g) W. F. Luder and C. A. Kraus, *ibid.*, **69**, 2481 (1947); (h) D. S. Burgess and C. A. Kraus, *ibid.*, **70**, 706 (1948). Nitrobenzene: (i) E. G. Taylor and C. A. Kraus, *ibid.*, **69**, 1731 (1947); (j) C. R. Witschonke and C. A. Kraus, *ibid.*, **69**, 2472 (1947). Acetone: (k) M. B. Reynolds and C. A. Kraus, *ibid.*, **70**, 1709 (1948).

TABLE I

CONDUCTANCE OF QUATERNARY AMMONIUM SALTS IN ETHYLENE DICHLORIDE AT 25°

$C \times 10^4$	Λ	$C \times 10^4$	Λ
A. Octadecyltributylammonium acetate		B. Octadecyltrimethylammonium acetate	
7.8121	22.919	11.988	5.1695
3.1549	29.727	4.9086	7.5172
1.7584	34.525	1.9348	11.273
0.79339	40.991	1.2544	13.498
.34531	46.764	0.66036	17.593
.24015	48.865	.42220	21.022
C. Octadecyltrimethylammonium chloroacetate		D. Octadecyltributylammonium thiocyanate	
5.3741	9.5356	7.8694	25.557
3.0953	11.915	3.5586	31.881
1.7491	14.936	1.4045	39.704
0.90093	19.280	0.85643	43.741
.38819	26.126	.46586	48.090
.26833	29.541		

E. Tetrabutylammonium perchlorate[3]

$C \times 10^4$	Λ
4.7874	32.327
2.4551	38.468
1.3895	43.758
0.76928	49.015
.39331	54.221
.25391	57.009

TABLE II

CONDUCTANCE OF QUATERNARY AMMONIUM SALTS IN PYRIDINE AT 25°

$C \times 10^4$	Λ	$C \times 10^4$	Λ
A. Octadecyltrimethylammonium fluoride		B. Octadecyltrimethylammonium chloride	
12.438	23.734	6.5512	17.279
5.4501	29.880	2.1972	26.209
2.6147	35.565	1.1573	32.832
1.5087	39.632	0.64850	39.297
0.78946	43.759	.37238	45.843
.338947	47.765	.21539	52.036
.19399	49.711		
C. Octadecyltrimethylammonium picrate		D. Octadecyltributylammonium acetate	
8.9779	34.869	4.7879	42.473
4.0331	40.346	1.7105	51.979
2.1653	44.223	0.81805	57.735
1.0570	47.913	.53785	60.316
0.54811	50.426	.34417	62.484
.29471	52.085	.22171	64.088
E. Octadecyltributylammonium chloroacetate		F. Dioctadecyldibutylammonium iodide[3]	
9.7564	35.180	1.8539	46.960
4.2778	42.760	1.2637	49.736
2.6418	47.146	0.79705	52.654
1.6338	51.200	.53558	54.740
0.91278	55.545	.32702	56.794
.58203	58.250	.18486	58.522
.25175	61.994		

TABLE III

CONSTANTS OF SALTS IN ETHYLENE CHLORIDE

Salt	Λ_0	Λ_0^+	Λ_0^-	$K \times 10^4$
Octd Bu_3N $OOCCH_3$	57.21	17.8[a]	39.4	1.33
Octd Me_3N $OOCCH_3$	63.1	23.7[a]	39.4	0.062
Octd Me_3N $OOCCH_2Cl$	59.0	...	35.3	0.123
Octd Bu_3N SCN	60.2	...	42.4	1.56
Bu_4NClO_4	66.2	26.2[b]	40.0	1.53

[a] Pickering.[2] [b] Fowler.[2]

TABLE IV

CONSTANTS OF SALTS IN PYRIDINE

Salt	Λ_0	Λ_0^+	Λ_0^-	$K \times 10^4$
Octd Me_3N F	53.88	...	32.0	2.93
Octd Me_3N Cl	73.3	..	51.4	0.358
Octd Me_3N Pi	55.62	21.9	33.7[a]	7.66
Octd Bu_3N $OOCCH_3$	68.94	17.1[b]	51.8	3.88
Octd Bu_3N $OOCCH_2Cl$	67.25	17.1	50.1	3.90
$Octd_2Bu_2N$ I	62.36	14.0	48.4[c]	4.21

[a] Luder.[2] [b] Pickering.[2] [c] Burgess.[2]

due to the difficulty with which the tetrabutylammonium salts of these ions may be purified. In the case of low melting quaternary ammonium salts of high solubility, it is advantageous to employ long chain salts which crystallize from solution more readily.

In ethylene chloride, the conductances of the acetate and chloroacetate ions are much lower than those of other ions having the same number of atoms other than hydrogen. Thus, the conductance of the chloroacetate ion is 35.3 while that of the perchlorate ion, having the same number of atoms, is 40.0. In pyridine, on the other hand, the conductance of the chloroacetate ion is 50.1 while that of the perchlorate ion is 47.6.[2g] In comparisons of this kind, it should be borne in mind that the viscosity of pyridine is 12% greater than that of ethylene chloride. The low conductance of the fluoride ion in pyridine (32.0) is noteworthy although, perhaps, not unexpected. It may be pointed out that the conductance of the picrate ion, containing 16 atoms other than carbon, is 8% greater in pyridine than in ethylene chloride, although, on the basis of the viscosities of the solvents, it should be 12% less.

The treatment of ion conductances, or perhaps better, ion resistances, on the basis of Stokes' concept of a spherical particle moving through a viscous medium, has not proved fruitful and in some respects has been misleading. With certain large symmetrical ions, such as the tetrabutylammonium ion, the conductance viscosity product has approximately the same value in different solvents (excepting in water).[4] When, however, we consider smaller ions, there is no correlation between ion conductances and the size of the atoms from which the ions are derived, nor is there correlation between ion conductance and the number of atoms in an ion.

Thus, in water, the conductance of the bromide ion is markedly greater than that of the chloride or iodide ion and the conductance of the iodide ion is somewhat greater than that of the chloride ion.[5]

In pyridine, the bromide[4] and chloride ions have

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[3] For these measurements we are indebted to Mr. Edward C. Baker of this Laboratory.

[4] H. M. Daggett, E. J. Bair and C. A. Kraus, THIS JOURNAL, **73**, 799 (1951).

[5] C. A. Kraus, *Ann. New York Acad. Sci.*, **51**, 794 (1949).

practically the same conductance, which is markedly greater than that of the iodide ion[2g] (6%). In ethylene chloride, the conductances of the iodide,[6] bromide and chloride[2h] ions stand in the ratio of the numbers 1:1.12:1.30. In this connection, we may recall the very low conductance of the sodium, lithium and fluoride ions in pyridine.

The highest conductance measured for any ion in pyridine is 52.6 for the nitrate ion containing four atoms; that of the chloride ion is 51.4. The perchlorate ion, with five atoms, has a conductance of 47.6.[2g] In ethylene chloride, the perchlorate and the nitrate[2c] ions have practically the same conductance, 40.0 and 40.1, respectively.

In pyridine, the choline ion ($HOC_2H_4 \cdot Me_3N^+$) with seven atoms has a conductance of 33.4, the conductance of the ethyltrimethylammonium ion (6 atoms) is 41.8.[2h] In ethylene chloride, the conductance of the choline ion is 40.4 while that of the ethyltrimethylammonium ion is 42.1.[2d] In nitrobenzene, the two ions have the same conductance, 17.1.[2i]

We have already pointed out that conductances in pyridine are generally higher than in ethylene chloride although the latter solvent has the lower viscosity. There is another marked difference between the two solvents. In ethylene chloride, positive and negative ions containing the same number of atoms and of similar structure have approximately the same conductance. Thus, the conductance of the BF_4^- ion is 42.7,[2f] while that of the tetramethylammonium ion is 42.6[2c]; that of the perchlorate ion is 40.0. In pyridine, the conductance of the perchlorate ion is 47.6[2g] while that of the tetramethylammonium ion is 43.0.[2h] In ethylene chloride the conductance values for the acetate and chloroacetate ions, are, respectively, 39.4 and 35.3; in pyridine, they are 51.8 and 50.1.

It appears that while positive and negative ions of the same size and similar structure have approximately the same conductance in ethylene chloride, the negative ions have a markedly greater conductance than positive ions in pyridine.

The conductance of an ion is determined by its interaction with the dipole molecules of the solvent medium. It is doubtful if the term "size" has physical meaning here.

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[6] H. L. Pickering and C. A. Kraus, THIS JOURNAL, 71, 3288 (1949).

[CONTRIBUTION FROM THE RESEARCH INSTITUTE OF TEMPLE UNIVERSITY]

Perfluoroalkyl Halides Prepared from Silver Perfluoro-fatty Acid Salts. I. Perfluoroalkyl Iodides

BY MURRAY HAUPTSCHEIN AND ARISTID V. GROSSE

A general method for the synthesis of perfluoroalkyl iodides and diiodides by the action of iodine on the corresponding silver perfluoro-fatty acid salt is described. The preparation of iodotrifluoromethane, iodopentafluoroethane, and the new compounds 1-iodoheptafluoropropane and 1,3-diiodohexafluoropropane are reported as representative examples. Various physical constants and the infrared spectra of the latter three compounds are given.

We wish to report an extension and generalization of the method recently reported by Henne and Finnegan[1] for the preparation of iodotrifluoromethane. The present paper deals with the preparation of the important perfluoroalkyl iodides, but the method has also been demonstrated to be equally well adapted to the preparation of perfluoroalkyl chlorides and bromides which will be published in future papers.

Iodotrifluoromethane, iodopentafluoroethane, 1-iodoheptafluoropropane and 1,3-diiodohexafluoropropane have been synthesized by reaction with silver trifluoroacetate, silver pentafluoropropionate, silver heptafluoro-*n*-butyrate and silver hexafluoroglutarate, respectively, in the presence of an excess of iodine. The latter two representative reactions are given by the equations

$$CF_3CF_2CF_2CO_2Ag + I_2 \longrightarrow CF_3CF_2CF_2I + AgI + CO_2 \quad (1)$$

and

$$AgO_2CCF_2CF_2CF_2CO_2Ag + 2I_2 \longrightarrow ICF_2CF_2CF_2I + 2AgI + 2CO_2 \quad (2)$$

Preliminary attempts were made to carry out these degradations in refluxing chlorobenzene. However, practically no carbon dioxide gas was generated, and the principal products appeared to be the free perfluoro acid and *p*-iodochlorobenzene formed presumably from the attack of the perfluoroacyl radicals on the solvent by abstraction of a hydrogen atom and iodination of the aromatic nucleus. It was found, however, that by the controlled thermal decomposition of the dry silver salt and a ten per cent. excess of iodine, *in the absence of a solvent*, iodotrifluoromethane, iodopentafluoroethane, 1-iodoheptafluoropropane[2] and 1,3-diiodohexafluoropropane were formed in 95, 86, 87–93 and 18% yield, respectively. In the latter case, evidence is presented in the experimental section which indicates strongly that the reaction proceeded to a large extent by a route different from that shown in equation 2, with the production of perfluorobutyrolactone. The formation of the product can be easily accounted for by the cyclization of the gamma iodo salt, $ICF_2CF_2CF_2CO_2Ag$, to form silver iodide and the lactone. The physical constants of the perfluoroalkyl iodides are presented in Table I, and the infrared spectra[3] are shown in Figs. 1, 2 and 3. As

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[1] A. L. Henne and W. G. Finnegan, THIS JOURNAL, 72, 3806 (1950). Our work has been carried out independently of these investigators.

[2] R. N. Haszeldine, *J. Chem. Soc.*, 2856 (1949), found that 1-iodoheptafluoropropane was one of the products formed in the reaction of iodotrifluoromethane with tetrafluoroethylene, but no physical constants were reported.

[3] Determined with a Baird Associates Infrared Recording Spectrophotometer by Samuel P. Sadtler and Sons, Inc., Philadelphia.