mole. Some of this disagreement can be accounted for by the fact that they used a shallower black body hole, 1 mm. in diam. and 3 mm. deep; we found, by a comparison of brightness temperatures for holes of different depths and diameters, that at 1100° a cavity of these dimensions gives temperatures 11 deg. lower than the black body we used. This error is in the right direction to account for the disagreement but is not of sufficient magnitude. In general, the Marshall, Dornte and Norton values of vapor pressure are double or slightly more than double our own. This corresponds to a temperature difference of about 35 deg., which still leaves more than 20 deg. in temperature, or 50% in vapor pressure, to be accounted for. Possibly their "electrolytic" iron contained some volatile impurity that contributed significantly to the vapor pressures.

The vapor pressures obtained by Jones, Langmuir and Mackay,[2] who measured the evaporation loss from a heated filament, are also about double our own. No information is given on the source or purity of their iron.

COLUMBUS 10, OHIO RECEIVED APRIL 4, 1951

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. LIV. The Conductance and Molecular Weight of Some Salts in Benzene at Higher Concentrations[1]

BY HOWARD S. YOUNG[2] AND CHARLES A. KRAUS

Cryoscopic measurements were carried out with solutions of octadecyltri-*n*-amyl-, octadecyltri-*n*-butylammonium thiocyanate and tri-*n*-butylammonium iodide. Association numbers for the first two salts are the same within the limit of experimental error. The association of the iodide is much smaller than that of the two thiocyanates. The conductances of solutions of the three salts were also measured at 25°. The two thiocyanates have complex conductance curves resembling those of other similar quaternary ammonium salts. The conductance of the iodide is much lower than that of the other two salts at low concentrations and is higher at high concentrations. The results are discussed.

I. Introduction

Cryoscopic[3] and conductance measurements[4] with dilute solutions of 1–1 salts in benzene, combined with molecular polarization values derived from dielectric constant measurements[5,6] have demonstrated that the association of ion dipoles is greatly dependent upon the size and symmetry of their ions. All measured properties are in accord with the view that interactions are governed, chiefly, by electrical forces. Recently, these measurements have been extended to considerably higher salt concentrations by Strong[6] and Copenhafer.[7] It was found that salts, exhibiting high association cryoscopically, yield complex curves of conductance *vs.* concentration; less strongly associated salts on the other hand, yield much simpler curves. In, general, salts of large, symmetrical cations and small anions were found to be the more highly associated.

The most highly associated salt measured cryoscopically by Copenhafer was *n*-octadecyltri-*n*-butylammonium formate. In view of the low solubility of this salt, it was thought worthwhile to investigate more soluble salts of the same cation type. Accordingly, we have studied solutions of *n*-octadecyltri-*n*-butyl- and *n*-octadecyltri-*n*-amylammonium thiocyanate with regard to their cryoscopic as well as their electrical behavior. In addition, we have investigated the less strongly associated salt, tri-*n*-butylammonium iodide, over a considerable range of concentration.

II. Experimental

1. **Materials.**—Benzene was purified by the method of Batson and Kraus.[3b]

Tri-*n*-butylammonium iodide was furnished us by Dr. H. L. Pickering who prepared it by treating the purified amine with gaseous hydrogen iodide; it was recrystallized from anhydrous ethyl acetate, m.p. 101.2–101.7° (cor.). *n*-Octadecyltri-*n*-butylammonium thiocyanate was prepared from the nitrate by metathesis with potassium thiocyanate in absolute alcohol according to the procedure described by Strobel.[8] The product was recrystallized from hexane to which had been added a small quantity of isopropyl alcohol, m.p. 66.5–67.2° (cor.). *n*-Octadecyltri-*n*-butylammonium nitrate, m.p. 89.2–90.0° (cor.), was prepared from the iodide by metathesis with silver nitrate, m.p. 101.0–101.3° (cor.). *n*-Octadecyltri-*n*-amylammonium thiocyanate was prepared by Mr. C. H. Keith, using a procedure paralleling that employed for the butyl compound, m.p. 55.8–58.0°. This thiocyanate was found to be approximately 60% more soluble in benzene at its freezing point than is the corresponding butyl derivative.

2. **Apparatus and Procedure.**—Conductance measurements were carried out at 25° using the apparatus and procedure described by Strong.[6] Densities of the more concentrated solutions were determined by means of a Weld specific gravity bottle; the results are given in Table I, where m is the molal concentration and d is the density.

The apparatus employed in freezing point measurements was that described in earlier papers[3,9]; the thermel was constructed by Dr. H. L. Pickering. A value of 5.088° was employed for the cryoscopic constant of benzene.

Difficulty was experienced in determining the concentration of solutions of the long chain salts by means of the analytical method described by Barton,[9] owing to their tendency to retain traces of solvent. Although this difficulty

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[1] Taken in part from the dissertation of Howard S. Young presented in partial fulfillment of the requirement for the degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1948.

[2] University Fellow in Brown University, 1947-1948.

[3] (a) C. A. Kraus and R. A. Vingee, THIS JOURNAL, **56**, 511 (1934); (b) F. M. Batson and C. A. Kraus, *ibid.*, **56**, 2017 (1934); (c) D. A. Rothrock, Jr., and C. A. Kraus, *ibid.*, **59**, 1699 (1937).

[4] (a) C. A. Kraus and R. M. Fuoss, *ibid.*, **55**, 21 (1933); (b) R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 3614 (1943); (c) W. F. Luder, P. B. Kraus, C. A. Kraus and R. M. Fuoss, *ibid.*, **58**, 255 (1936).

[5] (a) G. S. Hooper and C. A. Kraus, *ibid.*, **56**, 2265 (1934); (b) J. A. Geddes and C. A. Kraus, *Trans. Faraday Soc.*, **32**, 585 (1936); (c) C. A. Kraus and G. S. Hooper, *Proc. Nat. Acad. Sci.*, **19**, 939 (1933).

[6] L. S. Strong and C. A. Kraus, THIS JOURNAL, **72**, 166 (1950).

[7] (LIII) D. T. Copenhafer and C. A. Kraus, THIS JOURNAL, **73**, 4557 (1951).

[8] H. A. Strobel and H. C. Eckstrom, *J. Chem. Phys.*, **16**, 817 (1948).

[9] B. C. Barton Thesis, Brown University, 1939.

TABLE I

DENSITIES OF SOLUTIONS OF SALTS IN BENZENE AT 25°

n-Octadecyltri-*n*-butylammonium thiocyanate		*n*-Octadecyltri-*n*-amylammonium thiocyanate		Tri-*n*-butylammonium iodide	
m	*d*	*m*	*d*	*m*	*d*
0.1925	0.8756			0.1141	0.8820
.3481	.8777	0.2025	0.8752	.2746	.8941
.5256	.8797	.4883	.8783	.4547	.9068
				.6950	.9225

could be largely obviated by employing a mercury diffusion pump, the method is very time-consuming. Accordingly, it was found more expedient to analyze the solutions conductometrically. The conductances of the salts in question were measured in benzene solutions at 25° and concentrations of samples were interpolated from the conductance curves. The cryoscopic results for *n*-octadecyltri-*n*-butylammonium thiocyanate are based on the weight pipet method; those for the other salts are based on conductometric analyses

In general, analyses made by the conductance method yielded lower salt concentrations than did those made by the pipet method. This was not unexpected because of the tendency of these salts to retain solvent. The two methods were compared in several instances with the results shown in Table II; it is felt that the conductometric data are the more reliable.

TABLE II

COMPARISON OF METHODS OF ANALYSIS

Salt	Molal concentration Cond.	Pipet	Dif., %
n-Bu_3NHI	0.2770	0.2776	0.22
	.3627	.3638	.31
Oct. Am_3NCNS	.006610	.006649	.60

III. Results

1. Conductances.—The results of conductance measurements are presented in Table III. Concentrations in moles per liter appear in column 1 and equivalent conductances in column 2. The data for octadecyltributylammonium thiocyanate have already been published.[10]

2. Cryoscopic Data.—Cryoscopic data are given in Table IV. Concentrations in moles per 1000 g. of solvent appear in column 1, the freezing point depressions in column 2 and values of the association number, *n*, the ratio of apparent to the formal molecular weight, in column 3. Included is one datum for *n*-octadecyl alcohol, which is seen to be associated very slightly at a concentration of 0.02 molal.

TABLE III

CONDUCTANCE OF SALTS IN BENZENE AT 25°

n-Octadecyltri-*n*-amylammonium thiocyanate		Tri-*n*-butylammonium iodide	
$C \times 10^3$	$\Lambda \times 10^3$	$C \times 10^3$	$\Lambda \times 10^3$
307.7	50.03	514.8	320.9
196.1	41.53	419.0	279.0
144.1	38.68	320.5	219.6
105.1	36.15	208.5	124.7
79.52	33.92	195.9	112.4
62.08	31.43	142.8	57.84
38.84	24.52	97.13	18.36
28.15	17.96	69.90	5.670
22.10	13.08	60.02	3.307
16.99	8.552	38.38	0.7840
13.71	5.942	26.05	.2714
9.303	3.327	13.09	.05613
6.786	2.293		
5.190	1.780		
3.376	1.263		
2.116	0.9122		
1.475	.7153		

IV. Discussion

1. Cryoscopic Measurements.—In Fig. 1, values of the association number, *n*, are shown graphically as a function of molal concentration. The curves for octadecyltri-*n*-butyl- and octadecyltri-*n*-amylammonium thiocyanate coincide within the limit of experimental error. With the butyl derivative, the concentration was carried to 0.151 *m*, the limit of solubility, where the association number reaches the value 40.1. There is no indication of an approaching maximum in the curve. Evidently, the octadecyl chain has a marked influence on association. At 0.15 *m*, tetrabutylammonium and tetraisoamylammonium thiocyanate have an association number approximating 25. They have maximum association numbers of 31.9 and 25.8 at $m = 0.28$ and $m = 0.12$, respectively.

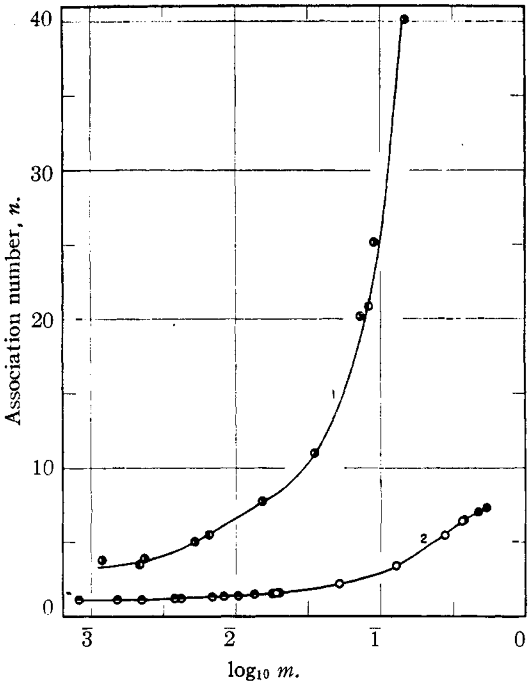

Fig. 1.—Association numbers of salts in benzene: 1, ◑, *n*-octadecyltri-*n*-butylammonium thiocyanate; ◐, *n*-octadecyltri-*n*-amylammonium thiocyanate; 2, tri-*n*-butylammonium iodide; ○, this investigation; ◓, Rothrock and Kraus (ref. 3c); ●, Pickering (unpublished observations).

While octadecyltributyl- and octadecyltriamylammonium thiocyanates exhibit greater association than the corresponding tetraisoamylammonium salt at high concentrations, at lower concentrations, the association of the last named salt is somewhat the greater, 6.5 and 7.8, respectively, at 0.01 *m*. For the corresponding tetrabutylammonium salt, the association number is 4.2.[7] Thus, while the two symmetrical quaternary amyl and butyl derivatives have very different association numbers, the corresponding long chain trialkyl salts exhibit

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(10) H. A. Strobel and R. H. Cole, *J. Chem. Phys.*, **17**, 1155 (1949).

TABLE IV

CRYOSCOPIC DATA FOR SALTS IN BENZENE

n-Octadecyltri-*n*-butylammonium thiocyanate			Tri-*n*-butylammonium iodide		
$m \times 10^3$	$\Delta T° \times 10^3$	n	$m \times 10^3$	$\Delta T° \times 10^3$	n
1.20	1.60	3.82	19.15	61.58	1.582
2.35	3.05	3.92	52.70	120.36	2.228
5.27	5.32	5.04	130.4	194.0	3.420
15.11	9.94	7.73	277.0	258.6	5.450
34.92	16.11	11.03	362.7	288.4	6.399
72.15	18.18	20.19	375.8[a]	293.3[a]	6.519[a]
90.06	18.19	25.19	467.7[a]	338.4[a]	7.032[a]
150.9	19.15	40.09	535.0[a]	374.2[a]	7.274[a]
n-Octadecyltri-*n*-amylammonium thiocyanate			*n*-Octadecyl alcohol		
2.20	3.20	3.50	17.37	86.20	1.025
6.61	6.12	5.50			
83.93	20.46	20.87			

[a] Measurements by Dr. H. L. Pickering.

the same degree of association. The long chains would appear to be a factor in the association process.

The values of the polar moments of the salts and the size of their anions, likewise, are of importance in the association process. Thus, the polar moment of tetraisoamylammonium thiocyanate[5b] is 15.4 × 10^{-18} while that of tributylammonium iodide is 8.29 × 10^{-18}. At 0.01 *m*, the association number of the tetraamyl salt is 7.8, that of tributylammonium iodide is 1.4.

The size of the negative ion is, in some respects, more important than the value of the polar moment. The polar moments of tetraisoamylammonium picrate and thiocyanate[5b] are, respectively, 18.3 and 15.4 × 10^{-18}; the association numbers at 3.87 × 10^{-3} *m* are 1.40 and 16.0. The dipole moments of tributyl ammonium picrate and iodide are 13.1 and 8.09 × 10^{-18}, respectively; their association numbers at 10^{-2} *m* are 1.07 and 1.40, respectively.

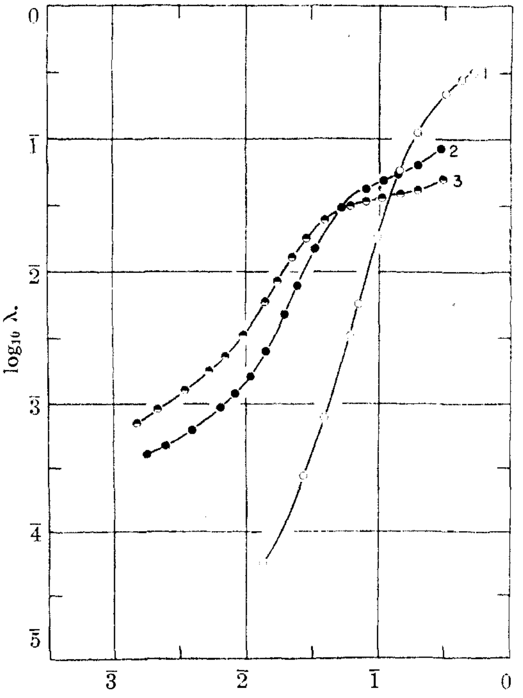

Fig. 2.—Conductance of electrolytes in benzene at 25°: 1, tri-*n*-butylammonium iodide; 2, *n*-octadecyltri-*n*-butylammonium thiocyanate; 3, *n*-octadecyltri-*n*-amylammonium thiocyanate.

2. **Conductance Measurements.**—Conductance curves for the salts measured are shown in Fig. 2, logarithms of equivalent conductance being plotted against logarithms of concentration. The curves for octadecyltri-*n*-amyl- and octadecyltri-*n*-butylammonium thiocyanate are very similar. The amyl derivative has somewhat the higher conductance at low concentrations and the lower conductance at higher concentrations. Both curves have two inflection points and both give indication of increasing to higher values at higher concentrations. The curves closely resemble those found by Strong[6] for dioctadecyldibutylammonium thiocyanate. They also resemble the curves of symmetrical quaternary ammonium salts of small anions.[4b]

At low concentrations, the conductance of tributylammonium iodide is much lower than that of the two quaternary salts but, at higher concentrations, the reverse is true. The curve resembles that of triisoamylammonium picrate; there are no inflection points.

The association of ion dipoles to quadrupoles and more complex structures and the dissociation of ion-pairs into their component ions are governed by much the same constitutional and structural factors. Salts of large quaternary ammonium ions and small anions, having dipole moments in the neighborhood of 15 × 10^{-18}, are highly associated and their conductance curves have much the same form. With the same cation, the ionic dissociation as indicated by conductance values, is the larger, the larger the anion and, presumably, the larger the dipole moment. Thus, the conductance values of tetraisoamylammonium iodide, bromide, chloride and fluoride at 3.2 × 10^{-5} *N* are, respectively, 1.7, 1.1, 0.65 and 0.32 × 10^{-5}. Between 0.001 and 0.01 *N*. these salts have practically the same conductance.[4b] At higher concentrations there is, again, greater divergence.

Yet the dipolar moment, alone, is not determinative of either the association or the ionization of a salt. Tetraisoamylammonium picrate and thiocyanate of polar moments 18.3 and 15.4 × 10^{-18}, respectively, have practically the same conductance at low concentrations,[4b] although the thiocyanate is highly associated and the picrate only slightly associated. Tributylammonium iodide, with a polar moment of 8.1×10^{-18}, is more highly associated and is a better conductor than triisoamylammonium picrate with a polar moment of 13.3×10^{-18}. In general, other factors being equal, salts with large dipole moments are better conductors than salts with small moments. On the other hand, salts with large unsymmetrical cations and large anions are poorer conductors and are less associated than similar salts with smaller anions. By and large, the conductance of a salt is not dependent on its tendency to associate, although salts of high association are generally rather good conductors. At high concentrations, the conductances of all salts are of the same order of magnitude, irrespective of their polar moments, or the size and structure of their constituent ions.

As Strobel[10] has shown, the form of the conductance curve of octadecyltri-*n*-butylammonium thiocyanate changes little between 25 and 5.25°; however, the temperature coefficient is unexpectedly high. At 0.065 *N*, the conductance at 25° is approximately 2.5 times that at 5.25°. The normal temperature coefficient due to viscosity change might be expected to be of the order of 1.5%; the high value of 7.5% indicates that the number of charged carriers in solution increases markedly with temperature.

PROVIDENCE, R. I. RECEIVED MARCH 2. 1951

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

The Hydrolysis of 3-Chloro-3-methyl-1-butyne and 1-Chloro-3-methyl-1,2-butadiene[1]

BY G. F. HENNION AND D. E. MALONEY[2]

The object of this work was to elucidate the significance of resonance stabilization of the carbonium ions $R_2\overset{\oplus}{C}—C\equiv CH \longleftrightarrow R_2C{=}C{=}\overset{\oplus}{C}H$. For this purpose the behavior of 3-chloro-3-methyl-1-butyne (I) and 1-chloro-3-methyl-1,2-butadiene (II) under conditions which induce hydrolysis of reactive halides has been studied. In 80% alcohol at 25° I undergoes extremely slow solvolysis; II does not react under these conditions. In the presence of added base I and II "hydrolyze" by second order kinetics, but I very much faster than II. Surprisingly, both base-induced reactions produce 3-methyl-1-butyn-3-ol ethyl ether (III) as the major product and are thought to be initiated by proton removal. It is concluded that dialkylethynylcarbonium ions have (relatively) little formation tendency in aqueous solutions, contrary to expectations from the resonance notion.

Discussion

In a recent paper[3] we reported that 3-chloro-3-methyl-1-butyne (I) and 1-chloro-3-methyl-1,2-butadiene (II) are readily hydrolyzed by alkalies. The behavior of I and II under conditions which induce hydrolysis of reactive halides has now been studied in some detail. Specifically, we sought to determine if resonance stabilization of the carbonium ions $R_2\overset{\oplus}{C}—C\equiv CH \longleftrightarrow R_2C{=}C{=}\overset{\oplus}{C}H$ is appreciable in the manner shown. It appears that there are steric as well as electronic differences in the solvated forms of these ions or activated complexes in which the organic reactants take on an ionic form. A simple approach to this problem is the study of the reactivities of substances potentially capable of forming such ions, *e.g.*, the chlorides I and II.

It may be well to mention that I rapidly precipitates silver chloride from alcoholic silver nitrate containing nitric acid; II does not. Neither I nor II reacts with potassium iodide in acetone. Yet both react with sodium hydroxide in 80% alcohol at room temperature as evidenced by the slow though abundant crystallization of sodium chloride.

In "80% alcohol"[4] I has been found to undergo *very slow* solvolysis (S_N1 reaction). The first order rate constant at 25° is only 7.4×10^{-4} hr.$^{-1}$, a value approximately 1/75 of that for *t*-amyl chloride under identical conditions.[5,6] Although this seems to indicate little resonance stabilization of the dimethylethynylcarbonium ion, it should be noted that I does not manifest much B-strain[6] and that the ethynyl group is strongly electron attracting (-I effect). The reluctance of I to ionize can be ascribed, at least in part, to these two factors. The S_N1 reaction proceeds somewhat more rapidly, as expected, when the water content of the solvent is increased. Thus in 60% alcohol $k_1^{25°}$ is about 4.3×10^{-3} hr.$^{-1}$ and in 60% acetone the value is 1.93×10^{-3} hr.$^{-1}$.

Under the conditions cited above the chloroallene (II) fails to undergo solvolysis. Solutions of II in 80% alcohol have been maintained at 25° for ten days without forming a detectable amount of hydrochloric acid.

In the presence of sodium hydroxide (S_N2 conditions) both halides appear to react by second order kinetics. The $k_2^{25°}$ values for I in 80% alcohol, varying the halide/base ratio as well as the halide concentration, ranged from 1.2 to 1.4 l./mole hr. and were reasonably constant in each run. The chloroallene (II) showed kinetics somewhat less satisfactory, the $k_2^{25°}$ values decreasing with time in every run from about 1×10^{-2} to 0.8×10^{-2} l./mole hr. Seeking an explanation for this difficulty, it was observed that II undergoes, as a side reaction, a prototropic rearrangement to 1-chloro-3-

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(1) Paper LVI on substituted acetylenes; previous paper, THIS JOURNAL, **72**, 5317 (1950).

(2) du Pont Predoctoral Fellow, 1950–1951.

(3) G. F. Hennion, J. J. Sheehan and D. E. Maloney, THIS JOURNAL, **72**, 3542 (1950).

(4) Concentration of solvents is given in per cent. by volume.

(5) E. D. Hughes and B. J. McNulty, *J. Chem. Soc.*, 1283 (1937).

(6) H. C. Brown and R. S. Fletcher, THIS JOURNAL, **71**, 1845 (1949).