

low dielectric constants,<sup>18-20</sup> illustrated by the log  $\Lambda$ -log  $m$  relationships (Fig. 3a,b). The approach to the limiting slope of  $-1/2$ , shown as the dashed line in Fig. 3a, and the minimum in the log  $\Lambda$ -log  $m$  plot for  $\text{CH}_3\text{CN}\cdot 2\text{HCl}$  are qualitatively in accord with the ion-pair and triple-ion concepts of the ion association theories<sup>18-20</sup> for strong electrolytes (salts) in media of low dielectric constants if a significance other than a fortuitous agreement is seen in these results. By contrast the log  $\Lambda$ -log  $m$  relation for the HBr solid substrates does not approach the

(18) C. A. Kraus and R. M. Fuoss, *THIS JOURNAL*, **55**, 21 (1933).

(19) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Academic Press, Inc., New York, N. Y., 1955.

(20) H. S. Harned and B. B. Owen, "Electrolyte Solutions," 3rd Ed., Reinhold Publ. Corp., New York, N. Y., 1958.

limiting slope of  $-1/2$  nor exhibit the minimum in the concentration range up to  $5 \times 10^{-3} m$ . The possibility that a conductance minimum in this graph may occur at higher concentration is not ruled out. This curve compares more closely with the behavior of the typical unassociated uni-univalent salts in solvents of low dielectric constants.

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TROY, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, RENSSELAER POLYTECHNIC INSTITUTE]

### Hydrogen Halides in Acetonitrile. III. Electrical Conductance<sup>1</sup>

BY GEORGE J. JANZ AND STEVEN S. DANYLUK

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The electrical conductances for aged solutions of HCl, HBr and HI in anhydrous  $\text{CH}_3\text{CN}$  have been investigated at 25° to characterize the properties of these solutes as electrolytes. The molar conductances for HCl are less than 1, for HBr, 10-20, and for HI, 35-50, respectively, for the entire range from dilute to concentrated solutions. The analysis of the molar conductances in light of existing treatments for weak electrolytes and ion association is considered. In systems such as  $\text{HX}\text{-CH}_3\text{CN}$ , where molecular type solvent-solute interactions contribute to the ionic processes, the preceding do not give an adequate account of the conductance-concentration curve. A conductance equation, based on an empirical fit to the data, is proposed for these more complex systems.

The conductance-time effect and the solid substrates observed for solutions of the hydrogen halides in  $\text{CH}_3\text{CN}$  under anhydrous conditions already have been discussed.<sup>2,3</sup> The electrical conductances of the hydrogen halide- $\text{CH}_3\text{CN}$  solutions are the subject of this communication.

Qualitative observations, based on vapor pressures,<sup>4,5</sup> polarographic behavior<sup>5</sup> and conductance,<sup>6,7</sup> indicate that the halogen acids are weak electrolytes, only slightly ionized, in  $\text{CH}_3\text{CN}$ . By contrast, the more recent quantitative conductance-concentration measurements for HCl by Pleskov<sup>8</sup> show that this acid behaves as a strong electrolyte in  $\text{CH}_3\text{CN}$ . A reinvestigation of the conductances of  $\text{HCl}\text{-CH}_3\text{CN}$  solutions, with extensions to the behavior of HBr and HI in this solvent, was undertaken in an attempt to resolve these contradictory views and to account for these properties in the light of current theories of interactions in ionic solutions.<sup>9</sup>

(1) Abstracted in part from a thesis submitted by S. S. Danyluk to Rensselaer Polytechnic Institute in partial fulfillment of the requirements for the Ph.D. degree.

(2) G. J. Janz and S. S. Danyluk, Part I, *THIS JOURNAL*, **81**, 3846 (1959).

(3) G. J. Janz and S. S. Danyluk, Part II, *ibid.*, **81**, 3850 (1959).

(4) A. Naumann, *Ber.*, **47**, 247 (1914).

(5) J. F. Coetzee, Ph.D. Thesis, Univ. Minn., 1956; *Dissert. Abst.*, **16**, 1071 (1956).

(6) H. Falkenhagen, "Electrolytes," Clarendon Press, Oxford, 1934, p. 208.

(7) M. Hlasko, *Bull. Acad. Sci. Crac.*, **3**, 339 (1932).

(8) V. A. Pleskov, *J. Phys. Chem., USSR*, **22**, 3, 351 (1948); see also L. F. Audrieth and J. Kleinberg, "Non-aqueous Solvents," J. Wiley and Sons, Inc., New York, N. Y., 1955.

(9) "Interaction In Ionic Solutions," *Disc. Faraday Soc.*, **24**, 1 (1957).

### Experimental

**Apparatus and Procedure.**—The preparation and purification of  $\text{CH}_3\text{CN}$  (b.p. 81.71°;  $\kappa < 2 \times 10^{-8} \text{ ohm}^{-1} \text{ cm.}^{-1}$ ), and HCl, HBr and HI and methods of analyses already have been described.<sup>2</sup> All measurements were made in thermostated oil-baths ( $\pm 0.002^\circ$ ), using a Jones-Dike conductance bridge and accessories.<sup>2</sup>

As in the preceding studies,<sup>2,3</sup> a special effort was made to maintain anhydrous conditions in all procedures. Because of the conductance change with time, the acetonitrile-hydrogen halide solutions were allowed to "equilibrate" before dilution of the stock solutions. The stock flask, in which the solutions were prepared directly by passing the purified hydrogen halide from the generator into the nitrile, and the weight pipet were of special design with  $\text{Mg}(\text{ClO}_4)_2$  guard tubes at the exits. With suitable adapters on the flasks all transfers of solvent and solutions could be made with dry  $\text{N}_2$  gas pressure. A flask-type conductance cell of great versatility for work with anhydrous organic solvent systems is shown in Fig. 1a, b. A very low cell constant (0.05483  $\text{cm.}^{-1}$ ) was attained by the use of the concentric cylindrical platinum electrodes shown in detail in Fig. 1b. The electrode leads were spaced 5 in. apart to minimize the Parker effect. The volume of the electrode chamber was about 25 ml. The 3-way mercury seal stopcock C permits the addition of solution from the stock flask at D, or aliquot sample removal (for analysis) *via* F by use of nitrogen gas pressure at E. Rinsing of the siphon tube F is achieved by alternately pressurizing and venting the cell contents with  $\text{N}_2$  at outlets D and E. Additions from the weight pipet were facilitated by port B. In addition to the preceding design, a flask dilution cell in which a Shedlovsky-type conductance cell of about 2-ml. volume with truncated platinum cone electrodes (cell constant, 0.9998  $\text{cm.}^{-1}$ ) similarly modified for use with non-aqueous solutions under anhydrous conditions was used in the present investigations. In addition to the use of equilibrated stock solution-dilution technique, the molar conductance-concentration behavior was investigated using solutions prepared individually at various concentrations and aged directly in the cells. An investigation of the effect of water upon the molar conduct-

ance, by repeated additions of conductivity grade water from a micro-pipet to an initially anhydrously prepared and equilibrated acetonitrile-HCl solution, also was made. The solvent conductance correction,  $2-5 \times 10^{-8}$  ohm $^{-1}$  cm. $^{-1}$ , was applied to measurements where necessary.

**Data and Results. HCl.**—The molar conductances for a series of eight experiments at 25° over the concentration range  $0.655-9.6 \times 10^{-4}$  *m* are summarized in Table I, to-

TABLE I  
MOLAR CONDUCTANCES OF HYDROGEN CHLORIDE IN ACETONITRILE AT 25°

Concn. (moles/l.)	Molar conductance (ohm $^{-1}$ cm. $^2$ mole $^{-1}$ )	Concn. (moles/l.)	Molar conductance (ohm $^{-1}$ cm. $^2$ mole $^{-1}$ )
Run 1		Run 2	
0.165	0.557	0.0058	0.881
.403	.809	.024	.785
.597	.915	.093	.785
		.265	.765
		.665	.804
Run 3		Run 4	
0.00191	1.347	0.00828	0.822
.00236	1.203	.00364	.845
.00377	1.024	.00311	.850
.00592	0.915	.00136	.856
.0162	.805	.000956	.880
Run 5		Run 6	
.00720	0.533	0.00935	0.671
.00283	.554	.0236	.665
.00153	.560	.0360	.673
		.0655	.684
		.211	.698
Run 7		Run 8	
0.00125	0.743	0.00532	0.721
.00196	.735	.0110	. . .
.00353	.705	.0251	.703
.0118	.609	.0495	.732
		.0766	.787
		.138	.803
Initial (zero-time) soln.		Equilibrated soln. (smoothed values)	
0.0245	0.188	0.0010	0.800
.0347	.111	.0032	.755
.0405	.121	.0100	.733
.0659	.106	.0316	.726
.0818	.116	.1000	.731
.0955	.194	.3160	.746
.0991	.153		
.123	.148		
		Effect of water (% H <sub>2</sub> O)	
		0.0497	0.00
		.0497	0.91
		.0497	1.36
		.0497	2.24
		.0497	6.04
			0.232
			9.41
			12.6
			14.7
			24.7

getlier with the values obtained by extrapolation to zero time of the conductance of freshly prepared solutions.<sup>3</sup> The smoothed values of the molar conductance for the equilibrated or aged solutions obtained from a large scale graph of the above data are also listed in Table I. The following points should be noted with reference to these experiments. Run 1 was carried out by repeated additions of HCl and repeated agings to equilibrium values between additions; all other runs were dilution runs in which the most concentrated solution was the aged or equilibrated stock solution. The following were the aging periods for

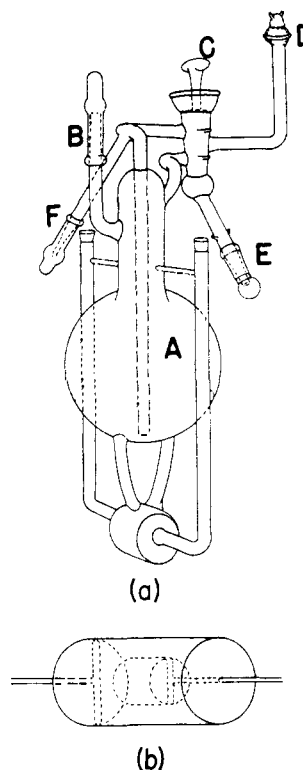


Fig. 1.—Flask-type conductance cell with concentric cylindrical electrodes: (a) cell; A, 500-ml. Pyrex flask; B, 10/30 standard-taper joint (entry port); C, 3-way mercury-seal stopcock; D, 18/9 ball-socket joint (outlet tube); E, 10/30 standard-taper joint (gas exit tube); F, 10/30 extension-tip joint; (b) electrode assembly detail.

these stock solutions: run 2, 55 hr.; 3, 800 hr.; 4, 170 hr.; 5, 850 hr.; 6, 70 hr. (solution prepared by vacuum transfer techniques)<sup>3</sup>; 7, 875 hr.; 8, 120 hr. It was noted that dilute solutions showed a smaller over-all increase in conductance with time than concentrated solutions.<sup>2</sup> This would lead to a scatter or irreproducibility in the dilution-conductance measurements since the values would be a function of the values attained by the initial stock solution in the aging period. The cause for this effect is not obvious, but a similar effect has been reported for pyridine-iodine solutions.<sup>10</sup> The scatter in the graph of  $\log \Lambda - \log m$  for the equilibrated molar conductances shown in Fig. 2A, reflects the irreproducibility of these measurements, far outside the limits of experimental error in the measurements. A very flat minimum at about  $4 \times 10^{-2}$  *m* is noted in the graphical analysis. The data with the values for the zero-time conductances show much more pronounced minima, Fig. 2B, at  $5 \times 10^{-2}$  *m*.

A graph of  $\Lambda \sqrt{m}$  vs.  $\sqrt{m}$  for the smoothed conductance values gave two straight line functions, intersecting at  $3.3 \times 10^{-2}$  *m*. This corresponds closely with the value for the minimum in the  $\log \Lambda - \log m$  relation for the equilibrated solutions. The empirical equations

$$\Lambda = 0.69 + \frac{4 \times 10^{-3}}{\sqrt{m}}; 10^{-4} < m < 4 \times 10^{-2}$$

$$\Lambda = 0.76 - \frac{5 \times 10^{-3}}{\sqrt{m}}; 10^{-2} < m < 0.7$$

express the molar conductance for the range of concentrations noted above.

In Table I are listed some of the data for the quantitative addition of conductance water (weight per cent.) to a  $4.97 \times 10^{-2}$  *m* HCl-CH<sub>3</sub>CN solution that had been aged to attain ionization equilibrium. In the range 0-1.5% H<sub>2</sub>O, the conductance increase is very rapid. The molar conductance

(10) E. F. Audrieth and E. J. Birr, THIS JOURNAL, 55, 668 (1933).

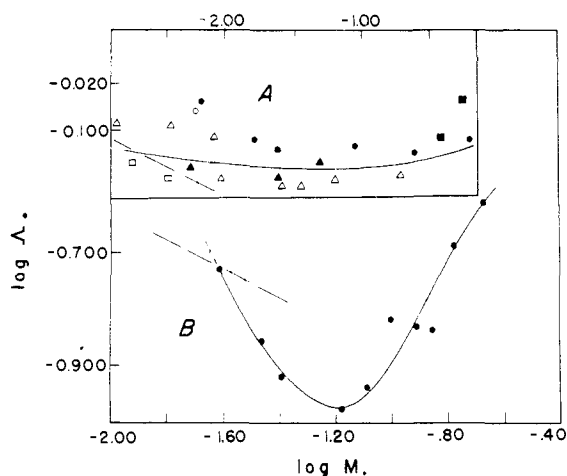


Fig. 2.—Molar conductance—concentration variation: A, equilibrated  $\text{CH}_3\text{CN-HCl}$ ; B, initial (zero-time) solutions.

for a  $4.97 \times 10^{-2} m$   $\text{HCl-CH}_3\text{CN}$  solution as reported in the data of Pleskov<sup>8</sup> was 145. It is readily apparent that the cause of the higher values in the Pleskov data must be attributed to some other factor than a water effect.

**HBr.**—The results for the HBr dilution runs and the smoothed values for the molar conductances obtained as above are summarized in Table II. The data for runs 1 and

TABLE II  
MOLAR CONDUCTANCES OF ACETONITRILE-HYDROGEN BROMIDE SOLUTIONS AT 25°

Concn. (moles/l.)	Molar conductance ( $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ )	Concn. (moles/l.)	Molar conductance ( $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ )
Run 1		Run 2	
0.00074	17.0	0.00111	23.3
.00139	14.5	.00121	22.7
.00307	13.4	.00144	21.6
.0103	12.5	.00183	20.3
.0256	13.9	.00235	18.9
.0381	14.3	.00281	18.3
.0667	15.1	.00369	16.8
.0803	15.4	.00536	14.0
.135	15.9	.00753	11.3
		.0113	11.1
		.0262	11.1
Run 3		Equilibrated solu. (smoothed values)	
0.000176	22.8	0.000225	21.4
.000259	20.5	.00040	18.6
.000346	19.0	.00090	15.8
.000584	17.0	.00160	14.4
.000761	16.2	.00250	13.6
.00109	15.3	.00500	12.6
.00163	14.4	.00750	12.3
.00247	13.6	.0100	12.0
.00353	13.0	.0150	12.4
.00461	12.7	.0250	13.6
.00585	12.4	.0500	14.8
.00805	12.0	.0750	15.4
.0123	11.7	.130	15.9

3 are illustrated graphically in Fig. 3; the molar conductance passes through a minimum at  $1.04 \times 10^{-2} m$  (cf.  $4 \times 10^{-2} m$  for HCl). The time effect is not so pronounced in  $\text{HBr-CH}_3\text{CN}$  solutions and the better reproducibility in measurements may be attributed to this factor. The somewhat higher values in the region of very dilute concentrations for run 2 may be attributed to traces of impurity in the solution

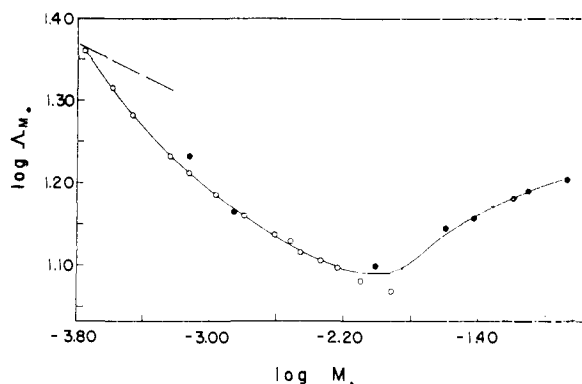


Fig. 3.—Variation of molar conductance with concentration:  $\text{CH}_3\text{CN-HBr}$  solutions.

most probably introduced experimentally in spite of the most careful techniques.

The graph of  $\Lambda\sqrt{m}$  vs.  $\sqrt{m}$  for the smoothed HBr data (Table II) gave straight line plots from which the equations

$$\Lambda = 10.2 + \frac{0.165}{\sqrt{m}}; 10^{-4} < m < 1.20 \times 10^{-2}$$

and

$$\Lambda = 17.7 - \frac{0.65}{\sqrt{m}}; 1.2 \times 10^{-2} < m < 0.1$$

were found to express the molar conductances over the concentration ranges noted above. The intersection of these lines,  $1.20 \times 10^{-2} m$ , is in close accord with the value,  $1.04 \times 10^{-2} m$ , for the minimum of conductance in this system.

**HI.**—The work with HI was limited to only one dilution run to obtain results for qualitative comparison with the preceding two hydrogen halides. The results as summarized in Table III should be regarded as of qualitative

TABLE III  
MOLAR CONDUCTANCE OF HYDROGEN IODIDE IN ACETONITRILE AT 25°

Concn. (moles/l.)	Molar conductance ( $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ )
0.00077	49.0
.00105	48.3
.00165	47.0
.00285	45.3
.00491	36.5

rather than quantitative significance accordingly. In the region of very dilute solutions, unlike the preceding two solutes, the  $\Lambda\sqrt{m}$  plot apparently approaches a straight line relationship. Further work is required to establish the exact behavior of HI in  $\text{CH}_3\text{CN}$ .

### Discussion

**Molar Conductances of Hydrogen Halides.**—No previous conductance values for HBr and HI have been reported, but a comparison of the results for HCl with the data of Pleskov<sup>8</sup> is possible. The values reported by Pleskov are about 200 times greater than those found in this investigation, e.g.,  $0.001 m$  HCl, Pleskov,<sup>8</sup> 178, this work, 0.800;  $0.01 m$  HCl, Pleskov,<sup>8</sup> 142, this work, 0.73<sub>3</sub>;  $0.10 m$  HCl, Pleskov,<sup>8</sup> 110, this work, 0.73<sub>1</sub>. Sufficient information is not available<sup>8</sup> to resolve this major discrepancy in values. The higher values of Pleskov cannot be attributed to the possible presence of water (*viz.*, Table I). The present conductances listed in Table I, as smoothed values are recommended as the best reference val-

ues for experimental or theoretical work with HCl-CH<sub>3</sub>CN solutions.

Comparison of the magnitudes of the molar conductances for the three hydrogen halides in CH<sub>3</sub>CN is of interest. The molar conductances of HCl are less than 1 for HBr, 10–20, and for HI, 35–50, respectively (Tables I, II and III). The conductances increase in the order of increasing polarizability of the solute molecules; acetonitrile acts as a differentiating solvent for the hydrogen halide species.

An inspection of the conductance-concentration curves, for the equilibrated and zero-time solutions, for HCl (Fig. 3) shows that the minimum in conductance remains in the same concentration region ( $4\text{--}5 \times 10^{-2} m$ ) in spite of the increase in conductance due to the time effect. It would appear that the ionic interactions or species in the aged solutions that contribute to the conductance are similar to those present initially at zero-time. This is in accord with arguments from the preceding communications<sup>2,3</sup> that the species HCl<sub>2</sub><sup>-</sup> and a solvated proton contribute to conductance in these solutions.

Inspection of the results shows that while the properties of HCl and HBr are those of typical univalent salt type electrolytes in non-aqueous solvents of low dielectric constants,<sup>11</sup> the limiting slopes of the log  $\Lambda$ -log  $m$  plots differ markedly from the theoretical value,  $1/2$ , predicted for ion pair species (*cf.* 2, 3, dashed lines). The properties of these solutions, as will be evident in this communication, do not lend themselves readily to structural interpretation by the theoretical treatments based on the properties of weak electrolytes or the coulombic type ion-ion and ion-solvent interactions.

If the properties of these solutes be regarded as those of weak electrolytes, an estimate of the apparent degree of dissociation of HBr is possible since the value of  $\Lambda_0 = 176$  may be estimated from the data of Coetzee<sup>8</sup> and Walden.<sup>12</sup> Using the approximation method of Davies,<sup>13</sup> the degrees of dissociation in 0.0001, 0.001 and 0.01  $m$  HBr solutions are found to be 0.13, 0.09 and 0.07, respectively. While these values have only qualitative significance, it is readily apparent that from this viewpoint all three hydrogen halides may be classed as weak electrolytes, with HCl being only very slightly ionized in anhydrous CH<sub>3</sub>CN.

The molar conductances for the three hydrogen halides in a number of organic solvents, compared for 0.01  $m$  solutions, are listed in Table IV. While the values for HCl are approximately the same for the three nitrogenous solvents, the values for HBr and HI are somewhat higher in CH<sub>3</sub>CN than in pyridine and aniline. This may be due, in part, to the higher dielectric constant of the nitrile, *i.e.*, CH<sub>3</sub>CN, 37.5; pyridine, 12.0, and aniline, 6.9, respectively at 25° since the acid-base interactions in acetonitrile are undoubtedly much less than in the other two solvents.

**Theoretical Considerations.**—An analysis of the molar conductance results in the light of existing

(11) R. H. Stokes and R. A. Robinson, "Electrolyte Solutions," Academic Press, Inc., New York, N. Y., 1955.

(12) P. Walden and E. J. Birr, *Z. physik. Chem.*, **144A**, 269 (1929).

(13) C. W. Davies, "The Conductivity of Solutions," John Wiley and Sons, Inc., New York, N. Y., 1930.

TABLE IV

CONDUCTANCES OF HYDROGEN HALIDES IN ORGANIC SOLVENTS<sup>a</sup>

Acid	Methyl alcohol	Ethyl alcohol	Isobutyl alcohol	Pyridine	Aniline	Acetonitrile
HCl	157	54.0	7.50	1.30	0.100	0.733
HBr	161	60.0	11.4	9.35	.225	12.0
HI	167	63.8	14.5	13.8	.450	35 <sup>b</sup>

<sup>a</sup> Equivalent conductances recorded for  $1 \times 10^{-2}$  equiv./l.  
<sup>b</sup> Estimated.

theories is of interest. The smoothed values for the equilibrated solutions of HBr (Table II) were selected for this purpose.

**Weak Electrolytes.**—The simplest treatment for weak electrolytes is that of the classical theory and the Law of Mass Action in the form of the Ostwald Dilution Law. A plot of  $1/\Lambda$  vs.  $(C\Lambda/1000)$  gave a curve with a decreasing positive slope, obviating the determination of  $\Lambda_0$  and  $K_i$  by this approach. Fuoss and Kraus<sup>14</sup> and Shedlovsky<sup>15</sup> have developed conductance equations for weak electrolytes based on the Onsager equation and the degree of ionization,  $\alpha$ . The Shedlovsky equation provides a somewhat better method<sup>16</sup> for estimating  $\Lambda_0$  and  $K_i$ . Both the Fuoss and the Shedlovsky plots for the data gave curves of changing slopes rather than the straight line predicted theoretically for weak electrolytes. An approximate value of  $\Lambda_0 = 32$  may be estimated by this treatment. A third analysis for weak electrolytes based on the use of the degree of ionization calculated after the method of Davies<sup>13</sup> gave no promise of success with these data.

It would appear that the data for HBr cannot be accounted for readily in terms of the existing treatments for weak electrolytes.

**Ion Aggregate Formation.**—The features of the log  $\Lambda$ -log  $m$  curves (Figs. 2 and 3) are characteristic of ionic association, *i.e.*, ion aggregate formation in solvents of low dielectric constant. The minimum in conductance has been interpreted in terms of triple ions, due to coulombic forces of interaction in the ionic solutions. According to these treatments, for ion pair formation, the slope of the log  $\Lambda$ -log  $m$  curve should have the value  $-1/2$  as it approaches zero, whereas in triple ion theory, the graph of  $\Lambda m^{1/2}$ - $m$  is predicted to be a straight line of positive slope from which the various constants may be evaluated. In the present work, the results for HBr and HCl gave limiting values of the slope quite different from the theoretical value for ion pair formation (Figs. 2, 3), and the graphs of  $\Lambda m^{1/2}$  vs.  $m$  were lines of decreasing positive slope, *i.e.*, non-linear.

Unilateral triple ion formation has been proposed<sup>17</sup> to account for the conductances of picric acid in various organic solvents. Unilateral triple ion formation apparently is feasible in systems where hydrogen bonding can occur between the anion and ion pair, *i.e.*, picric acid,  $\text{Pi-H} \dots \text{Pi}^-$ . In accord with this treatment, the primary dissociation is followed by the formation of triple ions

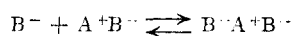
(14) R. M. Fuoss and C. A. Kraus, *THIS JOURNAL*, **55**, 476 (1933).

(15) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1933).

(16) R. M. Fuoss and T. Shedlovsky, *THIS JOURNAL*, **71**, 1496 (1949).

(17) C. M. French and I. G. Roe, *Trans. Faraday Soc.*, **49**, 314 (1953).

unilaterally



so that the resultant conductance equation has the form

$$\Lambda [C(K_2 + C)]^{1/2} = \Lambda_{01}(K_1K_2)^{1/2} + \Lambda_{03}\left(\frac{K_1}{K_2}\right)C^{1/2}$$

where  $K_1$  and  $K_2$  are the dissociation constants for ion pairs and the unilateral triple ions, respectively, and  $\Lambda_{01}\Lambda_{03}$  have the conventional significance. The graph of  $\Lambda [C(K_2 + C)]^{1/2} - C^{1/2}$  is predicted to be linear, from which the constants of the above equation are evaluated. For the HBr data, using a series of approximations, it was found that a linear plot was obtained only for values of  $K_2 \leq 10^{-4}$  in the region up to  $10^{-2} m$ ; an unequivocal determination of  $K_2$  and the constants in the above equation is not possible. The treatments of interactions in solutions based on coulombic forces only, thus, seem not adequate as an account of the conductances of the hydrogen halides in anhydrous  $\text{CH}_3\text{CN}$ . Additional effects, such as the molecular solute-solvent interactions, would account for deviations from the above theoretical treatments.

**Empirical Conductance Equation.**—The molar conductances of HCl and HBr have been found to fit an empirical equation of the form

$$\Lambda = A + B/\sqrt{m}$$

In view of the solute-solvent interactions possible in this system based on the ketoid acceptor properties of the ( $\text{C}\equiv\text{N}$ ) group,<sup>2,3</sup> an analysis of the conductance data for HCl in non-aqueous solvents,<sup>18</sup> generally has been undertaken. Preliminary results show that for HCl in acetone and benzaldehyde and for HCl and HBr (as pyridine·HX) in pyridine, an equation of the above form adequately accounts for the conductance-concentration variation, just as in  $\text{CH}_3\text{CN}$ , *i.e.*, for systems where solvent-solute compound formation occurs. Further investigations on this point are in progress in this Laboratory.

On the basis of the interactions possible in the HX- $\text{CH}_3\text{CN}$  solutions,<sup>2,3</sup> the ionic species  $\text{CH}_3\text{CNH}^+$ ,  $\text{X}^-$ ,  $\text{HX}_2^-$  and  $\text{CH}_3\text{C}(\text{X})=\text{NH}_2^+$  undoubtedly all contribute to the electrical conductance of these solutions. It would appear that the  $\text{HX}_2^-$  and  $\text{CH}_3\text{C}(\text{X})=\text{NH}_2^+$  species may be predominant in concentrated solutions.

**Acknowledgments.**—This work was made possible in part by financial support received from the U. S. Air Force, Air Research and Development Command, Office of Scientific Research, and the U. S. Atomic Energy Commission, Division of Research.

(18) G. J. Janz and S. S. Danyluk (unpublished work), R.P.I., 1958.

TROY, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

## The Photolysis and Fluorescence of Acetone and Acetone-Biacetyl Mixtures<sup>1</sup>

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The photolysis of acetone vapor has been redone at 3130 Å. to very low conversions and the fluorescence and photolysis of acetone-biacetyl mixtures have been studied. If biacetyl is present during the photolysis of acetone at 3130 Å., an energy transfer occurs between excited acetone molecules and biacetyl; the acetone photodecomposition and phosphorescence are diminished, and biacetyl phosphorescence is observed. Since biacetyl is a reaction product of acetone photolysis, the quantum yield of acetone decomposition decreases as the time of irradiation increases. The ratios of reaction products also change with time of irradiation. A detailed mechanism is presented for the primary process in acetone and for the energy transfer between acetone and biacetyl.

### Introduction

Extensive studies have been made of the vapor-phase photodecomposition and fluorescence of acetone. Recently a comprehensive review of the primary process in simple ketones has been published.<sup>3</sup> In the photolysis of acetone at room temperature biacetyl is a product. Okabe<sup>4</sup> and others have shown that biacetyl complicates both the photochemistry and fluorescence of acetone. If acetone is excited by 3130 Å. radiation, the biacetyl fluoresces. Because of this energy transfer the previous interpretation may be incomplete.

Recently Roebber, Rollefson and Pimentel<sup>5</sup> have proposed two primary processes as follows: (1) a direct dissociation of excited molecules into methyl and acetyl radicals; (2) a collision induced dissociation into two methyl radicals and carbon monoxide. These alternative processes will be discussed in a later section of the present article.

The photolysis of acetone has been redone to very low conversions. Also the fluorescence and photolysis of acetone-biacetyl mixtures have been studied. This paper presents the results of these studies.

### Experimental

Eastman spectroscopic grade acetone was used. The acetone was placed over Drierite for two days and distilled. The middle third was collected. Its mass spectrum showed no impurities. Eastman white-label biacetyl and diacetone alcohol were used. The purification of the biacetyl was the same as for acetone. The biacetyl used in the fluorescence studies was not dried, but it was fractionated. A

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