would preclude any fanciful mechanism involving hydrogen ion as a reactant in the rate determining step. It would require the absorption of more than 10000 calories per mole to obtain hydrogen ion under the conditions of these experiments.

Summary

The fading of solutions of 3,3'-dicarbazylphenylmethyl chloride in mixtures of acetone, water, methanol and sodium hydroxide have been investigated. Fixed concentrations of acetone and water were used. The concentrations of methanol and sodium hydroxide and the temperature were varied.

When the concentrations of sodium hydroxide and methanol were constant, the rate of fading was found to be proportional to the total concentration of the quinoids. The proportionality constant obeyed the law, $k = \{k_1 + k_2(\text{NaOH})\}/ \{1 + K(\text{NaOH})\}$ when the concentration of sodium hydroxide was varied, but that of methanol was fixed. When the concentration of sodium hydroxide was fixed and that of methanol was varied, the proportionality constant was a linear function of the concentration of methanol. The logarithm of the proportionality constant was found to be a linear function of the reciprocal of the absolute temperature.

Properties of Electrolytic Solutions. XXV. The Conductance of Choline and Related Picrates in Ethylene Chloride at 25°

BY D. J. MEAD, J. B. RAMSEY, D. A. ROTHROCK, JR., AND C. A. KRAUS

I. Introduction

It is well known that the strength of organic acids and bases is markedly influenced by the presence of electronegative substituents and by their position with respect to the charge on the ion. There is no clear evidence that such substituents have a similar effect in the case of salts, largely because such salts have been investigated in water, a solvent of high dielectric constant, in which salts are normally completely dissociated into their constituent ions.

In a later paper, some results will be presented showing what influence electronegative elements have on the dissociation constant of salts when introduced into the negative ion. In the present paper, we are concerned with the influence which electronegative atoms or groups have on the dissociation constant of salts of the onium type when introduced into the positive ion.

Among the simpler compounds in which negative atoms or groups occur in onium ions, are the cholines. The conductance of picrates of various ions of the choline type have been measured. The choline ion, itself, hydroxyethyltrimethylammonium, contains a hydroxyl group attached to the end carbon atom of the ethyl group. In place of the hydroxyl group, other groups or elements may be introduced. Of interest is the methoxymethyltrimethylammonium ion, which is isomeric with the choline ion. Other compounds studied are the picrates of ethyl-, bromoethyl-, acetylethyl-, bromomethyl and iodomethyltrimethylammonium. Investigated also, were arsenocholine and acetylarsenocholine picrates.

II. Experimental

Salts.—Choline, acetylcholine, arsenocholine and acetylarsenocholine picrates were kindly furnished by Professor Arnold DeM. Welch, now of Washington University, and Dr. M. H. Roepke, of the University of Toronto. Because of the limited quantities of the arseno derivatives available, these salts were recrystallized only once from pure ethanol. The choline and acetylcholine picrates were recrystallized twice from ethanol. The melting points were as follows: choline picrate, 242–245°; acetylcholine picrate, 109–110°; arsenocholine picrate, 251–253°; acetylarsenocholine picrate, 125.6°.

While the purity of the salts, as finally obtained, was not as high as might have been desired, the results are probably not in error by more than a few tenths of a per cent. for the nitrogen cholines and one per cent. in the case of the arseno derivatives.

Methoxymethyltrimethylammonium picrate was prepared by metathesis of the chloride with potassium picrate in pure ethanol. The resulting mixture was filtered while hot and the salt obtained from the filtrate was recrystallized from pure ethanol; m. p. 198°. The chloride had been prepared by the reaction of trimethylamine and chloromethyl methyl ether in cold, dry ether, as described by Litterscheid and Thimme.[1] A white solid was formed during the reaction. The ether was removed at room temperature, leaving the chloride as a viscous liquid which dissolved as such in pure ethanol and reacted with potassium picrate as mentioned above.

Ethyltrimethylammonium picrate was prepared by metathesis of the chloride with silver picrate. The salt was recrystallized from ethanol; m. p., 307–308° (dec.).

Chloroethyltrimethylammonium picrate was prepared by metathesis of the chloride with silver picrate. The salt was recrystallized from alcohol containing 10% water; m. p. 209°. The chloride was prepared by reaction of ethylene chloride with trimethylamine.

Bromoethyltrimethylammonium picrate was prepared by metathesis of the bromide with sodium picrate in aqueous solution. It was recrystallized from water; m. p. 160°. The bromide had been prepared according to the method of Kruger and Bergel[2] by the reaction of trimethylamine with ethylene bromide at 120°.

Bromomethyltrimethylammonium bromide was prepared by the interaction of methylene bromide with trimethylamine in alcoholic solution. This salt was metathesized with silver picrate to prepare the corresponding picrate; m. p. 155°.

(1) Litterscheid and Thimme, *Ann. Chem.*, **334**, 50 (1904).

(2) Kruger and Bergel, *Ber.*, **36**, 2901 (1903).

Iodomethyltrimethylammonium picrate was obtained in a similar manner starting with methylene iodide and trimethylamine; m. p. 218°.

Measurements were carried out at 25 ± 0.01°, according to the methods described in earlier papers from this Laboratory.[3]

III. Results

In Table I, are shown the measured concentrations and equivalent conductance values obtained in one run for each salt. Concentrations are given in moles of salt per liter of solvent; the density of ethylene chloride at 25° has been taken as 1.2455.

TABLE I

CONDUCTANCE OF VARIOUS ELECTROLYTES IN ETHYLENE CHLORIDE AT 25°

Ethyltrimethyl ammonium picrate		Choline picrate	
$C \times 10^5$	Λ	$C \times 10^5$	Λ
52.09	22.06	56.73	8.353
22.60	29.33	21.84	12.54
11.44	36.37	13.78	15.20
4.058	47.96	7.968	19.01
1.394	58.83	4.968	22.91
		2.979	27.75

Chloroethyltrimethyl- ammonium picrate		Bromoethyltrimethyl- ammonium picrate	
47.29	11.85	22.69	16.26
22.08	16.12	10.95	21.59
10.52	21.55	5.532	27.71
4.679	28.97	2.712	35.09
2.454	35.81	1.511	41.62
1.206	43.80		

Acetylcholine picrate		Bromomethyltrimethyl- ammonium picrate	
60.28	12.72	33.60	11.09
28.93	16.97	13.32	16.28
14.17	22.21	4.448	25.06
7.326	28.04	1.483	36.61
3.311	36.01		
1.784	42.49		

Iodomethyltrimethyl- ammonium picrate		Methoxymethyltrimethyl- ammonium picrate	
34.71	12.35	46.04	17.29
16.04	16.94	22.40	22.64
7.589	22.69	10.53	29.53
4.038	28.54	5.815	35.76
1.795	37.09	2.859	43.70
1.052	42.91	1.360	51.78

Arsenocholine picrate		Acetylarseno- choline picrate	
42.08	11.48	24.11	15.44
21.46	15.13	14.34	18.94
13.35	18.32	7.135	24.60
6.827	23.77	3.823	30.52
3.952	28.99	2.146	36.53
1.896	36.96		

(3) See, for example, Mead, Fuoss and Kraus, Trans. Faraday Soc., **32**, 594 (1936); also, Cox, Kraus and Fuoss, ibid., **31**, 749 (1935).

IV. Discussion

The experimental results were treated according to the method of Fuoss[4] to obtain limiting conductances and dissociation constants of the electrolytes under consideration. In the computations, the viscosity was taken as 0.00785 and the dielectric constant as 10.23. The plots of F/Λ against $C\Lambda f^2/F$ are all linear within the limit of experimental error, 0.1%; they are not reproduced but similar plots will be found in earlier papers.[3] The values of Λ_0 and K are given in the second and fourth columns of Table II. Mead's values[3] for tetramethylammonium picrate have been included for purposes of comparison.

TABLE II

CONSTANTS FOR CHOLINE AND RELATED PICRATES IN ETHYLENE CHLORIDE AT 25°

Salt	Λ_0	Λ_0^+	$K \times 10^5$
$(CH_3)_4NPi$	73.8	42.6	3.26
$(C_2H_5)(CH_3)_3NPi$	73.3	42.1	4.60
$(HOC_2H_4)(CH_3)_3NPi$	71.6	40.4	0.66
$(ClC_2H_4)(CH_3)_3NPi$	69.0	37.8	1.25
$(BrC_2H_4)(CH_3)_3NPi$	68.5	37.3	1.32
$(CH_3COOC_2H_4)(CH_3)_3NPi$	66.1	34.9	1.96
$(CH_3OCH_2)(CH_3)_3NPi$	71.4	40.2	2.54
$(BrCH_2)(CH_3)_3NPi$	69.9	38.7	0.78
$(ICH_2)(CH_3)_3NPi$	67.0	35.8	1.10
$(HOC_2H_4)(CH_3)_3AsPi$	70.6	39.4	1.00
$(CH_3COOC_2H_4)(CH_3)_3AsPi$	65.1	33.9	1.39

Taking the limiting conductance of the picrate ion as 31.2,[5] limiting cation conductances have been calculated and are listed in column 3 of Table II.

The limiting cation conductances show a steady decrease on substitution of one of the methyl groups in the tetramethylammonium ion by the following groups, successively

$$C_2H_5 > HOC_2H_4 > ClC_2H_4 > BrC_2H_4 > CH_3COOC_2H_4$$
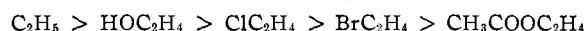
It thus appears that the cation conductances are determined primarily by the size of the substituent groups. In agreement with this view, we find that the conductances of the isomeric choline and methoxymethyltrimethylammonium ions are almost identical. The substitution of arsenic for nitrogen as the central atom of the cation results in only a slight lowering of the ionic conductance. For the halogenated derivatives, the results show appreciable decrease in ion conductance with increasing atomic weight. The low conductance of the iodomethyltrimethylammonium ion with respect to that of the corresponding bromo- derivative is noteworthy.

A glance at Table II will show that the introduction of electronegative atoms or groups on the substituent methyl groups of the onium ions causes a marked, although not large, decrease of the dissociation constant in all cases. The constant of ethyltrimethylammonium picrate is 4.60 $\times 10^{-5}$, while that of the corresponding tetra-

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

(5) Gleysteen and Kraus, THIS JOURNAL, **69**, 451 (1947).

methylammonium salt is 3.26×10^{-5}. The weakest of the substituted salts is choline (hydroxyethyltrimethylammonium) picrate, whose constant is 0.66×10^{-5}, while the strongest salt is methoxymethyltrimethylammonium picrate ($K = 2.54 \times 10^{-5}$), an isomer of the choline salt. The two isomeric ions have the same conductance but one contains the weakly polar methoxy group, the other, the strongly polar hydroxyl group.

Bromomethyltrimethylammonium picrate is a markedly weaker electrolyte than the corresponding bromoethyl salt ($K = 0.78 \times 10^{-5}$ and 1.32×10^{-5}, respectively). Evidently, the effect is the greater, the nearer the substituent lies to the central charge on the nitrogen atom. Larger dissociation constants result with substitution of larger atoms, as, for example, the bromomethyl derivative is weaker than the corresponding iodomethyl compound. The arsenocholine salt is stronger than the choline salt but the corresponding salt of acetylcholine is stronger than that of acetylarsenocholine.

In what manner the electronegative atoms or groups in the onium ions act in order to reduce the values of the dissociation constant of the ion-pair equilibrium is somewhat uncertain as yet. In the case of choline, hydrogen bonding with the negative ion might be suspected through the intermediation of the hydrogen of the hydroxyl group. That such hydrogen bonding occurs in the case of unsubstituted and partially substituted ammonium ions in nitrobenzene is well established.[6] However, the halogens, when introduced into the onium ions, have much the same effect as has the hydroxyl group It seems unlikely that the observed effect may be accounted for on the basis of hydrogen bonding.

(6) Witschonke, Thesis, Brown University, 1941.

The introduction of a negative element or group serves to introduce an electrical dipole into the ion. It is conceivable that interaction occurs between the ions and the dipoles. Perhaps the greatest objection to the dipole interpretation is the fact that the nearer the substituent atom lies to the charge on the nitrogen atom, the greater is its effect. Thus, the constant of the bromoethyl derivative is 1.32×10^{-5}, while that of the bromomethyl derivative is 0.78×10^{-5}. If dipole interaction is a controlling factor, we should expect the effect to be the greater the more exposed the position of the dipole.

On the basis of the available experimental results, it seems more reasonable to ascribe the effect of electronegative elements to a displacement of the center of charge in the ion. This accords with the fact that the effect is the greater, the nearer the negative atom, or group, lies to the nitrogen atom.

V. Summary

1. The conductance of the following picrates has been measured in ethylene chloride at $25°$: ethyltrimethylammonium, choline, acetylcholine, arsenocholine, acetylarsenocholine, bromoethyltrimethylammonium, bromomethyltrimethylammonium, iodomethyltrimethylammonium, and methoxymethyltrimethylammonium.

2. Values of Λ_0 and of K (dissociation constant) were obtained for all salts by the method of Fuoss.

3. The dissociation constants of salts containing negative atoms or groups in the cation are markedly lower than those of salts not containing such atoms.

4. Ion conductances have been evaluated.

PROVIDENCE, R. I.   RECEIVED NOVEMBER 6, 1946

Polarographic Characteristics of Chloro Complexes of +5 Antimony

BY JAMES J. LINGANE AND FUMIO NISHIDA

When present in the $+3$ state antimony is readily reducible at the dropping mercury electrode from its solutions in hydrochloric, nitric and sulfuric acids,[1-4] and even from sodium hydroxide solutions and in acidic, neutral and basic tartrate media,[4] but $+5$ antimony is not. Indeed, Page and Robinson[3] observed no reduction wave for $+5$ antimony (added as sodium antimony (V) gluconate) in $1 N$ hydrochloric acid, when conditions for reduction ought to be very favorable. Since in various other reactions in strongly acid

(1) V. Bayerle, Rec. trav. chim., 44, 514 (1925).
(2) K. Kacirkova, Collection Czechoslov. Chem. Commun., 1, 477 (1929).
(3) J. E. Page and F. A. Robinson, J. Soc. Chem. Ind., 61, 93 (1942).
(4) J. J. Lingane, Ind. Eng. Chem., Anal. Ed., 15, 583 (1943).

media, notably the oxidation of iodide ion and sulfurous acid, $+5$ antimony behaves as a fairly strong but rather slow oxidant the thermodynamic conditions for reduction at the dropping electrode from acid medium are certainly satisfied. The difficulty of obtaining a reduction wave must be attributed to a very small rate of reaction and a very large activation energy (overvoltage).

A similar situation exists in the case of stannic tin, and since in that case the overvoltage can be so greatly diminished by converting the aquo stannic ion to a chloro complex that a very well developed wave is obtained in concentrated chloride solutions,[5] it seemed likely that a similar reduction in overvoltage might be obtained with $+5$

(5) J. J. Lingane, THIS JOURNAL, 67, 919 (1945).