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

Hydrogen Halides in Acetonitrile. I. Ionization Processes[1]

BY GEORGE J. JANZ AND STEVEN S. DANYLUK

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Conductance measurements at 25° are reported for freshly prepared solutions of HCl, HBr and HI in anhydrous CH_3CN. At each concentration, the conductances increase, approaching maximum values as the solution ages. The nature of the time effect is examined with reference to the properties of the solvent, the solutes, and water. The time effect is attributed to a slow attainment of ionization equilibrium due to solvent–solute interactions, and subsequent ionization processes, with the formation of nitrilium type salts and imino-hydrohalides as the two most probable species in these solutions.

Acetonitrile, CH_3CN, the simplest alkyl derivative of hydrogen cyanide, is an excellent solvent for many inorganic substances,[3] and its ability to serve as a suitable ionizing medium for various electrolytes has been well established.[2–5] The dielectric constant (37.5 at 25°)[6] is much lower than that of hydrogen cyanide[3] (123 at 15.6°) but is slightly greater than that of methanol (32.63 at 25°).[6] Association in the liquid state is not as marked as in the case of methanol or ethanol (*cf.* Trouton's constant, 20.1, 24.9 and 26.5, respectively). Acetonitrile behaves as an amphiprotic solvent, exhibiting extremely weak acidic and slightly stronger basic properties, rather like acetone. Electron donor ability is not as marked as in the case of nitrogeneous solvents such as pyridine (*cf.* ionization potentials 11.96, 9.8, respectively). Polarographic measurements on solutions of various acids[7] indicate that acetonitrile also acts as a differentiating solvent.

As part of a program on the nature of simple electrolytes in anhydrous polar organic solvents, the properties of the hydrogen halides, HCl, HBr and HI in anhydrous acetonitrile have been investigated. Preliminary conductance measurements at 25° indicated that the conductances were not stable for specific solutions but increased to a maximum or "stabilized" value as the solutions aged. From saturated solutions, crystalline substrates were separable with well defined physical properties. The investigations of the substrates and the conductance–concentration relations for the solutions form Parts II[8] and Parts III[9] of this series, respectively. The present communication reports the results for the studies of the conductance–time effects in these solutions.

The increase of conductance with time in nonaqueous solutions of electrolytes has been attributed to various ionic processes. A brief survey, with special reference to the more recent contributions which reflect current thinking, is of interest. French and Roe[10] interpreted the increase in conductance with time for picric acid in acetonitrile[11,12] on the basis of a slow ionization process associated with proton acceptor properties of the solvent and with the ionic interactions leading to the formation of unilateral triple ions. The conductance change with time found for malonic esters (pseudo-acids) has been interpreted by Pearson and Mills[13] as due to the slow ionization of these substances. Pyridine–iodine solutions show a marked conductance–time effect.[14,15] According to Mulliken and Reid,[16] this may be interpreted as a slow passage from an "outer" to the "inner" charge-transfer complex due to an energy barrier of considerable height. The existence of well defined charge-transfer bonds was based on spectrophotometric measurements. Solutions of iodine and iodine monohalides have recently been reported to show conductance–time effects.[17–19] It was shown[19] that acetonitrile formed 1:1 complexes with iodine monohalides, and the gradual conductance increase was attributed to a slow transition of the "outer complex," $CH_3CN{\cdot}IX$, to the "inner complex" $CH_3CNI^+X^-$, by charge-transfer processes. With reference to the hydrogen halides in acetonitrile, the only conductance studies are those of Pleskov[20] for HCl, according to which HCl is a strong electrolyte and the conductivity does not alter with time.

Experimental

Acetonitrile.—Acetonitrile (reagent grade) was carefully purified to give a solvent with a water content less than 0.01% and free from contaminants such as acetamide, acetic acid and methylisonitrile. A variety of procedures for preparing pure, dry acetonitrile have been described.[6] In the present work, the following procedure was found most satisfactory. After standing over anhydrous $CaCl_2$ for several days, the nitrile was distilled and the middle fraction was stored over P_2O_5. A bright orange coloration[7,10,12] was noted. After 36 hr. over P_2O_5, the nitrile was decanted and redistilled as above. It was necessary to repeat this step at least 6 times before no discoloration was noted over P_2O_5. The nitrile then was distilled into a receiver containing freshly fused K_2CO_3 and in turn distilled from the carbonate. The acetonitrile thus obtained finally was refluxed and distilled alone, the middle cut was collected in a 2-liter flask of

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special design for storage and siphon transfer of the pure solvent.

In the preceding, as well as throughout this work, special attention was directed to the design of the flasks and procedures to maintain strictly anhydrous conditions. Contact with the atmosphere was permitted through guard tubes containing the nitrile or anhydrous $Mg(ClO_4)_2$. For the distillations above, an all-glass grease free assembly, with a 100 cm. × 2.5 cm. vacuum jacketed column packed with $^1/_8$ in. Hastalloy helices (Podbielniak Co., Chi.), a solenoid controlled take-off and a magnetic distilling adapter,[21] were used.

The physical properties of the nitrile thus obtained were: b.p. 81.7_1° (759.7 mm.); d^{25} 0.7768; n^{20}D, 1.34388; κ, 2–5 × 10^{-8} ohm^{-1} cm.$^{-1}$ (*cf.* lit. val., 81.6° (760 mm.); 0.77683; 1.34411 and 0.6–2.5 × 10^{-9}, respectively.) The water content, by the Karl Fischer titration, was found to be less than 1 × 10^{-3} *m* (<0.01 wt. %). The ultraviolet spectrum showed the absence of impurities having the carbonyl group. It was used without further purification.

Hydrogen Halides.—Anhydrous HCl was generated from H_2SO_4 and NaCl using the all glass apparatus described by Taniguchi and Janz.[22] Hydrogen bromide (Matheson Co., min. purity, 99.8%) was passed through $Mg(ClO_4)_2$ towers and used without further purification. In some instances HBr from H_3PO_4 and KBr carefully purified to remove last traces of bromine was used to confirm the results with the commercially obtained product. Hydrogen iodide was prepared catalytically from H_2 and I_2 in an all glass apparatus.[23] Because of the decomposition on exposure to light, the preparation of HI and subsequent measurements with the HI solutions were all carried out in a darkened room.

Apparatus for Conductance Measurements.—The conductances of all solutions were measured with a Leeds and Northrup a.c. conductance bridge and accessories designed by Jones and modified by Dike.[24] A light transformer oil was used in the thermostat baths, with temperature control to ±0.002° at 25°. Four conductance cells, with constants ranging from 1.129 to 0.0548_3 cm.$^{-1}$, were used, each modified so that the solutions could be prepared directly in the cells by bubbling the anhydrous hydrogen halide through a weighed amount of nitrile. The electrodes were not platinized. A design of the cell found most convenient for studies of the time effect is illustrated in Fig. 1. A 250-ml. flask A was sealed to the 20 ml. electrode chamber B by a 10 mm. diam. tube. The adapter C enabled dilution or removal of the cell contents. The port D permitted the use of HCl bubbling or N_2 gas venting adapters as required. The 15 mm. diam. disc electrodes were made from 0.15 mm. platinum sheet, with leads 4 in. apart to minimize the "Parker effect." The height of the solution above the electrodes had no effect on the resistance reading. The reproducibility of readings between fillings was better than 0.02%. Cell constants were determined in the conventional manner.

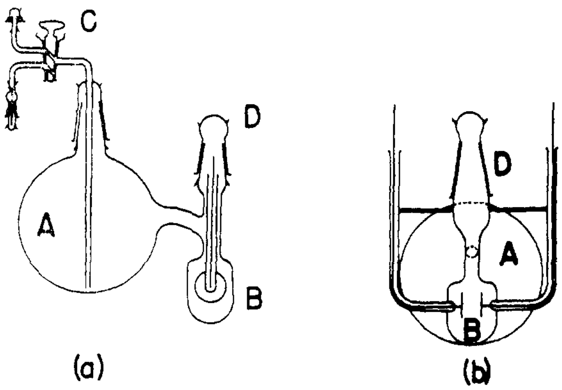

Fig. 1.—Disc electrode conductance cell for time effect measurements.

Procedure.—All glassware was thoroughly cleaned, oven-dried, swept with dry nitrogen and liberally rinsed with purified acetonitrile prior to use. For measurements of the conductance–time effect, the solutions were prepared directly in the cells as noted above. Measurements were started immediately after temperature equilibration had been achieved (usually 20–35 minutes), and subsequently at 5 minute intervals for the initial period. Solutions were analyzed by standard NaOH and Volhard titrations on the completion of the experiment.

The effect of a strong non-ionic proton acceptor, azobenzene, was investigated by the addition of a weighed amount of a sample (twice recrystallized from ethanol) to the solution in the conductance cell. Several experiments in which measured amounts of water had been added to the solution were carried out similarly. The effect of a dry nitrogen sweep through the "aged" or stabilized solution was investigated, the hydrogen chloride thus recovered being trapped in a series of NaOH bubblers.

Vacuum transfer techniques were used to check on the nature of an HCl solution. All the glass-ware and the conductance cell were sealed to a high vacuum manifold and pumped down to 10^{-6} mm. pressure for a period of 24 hr. before the experiment. Frequent purges with dry N_2 gas and flaming of the glassware were used to ensure the removal of traces of adsorbed water. Transference of the solution to the conductance cell was achieved by the usual evaporation–condensation technique via a breaker-seal in the system. Conductance–time measurements and solution analyses were carried out as in the preceding experiments.

Results

A summary of some of the data and results for the conductance–time effect for freshly prepared solutions of the three hydrogen halides in acetonitrile and miscellaneous related experiments is found in Table I. The nature of the increase in conductance with time is illustrated in Fig. 2 for four different concentrations of HCl. A special effort was made to ascertain that this conductance–time effect could not be attributed to hydrolysis of the nitrile due to the presence of trace amounts of water. Thus qualitative experiments established that the addition of acetonitrile to a solution that had at-

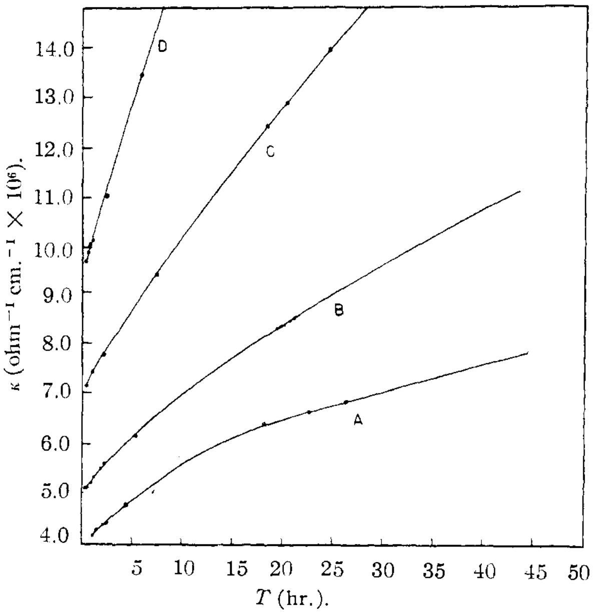

Fig. 2.—Variation of specific conductance with time: CH_3CN–HCl solutions: A, 0.0245 *m*; B, 0.0405 *m*; C, 0.0659 *m*; D, 0.0818 *m*.

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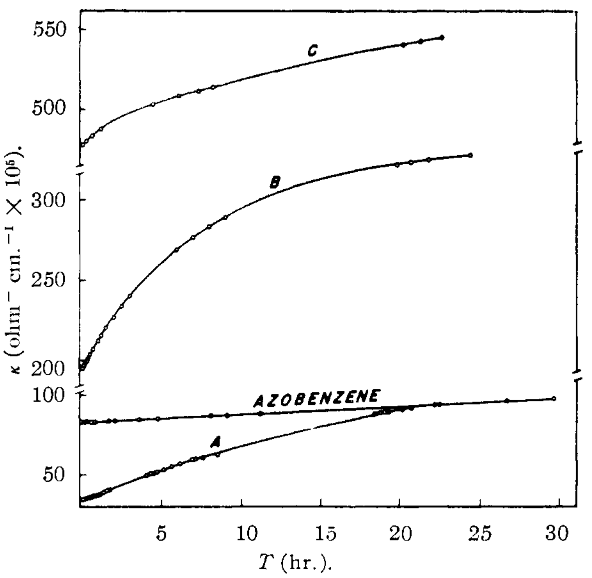


Fig. 3.—Re-initiation of "time effect" in initially equilibrated CH_3CN–HCl solutions and leveling effect of azobenzene: A, 0.165 *m* HCl; B, 0.403 *m* HCl; C, 0.597 *m* HCl.

tained ionization equilibrium did not initiate any further conductance–time variation, whereas the addition of acid (Table Ib and Fig. 3) did. Trace amounts of water and pieces of bright platinum did not re-initiate the time effect in equilibrated solutions. The results of the N_2 sweep showed that all of the HCl in CH_3CN–HCl solutions could be recovered in the NaOH bubbling trap and that the specific conductance of the remaining solution thus had been decreased to a fraction of its original equilibrated value, *e.g.*, the specific conductance for a 0.0288 *m* HCl solution was decreased from 15.8×10^{-6} ohm^{-1} cm.$^{-1}$ to 4.02×10^{-6} ohm^{-1} cm.$^{-1}$ by the N_2 sweep. Solutions formed by the addition of the solid substrates[8], $CH_3CN{\cdot}2HX$, to give concentrations equal to 0.446 *m* HCl and 0.0503 *m* HBr, respectively, showed the conductance–time effect exactly like the solutions prepared by dissolving the hydrogen halide in the nitrile (Table Ia and Ic). The investigation of the solid substrates, discussed[8] in detail in Part II of this series, established that the structures were of the nitrilium salt and imino-hydrohalide types in which the acid molecules are very labile and that the bonding is of a loose nature especially in the HCl system.

A rate analysis of the conductance–time effect was considered. In the CH_3CN–HI system, it was not feasible because of the secondary effects mentioned below. Attempts to determine the order of the reaction with reference to HCl in the initial period, using the differential rate expression

$$\frac{dx}{dt} = k(a)^n$$

gave log-log curves of increasing slope rather than constant values. A reliable C_∞ value likewise could not be gained in the CH_3CN–HCl solutions since stable conductances were not attained even after greatly prolonged periods. Further work may lead to an experimental approach more suitable for rate studies on these systems.

TABLE I

SPECIFIC CONDUCTANCE–TIME CHANGES FOR CH_3CN–HYDROGEN HALIDE SOLUTIONS

Concn. (moles/l.)	Initial[a] spec. conduc. (ohm^{-1} cm.$^{-1}$) $\times 10^5$	Final spec. conduc. (ohm^{-1} cm.$^{-1}$) $\times 10^6$	Elapsed time (hr.: min.)		Increase final conduc./initial conduc.
		(a) HCl solutions			
0.0245	0.459	0.776	30:24		1.69
.0347	.386	1.72	186:00		4.45
.0405	.490	1.120	44:05		2.29
.0659	.699	3.59	115:00		5.13
.0818	.947	3.95	71:11		4.17
.0955	1.85	5.51	67:25		2.98
.0991	1.51	.....	....		..
.138	1.98	11.1	151:40		5.61
.141	5.16	19.0	27:30		3.69
.165	3.40	9.19	40:45		2.70
.665	32.2	51.1	55:30		1.59
.174[b]	3.05	13.9	163:00		4.57
.123[c]	1.82	4.70	67:55		2.59
.211[c]	5.25	14.7	69:45		2.80
.446[d]	25.0	41.5	47:05		1.66
		(b) HCl solutions[e]			
0.165	3.49	9.19	20:45		2.63
.403	19.5	32.6	24:30		1.67
.597	47.7	54.6	22:40		1.14
.124[f]	8.31	9.95	34:35		1.19
		(c) HBr solutions			
0.0123	8.22	14.4	27:15		1.75
.0263	24.7	29.1	40:40		1.18
.0667		No appreciable time effect			
.00503[d]	3.17	8.65	46:40		2.73
		(d) HI solutions			
0.0053	17.5	20.0	47:10		1.14
		(e) Effect of water[g]			
				H_2O (Vol. %)	
0.066	14.7	36.6	47:20	0.25	2.49
.165	99.6	149.6	46:25	0.58	1.51
.136	146	152.	53:00	1.26	1.08

[a] Initial values by extrapolation to $t = 0$. [b] At 35°. [c] Vacuum transferred solution. [d] Solution of solid substrate, $CH_3CN{\cdot}2HX$ in CH_3CN. [e] HCl bubbled into equilibrated solutions. [f] Azobenzene also added. [g] Fresh HCl solutions.

The following points are to be noted specifically for the experiments with each acid. **HCl.**—The temperature dependence of the conductance was investigated over the range 0 to 35°. At each temperature, measurements were continued until the conductance had "stabilized" to a very nearly constant value. It was found that in the temperature range from 0 to 18° no detectable time effect occurred. Above 18°, the conductance–time effect became appreciable and was quite pronounced at 25 and 35° (Table Ia). On cooling to 0° to complete the cycle, the conductance did not return to the initial value at this temperature but was greater almost in direct proportion to the increase incurred at 25° in attaining ionization equilibrium.

The conductance time results for solutions prepared by the more laborious vacuum transfer techniques were quite similar to those for the freshly prepared HCl solutions (Table Ia). Addition of azobenzene (approximately 1:1 molar ratio with HCl) resulted in an almost instantaneous attainment of ionization equilibrium (Fig. 3 and Tables Ia, Ib). With reference to the effect of water, the time effect diminished rapidly as the concentration of water was increased to about 1% by volume. Addition of water, in trace amounts, to solutions that had attained "stabilized" conductance values did not re-initiate the time effect.

HBr.—The general nature of the conductance–time effect was quite similar to that with HCl (Fig. 1), *i.e.*, an initial rapid increase followed by a more gradual rise to a "stabilized" value. The magnitude of the time effect for an equivalent concentration of the acid was less for HBr than for HCl and diminished with increasing concentration of HBr.

HI.—The work with HI was limited to the few measurements necessary to check the general behavior of this system relative to the preceding. In the HI solutions, it was noticed that the specific conductance initially decreased to a minimum value and then increased with time rather similar in nature to the effect with HCl (Fig. 1), although considerably smaller in magnitude. The above changes in conductances were paralleled by changes from a colorless solution through light yellow to dark yellow solutions.

Discussion

It is concluded from the preceding results that traces of water (<0.01%) are not responsible for the observed conductance–time effect for solutions of the hydrogen halides in acetonitrile. Rather the latter must be attributed to the slow attainment of ionization equilibrium in these solutions. The existence of a "time effect" has been attributed[10] to the proton acceptor properties of the solvent. Ketones and nitriles have less tendency to solvate the free proton than water[7]; they exhibit a considerable time effect whereas water does not. The greatly diminished time effect when azobenzene was added to a freshly prepared HCl solution is in accord with this. Azobenzene, a non-electrolyte, has a much greater proton affinity and thus would hasten the rate of attainment of ionization equilibrium. Nitriles have relatively high ionization potentials, *e.g.*, CH_3CN, 11.96 e.v., and donor–acceptor interactions with subsequent formation of ionic species may be expected to proceed more slowly than in solvents with lower ionization potentials.

The polarizabilities of the molecules, solvent and solute species both, must also be considered. In acetonitrile, where the C≡N group is subject only to the weak perturbation from the slightly polar methyl group, ionization of picric acid was very slow, apparently incomplete after four weeks.[10–12] In benzonitrile, in which the C≡N group is subject to strong interactions with the delocalized electrons of the phenyl ring, ionization was complete in 3 hr. The greater polarizabilities of HBr and HI to that of HCl (3.49×10^{-22}, 6.00×10^{-22} and 2.56×10^{-22} cc., respectively)[25] undoubtedly contribute to the decreased time effects in the HBr and HI solutions. Although the rate analysis for the processes in the hydrogen halide–CH_3CN system could not be achieved unequivocally, it is apparent that the conductance–time change is ultimately dependent on the electron donor properties of the nitrile and the polarizability of the acid molecule.

According to the donor–acceptor classification of Mulliken,[26] acetonitrile may function in a dual manner, as onium electron donor (an n base, containing a relatively easily ionizable lone pair of electrons) and as a π-ketoid acceptor (leading to interactions by the formation of one σ-bond and the rupture of one π-bond). Hydrogen halides are dissociative $h\sigma_D$ acceptors (leading to interactions by the dissociation of σ-bond). Accordingly two mechanisms may be proposed to account for the interactions in the acetonitrile–hydrogen halide solutions.

The first is one in which CH_3CN acts as an onium donor and HX as an $h\sigma_D$ acceptor, and simple acid–base interactions occur, *i.e.*

$$\mathrm{CH_3CN + HX \rightleftarrows CH_3CN\cdot HX} \qquad (1)$$

$$\mathrm{CH_3CN\cdot HX \rightleftarrows CH_3CNH^+X^-} \qquad (2)$$

$$\mathrm{CH_3CNH^+X^- \rightleftarrows CH_3CNH^+ + X^-_{solv}} \qquad (3)$$

Thus the nitrile and acid form a 1:1 addition compound, *i.e.*, an "outer" charge-transfer complex in which the bonding of the acid is still largely of the σ-type. The rearrangement from an "outer" to an "inner" charge complex (2, above) is followed by the ionization of the "inner" complex (3, above) to yield solvated ions in the solution. The solvated anion X^-_{solv} may interact with another acid acceptor, *i.e.*, HX, to form the bihalide triple ion,[27] *i.e.*:

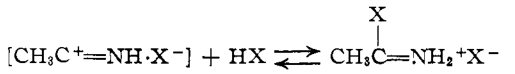
$$\mathrm{HX + X^-_{solv} \rightleftarrows HX_2{}^-_{solv}} \qquad (4)$$

The over-all interactions would be equivalent to the formation of nitrilium type salts, of empirical formula $CH_3CN\cdot 2HX$.

Equally probable is the action of acetonitrile by virtue of its π-ketoid acceptor properties. The canonical structures of the compound from the initial solvent–solute interaction (equation 1)

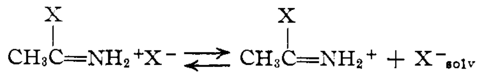
$$\mathrm{[CH_3C{\equiv}NH^+X^- \rightleftarrows CH_3C^+{=}NH\cdot X^-]} \qquad (5)$$

must be considered. Interaction with the second molecule of acid would be an attack by the electronegative halide atom on the carbon atom of the nitrile group



$$\mathrm{[CH_3C^+{=}NH\cdot X^-] + HX \rightleftarrows CH_3\overset{X}{\overset{|}{C}}{=}NH_2{}^+X^-} \qquad (6)$$

and consequent ionization of the imino hydrohalide



$$\mathrm{CH_3\overset{X}{\overset{|}{C}}{=}NH_2{}^+X^- \rightleftarrows CH_3\overset{X}{\overset{|}{C}}{=}NH_2{}^+ + X^-_{solv}} \qquad (7)$$

The increased polarizabilities of HBr and HI favor an enhancement of the imino-type interactions over that in the CH_3CN–HCl system. While the physical properties of the solid substrates may be explained by both of the above structures, *i.e.*, nitrilium salt or imino hydrohalide, the spectral evidence indicates that in the HBr substrate, the im-

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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]

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TROY, NEW YORK

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

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

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

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The nature of the solid substrates, $CH_3CN \cdot 2HX$, isolable from solutions of HCl, HBr and HI in anhydrous CH_3CN has been investigated. The structure of $CH_3CN \cdot 2HCl$ seems to be essentially that of a nitrilium salt, $(CH_3CNH^+)(HCl_2)^-$; whereas for $CH_3CN \cdot 2HBr$ and $CH_3CN \cdot 2HI$, 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, $RCN \cdot 2HX$, which yielded the original nitriles when treated with water. The formation of acetamide from these compounds by prolonged exposure to atmospheric moisture was postulated by an intermediate, $CH_3C(OH)NH \cdot HX$, 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 $CH_3CCl_2NH_2$, *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°); $2CH_3CN \cdot 3HCl$ (m.p. −88°); $CH_3CN \cdot 5HCl$ (m.p. −123.6°); $CH_3CN \cdot 7HCl$ (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 $C{\equiv}N$ group. Structures rather like imino acids were proposed in which the hydrogen halide is very loosely bonded to the nitrile.

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