ino-type structure is strongly developed,[8] with little evidence of the nitrilium type structure present.

In the latter series of interactions, the conductance–time effect may be understood as due to the finite rate of formation of the imino-type compound 6 and consequent ionization. In the charge transfer interaction scheme, the rearrangement from the "outer" to an "inner" complex 2 is normally postulated as the slow step. Charge-transfer processes are generally quite temperature insensitive.[28] The very marked temperature dependence of the time effect observed on the present investigation suggests that it may be attributed in large part to a slow reaction to form the imino-type compound. The enhancement of these interactions owing to the increased polarizabilities of HBr and HI would lead

to a more facile formation of the imino hydrohalides with these acids. The diminished time effects for the HBr and HI solutions are thus understood.

Any interpretation of the interactions in acetonitrile–hydrogen halide solutions should account for the formation of solid substrates and their physical properties and the molar conductance–concentration properties for the three hydrogen halides in acetonitrile. These are described elsewhere in detail.[8,9]

(28) M. Smith and M. C. R. Symons, *Disc. Faraday Soc.*, **24**, 206 (1957).

TROY, NEW YORK

Hydrogen Halides in Acetonitrile. II. Solid Substrates[1]

BY GEORGE J. JANZ AND STEVEN S. DANYLUK[1]

The nature of the solid substrates, $CH_3CN\cdot2HX$, isolable from solutions of HCl, HBr and HI in anhydrous CH_3CN has been investigated. The structure of $CH_3CN\cdot2HCl$ seems to be essentially that of a nitrilium salt, $(CH_3CNH^+)(HCl_2)^-$; whereas for $CH_3CN\cdot2HBr$ and $CH_3CN\cdot2HI$, an iminohydrohalide structure, $CH_3C(X)=NH_2{}^+X^-$, seems most probable. The physical properties, spectroscopic data and electrical conductance of these substrates in CH_3CN are reported.

In view of the increasing use of non-aqueous solvents in various physicochemical and analytical techniques, *e.g.*, polarography, acid–base titrimetry and the renewed interest in ionic processes in solution,[2] the need for precise measurements in these solvents is evident. The investigation of the hydrogen halides in polar organic solvents affords an opportunity to study the complicating factors of solute–solute, solute–solvent, as well as ionic interactions so frequently masked in levelling solvents like water. This communication reports the results of an investigation of the nature of the solid substrates that may be isolated from solutions of hydrogen halides in anhydrous acetonitrile at room temperatures. A knowledge of their structure is essential in understanding[3,4] the interactions in these solutions.

The formation of solid substrates from hydrogen halide–acetonitrile has been noted by various workers, but the views on the structure of these are quite conflicting. The problems may be illustrated best by a brief reference to the status of knowledge for the substrates from solutions of hydrogen chloride in acetonitrile. Hantzsch[5] showed cryoscopically and optically that the compounds were in many respects like nitrilium salts, RCN·2HX, which yielded the original nitriles when treated with water. The formation of acetamide from these com-

pounds by prolonged exposure to atmospheric moisture was postulated by an intermediate, $CH_3-C(OH)NH\cdot HX$, in the reactions. Hinkel and Treharne[6] obtained the dihydrogen chloride compound from the above system by chilling the solutions to $-17°$ and reported the structure to be $CH_3CCl_2-NH_2$, *i.e.*, acetamido dichloride. Decomposition to acetamido monochloride with the evolution of HCl at 6° and further interactions leading to dimers such as α-chloroethylidene acetamidine were cited in favor of this structural analysis. Inspection of the properties of the hydrogen chloride compound reported to Hinkel and Treharne suggests that these are more in accord with an ionic nature in the structure than the completely covalent acetamido dihalide structure advanced by these investigators. Most recently, Murray and Schneider[7] investigated the freezing point diagram by low temperature cryoscopic techniques for the complete range of compositions, 0–100% acetonitrile and hydrogen chloride. Well defined addition compounds of the various compositions were confirmed: $CH_3CN\cdot HCl$ (m.p. $-63.2°$); $2CH_3CN\cdot3HCl$(m.p. $-88°$); $CH_3CN\cdot 5HCl$(m.p. $-123.6°$); $CH_3CN\cdot7HCl$(m.p. $-125°$). The formation of a dihydrochloride, as noted by the previous investigators,[5,6] was not reported. The polyatomic compounds were considered in light of the intermolecular force field of the nitrile on the basis of the electron orbital structure and charge distribution in the $C≡N$ group. Structures rather like imino acids were proposed in which the hydrogen halide is very loosely bonded to the nitrile.

(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) *Disc. Faraday Soc.*, **24**, 1 (1957).

(3) G. J. Janz and S. S. Danyluk, Part I, THIS JOURNAL, **81**, 3850 (1959).

(4) G. J. Janz and S. S. Danyluk, Part III, *ibid.*, **81**, 3854 (1959).

(5) A. Hantzsch, *Ber.*, **64**, 667 (1931).

(6) L. E. Hinkel and G. J. Treharne, *J. Chem. Soc.*, 866 (1945).

(7) F. E. Murray and W. G. Schneider, *Can. J. Chem.*, **33**, 797 (1955).

A reinvestigation of the acetonitrile–hydrogen chloride substrate $CH_3CN \cdot 2HCl$, with extension to the dihydrobromide and dihydrogen iodide to resolve some of the problems above was undertaken as part of this present investigation.

Experimental

As in the preceding investigation,[3] particular emphasis was placed on the maintenance of rigid anhydrous conditions, and all apparatus was designed to fulfil this requirement. The solvent and solutes, and the conductance bridge and accessories have already been described.[3]

Procedures.—Preliminary measurements indicated that whereas a saturated solution of HCl in acetonitrile could be stored indefinitely at room temperature without formation of a crystalline substrate, crystals would readily form when the saturated solution had been chilled at $-20°$. At this temperature, after an induction period of 5 to 10 hr., a copious separation of crystals, stable in sealed tubes at room temperature, occurred. The addition compound in $CH_3CN-HCl$, accordingly, was prepared by saturating chilled ($-20°$) acetonitrile with dry HCl in an all glass apparatus designed with a sintered glass disc for filtration *in situ*. The arrangement of the assembly is shown in Fig. 1a, where G and H are the guard tubes and the vessels D and C can be chilled, if required, in Dewar flasks. Approximately 15 ml. of pure CH_3CN was siphoned from a storage flask into C under a dry N_2 atmosphere. Anhydrous HCl was forced from G *via* D to bubble through the sintered disc F into the nitrile in C chilled at $-20°$. Filtration after the experiment was accomplished simply by using a positive pressure of nitrogen gas from H to force the supernatant liquid into chamber D. Excess HCl was removed by a dry nitrogen sweep over the crystals retained on the sintered glass frit. The crystals could be transferred by inverting C to various vessels as required for further study using suitable adapters and nitrogen pressure, *i.e.*, without exposure to atmospheric conditions. The crystals were generally stored at $-20°$ until required for further measurements. In the case of the $CH_3CN-HBr$ and CH_3CN-HI solutions, the respective solid substances were isolated by saturating the nitrile at room temperature with the appropriate hydrogen halide, using the same glass apparatus.

For analysis of the crystals for halide content, the solids were formed directly in a small bubbling tube of the design shown in Fig. 1b. Dry gas was passed through the tube until all the nitrile in C had reacted. The exits A and B of the tube were sealed with a glass torch before weighing the samples. The entire tube was immersed in an aliquot of water, and the salt was dissolved by fracturing the thin membrane C in the weighing tube. The resultant solutions were analyzed by both standard base and Volhard titrations. Possible errors due to sample transfers and escape of hydrogen halide were thus minimized.

The conductivities of the solutions already have been described.[3] The solutions were prepared by adding the crystals to a known amount of acetonitrile in a weight pipet. Aliquots were used for transfer to the conductance cells and for analytical checks on the composition.

Melting points were determined in sealed capillary tubes in the conventional stirred apparatus. In the case of the hydrochloride substrate, re-formation of the crystals occurred on rechilling the tube to $-20°$ after such measurements.

Infrared absorption spectra were recorded with a Perkin–Elmer Model 21 Double Beam Spectrometer and cells with appropriate windows. An infrared cell design for volatile solids[8] was used to obtain the spectrum of the crystalline solid for the hydrogen bromide solutions. Attempts to obtain the spectra for the hydrogen chloride and hydrogen iodide crystalline substrates were not successful. The infrared spectra for solutions of the substrates in acetonitrile were likewise investigated.

The solubilities of the crystalline substrates were qualitatively determined in the conventional organic solvents. The behavior on exposure to the atmosphere also was investigated.
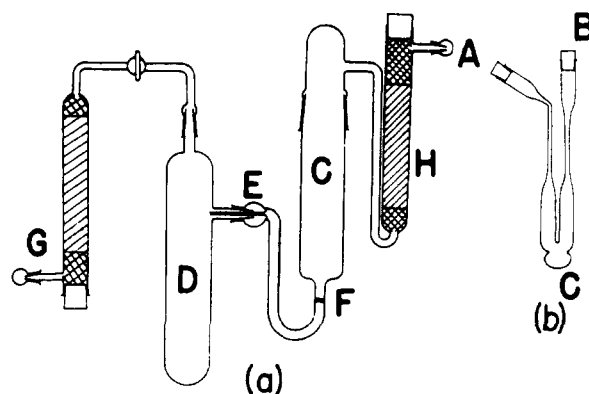
(8) G. J. Janz and S. S. Danyluk, *Appl. Spectroscopy*, **13**, in press (1959)

Fig. 1.—(a) All glass assembly for preparation of solid substrates in the CHCN–HX systems. (b) Microbubbling tube for preparation of substrates in sealed ampoules.

Results

The analyses were in close accord with the empirical formula $CH_3CN \cdot 2HX$ for the HCl and HBr substrates (HCl, found 64.0, theor. 63.7; HBr, found 79.0, theor. 79.8). For HI, the agreement (HI, found 81, theor. 86.1) leaves something to be desired but the analyses were complicated by the photochemical instability of this solid.

The solubilities of these solids in acetonitrile at $25°$ increased in the order: $CH_3CN \cdot 2HI < CH_3CN \cdot 2HBr < CH_3CN \cdot 2HCl$. In the more concentrated solutions evolution of the hydrogen halide was noted, indicating a decomposition of the compounds. The three compounds were found to be insoluble in CCl_4, $CHCl_3$ and benzene and only slightly soluble in diethyl ether.

In sealed tubes, these melting point characteristics were noted: $CH_3CN \cdot 2HCl$, sinters, $28°$; melted with evolution of some gas, $32°$; $CH_3CN \cdot 2HBr$, sinters, $81°$; m. with copious evolution of gas, $83-85°$; $CH_3CN \cdot 2HI$, m. $90-100$; only qualitative observations possible. On exposure to the atmosphere at $25°$, each of the above solids decomposed rapidly with the evolution of the acid and formation of CH_3CN. With $CH_3CN \cdot 2HCl$, a fine white crystalline solid also was formed, identified as acetamide hydrochloride by its m.p., analysis and infrared spectrum.

Infrared Spectra: $CH_3CN \cdot 2HCl$.—The unstable character and low melting point of the solid made the conventional solid sample techniques impractical. Attempts to gain the spectrum using a low temperature cell[9] were unsuccessful. The infrared spectrum for the solid dissolved in anhydrous acetonitrile accordingly was investigated, at concentrations 0.5 and 1.15 m, respectively. Comparison of the spectra with that for pure acetonitrile showed exact correspondence except for the following points. Both solutions showed a broad, strong absorption band in the region 2400–2700 cm.$^{-1}$. The HCl fundamental occurs at 2480 cm.$^{-1}$. The above shift in this band is generally associated with compound formation between solute and solvent molecules.[10] In the more concentrated solution

(9) G. J. Janz and W. E. Fitzgerald, *ibid.*, **9**, 4 (1955).

(10) M. L. Josien and G. Sourisseau, *Bull. soc. chim. France*, 178 (1955).

(1.5 m) two additional bands were noted at 1180 cm.$^{-1}$ (m) and 945 cm.$^{-1}$(w). The former may be attributed to the ν_2 bending vibration (1180 cm.$^{-1}$) of the dichloride ion,[11] HCl_2^-. The ν_1 stretching vibration (1565 cm.$^{-1}$) for the dichloride ion falls in the region of the broad, strong band associated with the methyl deformation vibrations and is masked accordingly by the absorption spectrum of the solvent. The assignment of the weak 945 cm.$^{-1}$ band is not obvious but lies in the region of the NH_2 rocking modes. It was noted that the infrared spectra of HCl–CH_3CN solutions prepared by bubbling HCl into the nitrile corresponded exactly to the spectrum of $CH_3CN \cdot 2HCl$ dissolved in the nitrile. No band corresponding to the C–Cl stretching mode (750 cm.$^{-1}$) was observed. The spectrum compares most closely with that predicted for a nitrilium salt, $CH_3CNH^+(HX_2^-)$. **$CH_3CN \cdot$ 2HBr.**—A comparison of the infrared spectrum for the solid with that for pure acetonitrile is shown in Fig. 2. The most striking features are the
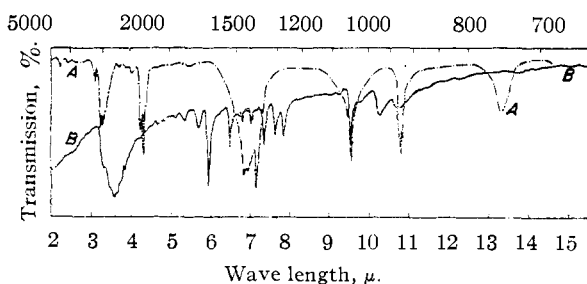

Fig. 2.—Infrared spectrum of the solid compounds, $CH_3CN \cdot$ 2HBr: A, pure $CH_3CN(l)$;   B, pure $CH_3CN \cdot 2HBr(s)$.

greatly diminished absorption of the C≡N stretching vibration (2275 cm.$^{-1}$ and the appearance of the strong 1630 cm.$^{-1}$ band in the spectrum of the solid. The latter may be assigned to the C=N stretching mode in imino type compounds[12] (1640–1690 cm.$^{-1}$). The disappearance of the (C≡N) stretching mode in the solid is understood in the light of such a structural change. The strong, broad band in the region 2550–3000 cm.$^{-1}$ in the solid compares closely to the strong absorption observed in this region (2300–2800 cm.$^{-1}$) by Chenon and Sandorfy[13] for a large number of primary amine hydrobromides and attributed to the R–H$^+$ . . . X$^-$ stretching mode. The spectrum for the solid is understood in the light of an imino hydrobromide type structure, $CH_3C(Br)=NH \cdot HBr$ for the solid substrate. **$CH_3CN \cdot 2HI$.**—Attempts to obtain the infrared spectrum of the dihydrogen iodide as a solid or in solution were unsuccessful as already noted.

Electrical Conductance.—The conductance-time effect of freshly prepared $CH_3CN \cdot 2HX$ solutions already has been noted.[3] The molar conductance-concentration variation for the compounds, $CH_3CN \cdot 2HCl$ and $CH_3CN \cdot 2HBr$ was determined in acetonitrile at 25° by dilution of a stock solution that had reached ionization equilibrium. The results are summarized in Table I. Conductance

(11) H. F. Herbrandson and N. Zutty (unpublished work), R. P. I., 1957.

(12) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1955.

(13) B. Chenon and C. Sandorfy, *Can. J. Chem.*, **36**, 1181 (1958).

measurements for the dihydroiodide compound were not undertaken owing to the secondary processes and reactions occurring in the solutions.[3,4] For the $CH_3CN \cdot 2HCl$ solutions, the conductance relation is illustrated graphically in Fig. 3a. The

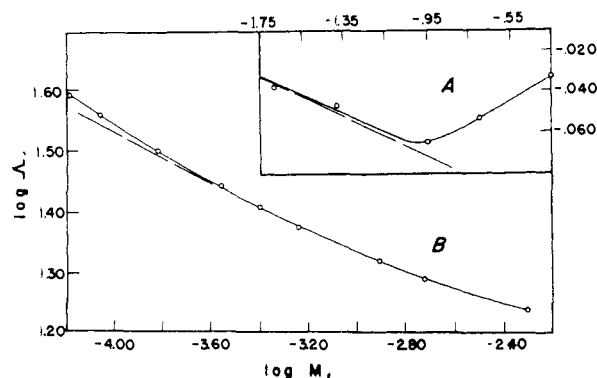Fig. 3.—Conductance of $CH_3CN \cdot 2HCl$ and $CH_3CN \cdot$ 2HBr in CH_3CN at 25°:   (A) $CH_3CN \cdot 2HCl$;   (B) $CH_3CN \cdot$ 2HBr. The dashed line is for a limiting slope of $-1/2$.

log Λ–log m curve passes through a minimum at approximately 0.1 m. At concentrations below 0.02 m, the conductance measurements suffered irreproducibility owing to the very high resistances of the solution (*i.e.*, comparable with that of the pure solvent). A more detailed analysis of the conductance–concentration relation is the subject of a later communication.[4] The solutions of $CH_3CN \cdot 2HBr$ have much higher equivalent conductances than the corresponding hydrochloride salt. The Λ–$\sqrt{m}$ relation reveals that this salt behaves as a typical weak electrolyte. The log Λ–log m relation shown in Fig. 3b does not pass through a minimum in the concentration range studied. The limiting slope of this graph in the region of dilute solutions was found to be -0.66. The conductance data can be expressed by an empirical equation

$$\Lambda = 14.0 + 0.230m^{-1/2}$$

within the limits of the experimental measurements, *i.e.*, the graph of $\Lambda\sqrt{m}$ *vs.* $\sqrt{m}$ is a straight line. A comparison of the values thus calculated with the experimental results is given in Table I. The deviations in the low concentration range are due to the increased experimental difficulties inherent in this range. The significance of this equation is considered in more detail when the behavior of HBr in CH_3CN solutions is discussed.[4]

Discussion

The formation of solid substrates in acetonitrile-hydrogen halide systems under strictly anhydrous conditions is confirmed. In general the compositions of the substrates correspond to the empirical formula $CH_3CN \cdot 2HX$, confirming the observations of previous investigators.[5,6,14,15] The exact composition of the hydroiodide compound has not been established unequivocally although a comparison of the other systems favors the dihydroiodide. Biltz[14] prepared $CH_3CN \cdot 2HI$ by passing HI through CH_3CN cooled in ice. The ease of formation and

(14) H. Biltz, *Ber.*, **25**, 2542 (1892)

(15) C. Engler, *Ann.*, **142**, 291 (1867)

TABLE I

CONDUCTANCES OF SOLID SUBSTRATES IN CH_3CN

(a) $CH_3CN \cdot 2HCl$

m (moles/l.)	0.446	0.201	0.114	0.0416	0.0205
Λ (ohms^{-1} cm.^{2} mole^{-1})	0.928	0.885	0.862	0.897	0.917

(b) $CH_3CN \cdot 2HBr$

m (moles/l.) $\times 10^3$	5.02	1.88	1.22	0.578	0.400
Λ obsd.	17.2	19.3	20.8	23.7	25.6
Λ calcd.[a]	17.2	19.3	20.6	23.6	25.5
m (moles/l.) $\times 10^3$	0.272	0.150	0.0881	0.065	
Λ obsd.	27.7	31.8	36.4	39.1	
Λ calcd.[a]	27.9	32.8	38.5	42.5	

[a] See equation 1, this paper.

thermal stability (in sealed systems) of these increase in the order

$$CH_3CN \cdot 2HCl < CH_3CN \cdot 2HBr < CH_3CN \cdot 2HI$$

The physical properties of the solid substrates are in accord with a considerable ionic character in these solids.

With reference to the CH_3CN–HCl system, compounds of the empirical structure have been reported both by Hantzsch[5] and Hinkel and Treharne[6] but not by Murray and Schneider.[7] Some recent measurements by Schneider[16] have shown that for a solution of acetonitrile containing 2 moles of HCl the freezing point of $-80°$ reported in the earlier measurements[7] cannot be reproduced if the mixture is put through a thermal cycle repeatedly. Cooling this solution to $-100°$, warming to $20°$ and cooling again cause a copious precipitation of a crystalline substrate and the original low freezing point is no longer reproduced. The crystals thus separated melt above $20°$, although an exact value was not reported. A nuclear magnetic resonance spectrum of the solution was in accord with that of a simple mixture of HCl and CH_3CN (or a solution of a salt).[16] The presence of the dichloride ion, HCl_2^-, in concentrated solutions of this compound was confirmed in the present investigation. A nitrilium salt type structure, $[CH_3CNH^+]HX_2^-$, seems most probable for this solid. This is in accord with the structure first proposed by Hantzsch.[5] No evidence for the acetamido-dichloride type compounds[6] was found in the present study. A transition from a molecular type addition compound, in which the binding forces are primarily the electrostatic forces of a hydrogen bond to a salt-like compound, could account for the discrepancy in the melting points noted by Schneider[16] and the need for a thermal cycle or incubation period. In accord with the concepts of charge-transfer theory[17] this would correspond to the transition from an outer complex to an inner complex by charge-transfer processes.

The occurrence of intermolecular complexes in a 1:1 ratio is readily anticipated as due to simple acid–base electrostatic interactions. The donor lone pair orbital in the N atom of the (C≡N) group is directed along the C≡N axis, and the 1:1

(16) W. G. Schneider, private communication, 1958.
(17) R. S. Mulliken, *J. Phys. Chem.*, **56**, 814 (1952).

addition compounds can be assigned the completely linear configuration: CH_3—C≡N—HX. The low melting points of these compounds (cf. CH_3-$CN \cdot HCl$, m.p. $-63.2°$[7]) are not compatible with salt-type structures and correspond to the outer complexes of charge-transfer concepts. Transformation to the inner complex, $CH_3CNH^+X^-$, by a charge transfer corresponding to σ-bond scission in the HX depends in part on the polarizability of the acid molecule. In accord with the polarizabilities within the hydrogen halide series (HCl < HBr < HI) the 1:1 compound with HI would have the most ionic character. As noted in the preceding contribution,[3] the time effect may in part be due to the charge-transfer step in the process of transformation of the initial 1:1 addition complex to the salt-type structure. The order of the time effect, i.e., smallest with the HI solutions, is in accord with the prediction based on the polarizabilities of the hydrogen halides.

The formation of the compounds having a 1:2 molar ratio of nitrile:hydrogen halide, respectively, follows from the preceding in light of the structural data gained in the present investigation. The solvated anion X^-(solv) may function as an n' onium donor.[17] Interaction with a second acid acceptor species would lead to the dihalide ion species, HX_2^-solv, and the over-all interaction would result in the nitrilium type salt, $CH_3CNH^+HX_2^-$, confirmed as the most probable structure for the $CH_3CN \cdot 2HCl$ compound. The possibility of an imino hydrochloride structure as found for $CH_3CN \cdot 2HBr$ is not, however, ruled out.

Alternately additional donor centers may be brought into play by virtue of the ketoid π-acceptor properties of the nitrile group.[17] Thus the formation of an imino type structure through the interaction of the second hydrogen halide molecule with the canonical structure of the 1:1 compound ($CH_3C^+=NHX^-$) is understood. The infrared spectrum for solid $CH_3CN \cdot 2HBr$ confirms the structure of this compound to be $CH_3C(Br)=NH^+Br^-$. The increased polarizabilities of HBr and HI would favor an enhancement of the imino-type interactions over that in the CH_3CN–HCl system. An imino hydroiodide structure seems most probable for the HI compound in accord with its physical properties, but spectroscopic confirmation of this was not successful in the present investigation. The time effect[3] in the conductance of these solutions is now understood as due to the finite rate of the interaction with the second hydrogen halide molecule to form the imino type salt. As already noted,[3] the temperature dependence of the time effect is understood most readily in the light of such interaction rather than charge-transfer processes.

The molar conductance–concentration relationships for $CH_3CN \cdot 2HCl$ and $CH_3CN \cdot 2HBr$ are quite similar to those for the solutions prepared using the respective acids as solutes and a detailed analysis of these results is deferred for later discussion accordingly.[4] It is sufficient to note for the present that solutions of $CH_3CN \cdot 2HBr$ have a higher conductance than solutions of $CH_3CN \cdot 2HCl$ and that both compounds have the properties of uni-univalent salt-type electrolytes in solvents of

low dielectric constants,[18-20] illustrated by the log Λ–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 Λ–log m plot for $CH_3CN \cdot 2HCl$ are qualitatively in accord with the ion-pair and triple-ion concepts of the ion association theories[18-20] 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 Λ–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.

TROY, NEW YORK

Hydrogen Halides in Acetonitrile. III. Electrical Conductance[1]

BY GEORGE J. JANZ AND STEVEN S. DANYLUK

The electrical conductances for aged solutions of HCl, HBr and HI in anhydrous CH_3CN 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 $HX-CH_3CN$, 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 CH_3CN under anhydrous conditions already have been discussed.[2,3] The electrical conductances of the hydrogen halide–CH_3CN solutions are the subject of this communication.

Qualitative observations, based on vapor pressures,[4,5] polarographic behavior[5] and conductance,[6,7] indicate that the halogen acids are weak electrolytes, only slightly ionized, in CH_3CN. By contrast, the more recent quantitative conductance–concentration measurements for HCl by Pleskov[8] show that this acid behaves as a strong electrolyte in CH_3CN. A reinvestigation of the conductances of $HCl-CH_3CN$ 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.[9]

(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 CH_3CN (b.p. 81.7$_1$°; $\kappa <2 \times 10^{-8}$ ohm^{-1} cm.$^{-1}$), and HCl, HBr and HI and methods of analyses already have been described.[2] All measurements were made in thermostated oil-baths ($\pm 0.002°$), using a Jones–Dike conductance bridge and accessories.[2]

As in the preceding studies,[2,3] 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 $Mg(ClO_4)_2$ guard tubes at the exits. With suitable adapters on the flasks all transfers of solvent and solutions could be made with dry 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 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 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 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-