CONDUCTANCES OF HYDROGEN HALIDES IN ANHYDROUS POLAR ORGANIC SOLVENTS

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I. INTRODUCTION

The electrochemical properties of ionophores (61) (ionic compounds) have been and are a continued area of interest and study. This subject has received increasing attention in recent times in view of the current interest in concepts of solvent–solute and solvent–ion interaction in these systems. Conductance equations for ionophores have been reinvestigated theoretically recently (62, 63a, 63b, 68) and their concentration range extended considerably. By contrast ionogens, particularly the hydrogen halides in organic solvents, have received rather little attention. In addition to solvent–ion interactions, there may occur solvent–solute interactions in these acidic systems (not generally so in salt–organic systems) provided the solvent has appreciable basic and/or acidic properties. As such they afford an opportunity for the advancement of knowledge in this little understood area.

The first systematic study of the electrical conductivity of hydrogen halides in nonaqueous solvents was started in the latter part of the nineteenth century (105). Considerable uncertainty was associated with this early work, however, and it was not until the measurements in aliphatic alcohols that accurate data became available. Of the hydrohalide acids, hydrogen chloride has been the most extensively investigated, particularly in hydroxylic solvents.

In the majority of organic solvents (lower aliphatic alcohols excepted) the hydrogen halides are relatively poor electrolytes; the equivalent conductances are frequently lower than 1 ohm^{-1}cm.^{2} at concentrations less than 10^{-2} N. Perhaps the most outstanding aspect of these systems is the nature of the conductance–concentration curves. The latter are often quite complex, exhibiting maxima and/or minima that are not readily explained.

II. PHYSICAL PROPERTIES OF ORGANIC SOLVENTS

Organic solvents for which hydrogen halide conductance data are available encompass a variety of polar groups, e.g., keto, nitro, amino, and the physical

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TABLE 1*

Physical properties of organic solvents†

Solvent	Dielectric Constant	Viscosity	Ionization Potential
		centipoises	*e. v.*
Methanol	32.63	0.5445	10.8–10.9
Ethanol	24.30	1.078	9.8–10.5
1-Propanol	20.1	2.004	—
1-Butanol	17.1	2.271_{30°	—
Isobutyl alcohol	17.7	3.91	—
Isoamyl alcohol	14.7	2.96_{30°	—
Acetaldehyde	21.1	—	10.18
Benzaldehyde‡	17.8_{20°	1.40	9.82
Acetone	20.70	0.2954	9.69
Diethyl ether	4.335_{20°	0.242_{20°	9.7–10.2
Pyridine	12.01	0.829_{30°	9.7–9.9
Quinoline	9.0	2.94_{30°	—
Dimethylamine	3.3_{100° (gas)	—	9.5–9.6
Ethylamine	4.3_{100° (gas)	0.346_{25°; $0.824_{-33.5^\circ}$	9.3–9.7
Aniline	6.89_{20°	3.770	—
o-Toluidine	5.95_{18°	4.418_{15°	—
Acetonitrile	37.5	0.345	11.96
Formamide	111.5_{20°	3.302	—
Acetamide	60.6_{94°	1.63_{94°	—
N,N-Dimethylformamide	38.3_{20°	0.88_{20°	—
Formic acid	58.5_{15°	1.966	11.33
Nitrobenzene	34.82	2.165	11.34–12.0

* The data in this table are in large part from Weissberger (204) and Conway (27).

† All values listed at 25°C. unless noted otherwise.

‡ No data available for cinnamaldehyde.

properties summarized in table 1 cover a wide range of values. More extensive tables of properties are given in several recent reference books (27, 204).

The dielectric constants of organic solvents are generally much lower than that of water ($D.C._{25^\circ} = 82.35$), though there are several solvents which do not follow this trend (e.g., formamide, $D.C._{20^\circ} = 111.5$). Considerable association into ionic aggregates would therefore be expected, increasing in magnitude with decreasing dielectric constant. However, empirical correlations between the dielectric constant and the strength of an electrolyte [Nernst–Thomson Rule (49)] are uniformly unsuccessful in hydrogen halide–organic solvent systems. This is well illustrated by hydrogen chloride, which is a relatively strong electrolyte in methanol ($D.C._{25^\circ} = 32.63$) and an extremely poor conductor in nitromethane ($D.C._{25^\circ} = 35.87$).

The viscosity of the solvent is of considerable importance in electrolyte solutions, for the ionic mobilities of ionophores are dependent to a large extent upon the magnitude of this property. Thus the mobilities vary inversely with the viscosity according to Stokes' law and Walden's rule (84). The dependence of the Walden product on dielectric constant has been recently discussed by Fuoss (63a). It is shown that the inconstancy of the Walden product may be attributed to interactions of the fields of the moving ions and those of the solvent dipoles in surrounding solvent.

Ionization potentials have been included in table 1, since they provide an insight into the electron-donor properties of the solvent molecules. This physical property is of considerable importance in determining the extent and nature of electron donor–acceptor interaction, i.e., Lewis acid–base interaction, between two unlike molecules (151, 152). Both the basicities of electron donors and the relative binding energies of addition compounds formed with electron acceptors decrease with increasing ionization potentials of the donor. For example, the base strengths of amines increase in the order $NH_3 < (CH_3)_2NH < (CH_3)_3N$, while the ionization potentials are 10.52, 9.5, and 9.2 (51), respectively. The extent of acid–base interaction is also dependent upon the electron affinity of the acceptor and the molecular configuration of both donor and acceptor.

III. CLASSIFICATION OF NONAQUEOUS SOLVENTS

For the purposes of this review nonaqueous solvents have been classified into two broad groups, acidic and basic. Following the definitions proposed by Mulliken (151, 152) acidic solvents are distinguished by their ability to accept a negative charge (electron acceptors) donated by a foreign species, while basic solvents are those which can donate a negative charge, e.g., an electron pair. Included in the acidic category are compounds such as acetic and formic acids; examples of bases are amines, pyridine, etc. Further subdivision into amphiprotic and aprotic groups is also possible but is of minor significance for organic solvent–hydrogen halide systems.

In addition to the above classification, solvents are also frequently compared on the basis of properties exhibited by electrolytes dissolved in them. Two groups of solvents may be distinguished: (*1*) levelling solvents in which members of a series of electrolytes are of approximately the same strength, e.g., hydrogen halides in methanol; and (*2*) differentiating solvents in which the members possess markedly different strengths, e.g., hydrogen chloride, hydrogen bromide, and hydrogen iodide in acetonitrile.

IV. SOLUBILITIES IN ORGANIC MEDIA

In general the hydrogen halides are moderately soluble in most polar organic solvents; solubilities in both polar and nonpolar solvents are summarized in several reference books (126, 180). Among some of the more recent measurements are those of Gerrard and coworkers for hydrogen chloride and hydrogen bromide (72, 73), those of Strohmeier and Echte (189) and of Kohn (121) for hydrogen chloride in alcohols, and those of Brown and Brady (16) and of O'Brien and coworkers for hydrogen chloride (158, 160). Karvé (111) has reported heats of solution for hydrogen chloride, hydrogen bromide, and hydrogen iodide in various organic solvents in connection with a thermochemical investigation of the constitution of these acids in solution.

Gerrard and coworkers (72, 73) have measured the solubility of hydrogen chloride in a wide variety of alcohols, carboxylic acids, and esters over a range of temperatures. The solubility was highest in alcohols and somewhat less in esters; acids were relatively poor solvents. These authors concluded that oxonium salts of the types $ROH_2^+X^-$, $RCOOH_2^+X^-$, and $RCOORH^+X^-$ were formed in the latter systems and, in the case of $ROH_2^+X^-$, served as intermediates in alkyl halide formation. The solubilities are dependent on the temperature and nature of the solvent, increasing markedly with decreasing temperature and increasing basicities (72).

For alcohols the solubility of hydrogen chloride can be correlated with the electron density on the oxygen. For example, the latter increases as follows: $CH_3 < CH_3CH_2 < CH(CH_3)_2 < C(CH_3)_3$, and the solubilities at 10°C., expressed as moles of hydrogen chloride per mole of alcohol are: methanol (0.857), ethanol (0.950), 2-propanol (1.030). The presence of electron-withdrawing substituents (such as halides) in the alkyl group of the alcohols decreases the solubility of the hydrogen halides; e.g., at 11°C. the solubility of hydrogen chloride decreases as follows in chlorinated ethanols: $ClCH_2CH_2OH > Cl_2CHCH_2OH > Cl_3CH_2OH$. Effects similar to the above were also observed in the acids and esters.

V. Compound Formation with Hydrogen Halides

Consideration of possible chemical interactions between the hydrogen halides and the organic solvents is important relative to the electrochemical properties of the solutions. A discussion of compound and salt formation, hydrogen bonding, and related effects in these systems follows. The reviews by Andrews (1) and McGlynn (139) and the classic work of Pfeiffer (164) are of interest in supplementing the present discussion.

Molecular interactions between hydrohalide acids and organic compounds cover a wide latitude ranging from the weak π complexes formed with aromatic hydrocarbons (15), e.g., hydrogen chloride in benzene, to salt formation characterized by the amines, e.g., $CH_3NH_3^+Cl^-$. In the majority of cases the molecular complexes formed are relatively unstable under normal conditions and dissociate readily into their components.

A compilation of the acid complexes formed with a number of organic solvents is given in table 2. On the basis of melting points only the amine, pyridine, and amide hydrohalides can be considered as salts. By comparison, compounds with the oxy solvents possess low melting points and in most cases dissociate on fusion into the free acid and base, suggesting that the bonding is predominantly associative; i.e., via hydrogen bonding. Some support for the latter is seen in the values of the enthalpy change for reaction between acids and ethers (74, 133, 134, 202). Thus the ΔH for the association of methyl ether with hydrogen chloride is -7 kcal. (74) and similarly with hydrogen bromide, -5 kcal. (134); i.e., the values are within the enthalpy range (3–10 kcal.) for hydrogen-bonding reactions.

The existence of molecular complexes in acid solutions has been confirmed by a wide variety of physical methods, apart from electrical conductivity. One of the most useful techniques has been the investigation of freezing point–composition diagrams for binary systems of acids and organic compounds. This method is particularly suited for the detection of compounds only isolable at low temperatures, e.g., $CH_3OH \cdot HCl$, m.p. -62°C. (131), and for systems in which complexes of various stoichiometric ratios occur, e.g., acetonitrile–hydrogen chloride (154) and ethyl ether–hydrogen chloride (131). Supercooling, as in oxy solvents (128), and possible secondary reactions limit the applicability of this approach in some systems.

Complex formation in solutions has also been detected by changes in the dipole moment of the acid molecule (46, 47, 48, 119, 120, 148). For example, Mizushima, Suenaga, and Kozima (148) reported that hydrogen chloride has a dipole moment of 2.22 Debyes in ethyl ether, 1.24 Debyes in toluene, and 1.20 Debyes in benzene at 20°C. as compared with 1.03 Debyes in air.

Vapor pressure (157, 158, 159, 160, 201) and viscosity measurements (38, 119, 120) have been used to show acid–base interaction in a number of systems. Deviations of vapor pressures from the values predicted by Henry's law were attributed by O'Brien and coworkers (157, 158, 159, 160) to interactions of the type $HX + S \rightleftharpoons S \rightarrow HX$. On this basis equilibrium constants were estimated for both hydrogen chloride and hydrogen bromide in several organic solvents. Viscosity measurements have been reported for binary systems of hydrogen chloride–alcohols (119, 120) and hydrogen chloride–ethers (38). In all cases the η–composition isotherms show marked deviations from ideality, passing through maxima in the concentration range corresponding to a 1:1 mole ratio of the components.

Evidence of solute–solvent interaction between acids and organic solvents may be gained from infrared (5, 19, 58, 80, 190, 205) and Raman spectral studies of the solutions (11, 12, 70, 71, 197). Shifts of the fundamental absorption bands, ν_{HX}, of hydrogen halides to longer wavelengths, accompanied by broadening of the bands, have been observed in a wide variety of organic solvents

TABLE 2

Molecular complexes of hydrogen halides and organic compounds

System	Mole Ratio of Components	Melting Point	References
Alcohols			
		°C.	
Methyl alcohol-HCl	1:1	−62	(131)
	3:2	−64	(141)
Methyl alcohol-HBr	4:1	−61 (incongruent)	(128)
	1:1	−14, −12	(128, 129, 140)
	1:4	−94	(128)
Methyl alcohol-HI	1:1	−48	(140)
Ethyl alcohol-HCl	1:1	−65	(131)
Ethyl alcohol-HBr	1:1	−30	(129)
n-Propyl alcohol-HCl	1:5	−120	(3)
n-Propyl alcohol-HBr	1:2	−85	(3)
n-Propyl alcohol-HI	1:2	−65(?)	(3)
Aldehydes and Ketones			
Acetaldehyde-HCl	2:3	−18	(141)
Acetaldehyde-HBr	2:3	−15	(141)
Acetaldehyde-HI	2:3	−34	(141)
Acetone-HF	1:1	55	(127)
	1:2	12-15	(127)
Acetone-HCl	1:1	−77	(143)
	2:5	—	(143)
	1:3	−81	(143)
Acetone-HBr	4:1	−35 (incongruent)	(128)
	1:1	−4, −23	(128, 129)
	1:4	−35	(128)
Acetone-HI	2:1	—	(3)
Esters			
Ethyl acetate-HCl	1:2	−75	(141)
Ethyl acetate-HBr	2:3	−40	(141)
Ethyl acetate-HI	1:1	−23	(141)
Acids			
Acetic acid-HCl	2:3	−53	(141)
Ethers			
Methyl ether-HCl	1:1	−96	(129)
	1:3, 1:4 (?)	−102	(129)
Methyl ether-HBr	1:1	−13	(129)
Methyl ether-HI	1:1	−22	(129)
Ethyl ether-HCl	1:1	−92	(3, 131)
	1:2	−88	(131)
	1:5	−92, −89	(3, 131)
Ethyl ether-HBr	3:1	−55 (?)	(128)
	1:1	−40	(128, 142)
	1:2	−46	(129)
Ethers—Continued			
		°C.	
Ethyl ether-HI	2:1	—	(3, 145)
	1:1	−18	(3)
Pyridines			
Pyridine-HCl	1:1	—	(146)
	1:2	47-51	(43, 44)
Pyridine-HBr	1:1	206 (225 decomposes)	(173)
	1:2	Melting starts at 36°; complete at 54°	(112)
Pyridine-HI	1:1	190-195	(31)
Quinoline-HCl	1:1	133, 134.5	(39, 163)
	1:2	46.7	(112)
	2:3	82	(39)
Quinoline-HI	1:2	41	(113)
Amines			
Methylamine-HCl	1:1	226	(83)
Ethylamine-HCl	1:1	107.5, 109	(137, 199)
Ethylamine-HBr	1:1	159	(199)
Ethylamine-HI	1:1	167, 189	(34, 199)
Dimethylamine-HCl	1:1	171	(199)
Dimethylamine-HBr	1:1	133	(170, 199)
Dimethylamine-HI	1:1	—	(199)
Dimethylamine-HF	1:2	—	(203)
Aniline-HCl	1:1	198	(136)
Aniline-HBr	1:1	280	(95)
Aniline-HI	1:1	—	(59)
Amides			
Formamide-HCl	1:3	—	(171)
Formamide-HBr	2:3	—	(171)
Acetamide-HCl	1:1	135	(108)
	2:1	130-132	(97)
Acetamide-HBr	2:1	140-142	(97)
Nitriles			
Acetonitrile-HCl	1:1	−63.2	(154)
	2:3	−88 (incongruent)	(154)
	1:5	−123.6	(154)
	1:7	−125	(154)
	1:2	30	(100)
Acetonitrile-HBr	1:2	75-80	(100)
Acetonitrile-HI	1:2 (?)	>100	(100)

(103, 104) and cannot be accounted for in terms of solvent effects alone, i.e., the dielectric constant. For example, in methanol solutions ν_{HCl} is shifted from 3.46 μ to a broad band at 4.0 μ. The data are not suitable for determining equilibrium constants or the stoichiometry of the complex, although they can give a qualitative indication of the basicities of solvents (5, 104).

Infrared spectra of solid complexes have been reported recently for a number of amine hydrohalides (23) and $CH_3CN \cdot 2HBr$ (100). The spectrum of the latter compound was markedly different from that of the pure components and was attributed to an imino hydrobromide structure, $CH_3C(Br){=}NH_2^+Br^-$. Briegleb and Lauppe (11, 12) have reported low-temperature Raman spectra for the compounds formed between alcohols, ethers, and hydrogen halides. The frequency assignments by the latter have been questioned by Gantmacher and coworkers (70, 71), and a need for further work is apparent.

VI. CONDUCTANCE DATA FOR HYDROGEN HALIDES

Of the conductance measurements reported for hydrogen halides in nonaqueous solvents, most are of limited accuracy (often 5 per cent). Discrepancies are most evident in dilute solutions and undoubtedly arise because of the presence of impurities in the solvent or because of chemical reactions. Limitations imposed by the hygroscopic nature and the high resistances of many nonaqueous solutions are further complicating factors.

A considerable amount of information regarding purification procedures and experimental techniques can be found in the experimental portions of papers discussed in this section. Information relative to the design and construction of conductance cells suitable for nonaqueous work can be found in several recent papers (7, 13, 50, 156).

For uniformity and comparison, phoreograms, i.e., graphical plots of the equivalent conductances (Λ) versus the square root of the concentration ($\sqrt{c}$), have been used to illustrate the conductance data. Where a number of separate investigations have been reported, the measurements judged most accurate have been used in constructing the graphs.

A. BASIC SOLVENTS

1. Alcohols

Conductances of hydrogen halides have been investigated most extensively in alcohols, the interest here lying in the catalytic properties of the acids in these solvents. Because of their inherent similarity to water, methyl and ethyl alcohol have been of particular interest.

The equivalent conductances of hydrogen chloride in methanol (D.C.$_{25°}$ = 32.6) have been reported at 25°C. by a number of authors (22, 76, 85, 90, 161, 172, 192), the most recent being Shedlovsky and Kay (183).

In figure 1 are illustrated the more extensive, although less accurate, measurements of Goldschmidt and Dahll (76). Analysis of the results indicates that this acid behaves as a strong electrolyte in methanol with only a small amount of association. Hartley and Rust (85) noted that the observed Onsager slope (84) was greater than the calculated value but did not determine the value of the thermodynamic dissociation constant, K_i. Shedlovsky and Kay (183) computed a dissociation constant of 0.059 and Λ_0 = 198.5 from a plot of the Shedlovsky conductance equation (182) for weak electrolytes:

$$\frac{1}{\Lambda S} = \frac{1}{\Lambda_0} + \frac{c\Lambda S f_{\pm}^2}{K_i \Lambda_0^2}$$

The explanation of the notation is given in Section VII.

Although limiting equivalent conductances (Λ_0) have been reported by a number of authors, agreement between independent values is not satisfactory (*cf.* table 4). The discrepancies may be attributed in part to different methods of estimating Λ_0; e.g., Λ_0 values of 193.2 (Hartley and Rust (85)), 196.7 (Thomas and Marum (192)), and 192.3 (Rosenberg (172)) were estimated graphically from Λ–$\sqrt{c}$ curves; Λ_0 values of 202.5 (Hlasko and Kamienski (90)) and 204.3 (Goldschmidt and Dahll (76)) were estimated from Λ–$\sqrt[3]{c}$ plots; the value Λ_0 = 193.2 (Ogston (161)) was estimated by the Fuoss–Kraus method (65) and Λ_0 = 198.5 (Shedlovsky and Kay) was determined by the Shedlovsky method for weak electrolytes. The presence of trace impurities (water and esters) and the occurrence of chemical reactions (*cf.* below) would also account for some of the differences.

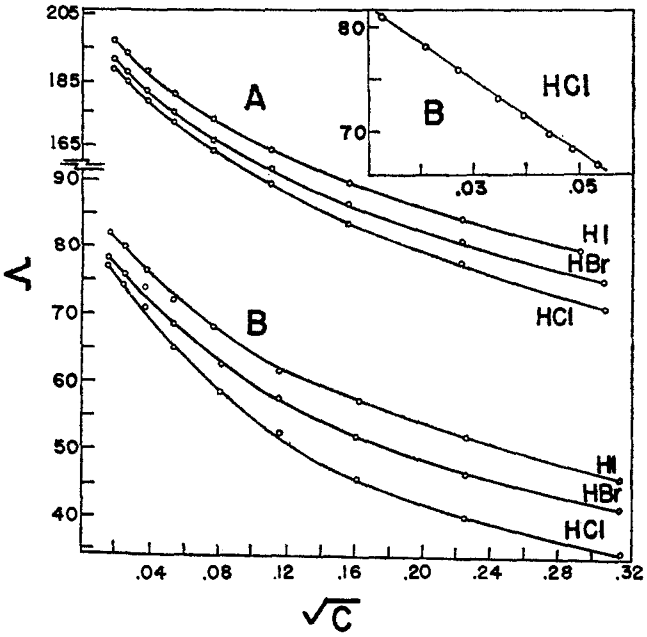


FIG. 1. Hydrogen halides in methyl and ethyl alcohols. A: Methanol, Goldschmidt (76). B: Ethanol, Goldschmidt (76). Insert: Bezman and Verhoek (8).

It is of interest to note that the addition of small amounts of water, less than 2 per cent, to alcohol–acid mixtures decreases the conductivity (76, 183). It appears that the proton-transfer mechanism in alcohols is disrupted by the presence of more strongly bonded H_3O^+ ions, i.e., the equilibrium

$$ROH_2^+ + H_2O \rightleftharpoons ROH + H_3O^+$$

lies far to the right.

The Λ_0 and K_i values of Shedlovsky and Kay (183) are recommended as the best values. Further work over an extended temperature range and subsequent analysis of experimental results in terms of the recent Fuoss (62) or Ramsey and Denison (35) concepts would provide additional needed data. Ogston (161) has reported the equivalent conductances and ionization constants for hydrogen chloride at 4° and 15°C. in methanol. The values $\Lambda_0 = 150.4$ (4°C.) and 173.0 (15°C.) and $K_i = 0.102$ (4°C.) and 0.112 (15°C.) were estimated by the method of Fuoss and Kraus (65).

Goldschmidt and Dahll (76) measured the conductivities of hydrogen bromide and hydrogen iodide and estimated (graphically) Λ_0 values of 206.6 and 212.2, respectively. The results differ considerably from the only other available values reported by Hlasko and Kamienski (90), i.e., $\Lambda_0 = 212.3$ (HBr) and $\Lambda_0 = 221.8$ (HI). As in the case of hydrogen chloride, both hydrogen bromide and hydrogen iodide show a small degree of ionic association. Recalculation of the Goldschmidt and Dahll data using the Fuoss–Shedlovsky methods does not yield meaningful results. Further experimental work to resolve the above discrepancies is necessary.

Strauss (188) recently measured the conductivity of hydrogen bromide in methanol solutions to 3000 atm. at 25°C. and found that the molal conductance decreased with increasing pressure, as shown in table 3.

TABLE 3

Variation of the molal conductance of hydrogen bromide in methanol with pressure

Pressure (atm.)	1	1000	2000	3000
Λ* (molal)	127.7	116.1	107.8	101.1

* Concentration of HBr, 0.028 molal.

The decrease was not as large as for comparable solutions of ionophores. Strauss estimated that the excess proton conductance, i.e., the conductivity contribution from proton-transfer mechanisms, accounted for approximately 66 per cent of the total hydrogen-ion conductance at atmospheric pressure, the remainder resulting from $CH_3OH_2^+$ ions. The decrease in excess proton conductance with increasing pressure was attributed to hindrance of rotation of the methanol at higher pressures.

The equivalent conductance data in ethanol ($D.C._{25°} = 24.30$), illustrated in figure 1B, confirm that hydrogen chloride is a moderately weak electrolyte in this solvent. The observed $\Lambda-\sqrt{c}$ slope, 360, is considerably greater than the calculated Onsager slope, $199_{25°}$. The agreement among the Λ_0 and K_i values at 25°C., reported independently in the literature, leaves something to be desired. For example, values for Λ_0 of 82.46 (El-Aggan, Bradley, and Wardlaw (41)), 83.8 (Hartley and Rust (85)), 84.25 (Bezman and Verhoek (8)), 84.7 (Thomas and Marum (192)), 89.1 (Goldschmidt and Dahll (76)), and 81.7 (Ogston (161)), and values for K_i of 8.23×10^{-3} (El-Aggan, Bradley, and Wardlaw (41)), 0.0112 (Ogston (161)), and 0.0113 (Bezman and Verhoek (8)) have been reported. The most recent Λ_0 values, 82.46 and 84.35, and values of the ionization constants, 8.23×10^{-3} and 11.3×10^{-3}, respectively, were determined by the method of Fuoss and Kraus and are recommended as best values. It should be noted that a somewhat better extrapolation of the conductance data for weak electrolytes, i.e., $10^{-3} \leq K_i \leq 1$, is possible if the Shedlovsky (182) treatment is used. Trace amounts of water in the ethanol decrease the conductivity (76), and the lower values of Λ_0 may be attributed in part to this effect. Chemical reactions, e.g., alkyl halide formation and esterification, would also contribute.

The limiting equivalent conductance and K_i of hydrogen chloride have also been determined at 4°C. and 15°C. (161). The Fuoss–Kraus extrapolation procedure yielded the following values: $\Lambda_0 = 53.25$ and $K_i = 0.0232$ at 4°C.; $\Lambda_0 = 67.30$ and $K_i = 0.147$ at 15°C.

Conductances for hydrogen bromide and hydrogen iodide have been reported in ethanol at 25°C. by Goldschmidt and Dahll (76). Both acids are somewhat stronger than hydrogen chloride (figure 1B), although they are still relatively weak electrolytes. Limiting conductances of 88.9 (HBr) and 93.2 (HI) were extrapolated graphically ($\Lambda-\sqrt[3]{c}$).

Conductance data are also available for the series hydrogen chloride, hydrogen bromide, and hydrogen iodide in n-propyl alcohol (79) ($D.C._{25°} = 20.1$), n-butyl alcohol (77) ($D.C._{25°} = 17.1$), and isobutyl alcohol (75) ($D.C._{25°} = 17.7$), and for hydrogen chloride and hydrogen iodide in isoamyl alcohol (105) ($D.C._{25°} = 14.7$). Data for these are illustrated in figure 2. A number of conductance measurements have been reported for hydrogen chloride in isoamyl alcohol–benzene mixtures at 30°C. by Bhide and Watson (9) and are illustrated in figure 3. Dolby and Robertson (36) measured the conductivity of hydrogen chloride in phenol at two concentrations and observed that the equivalent conductances were considerably less than 1 at 50°C. The accuracy of conductance measurements in these alcohols is considerably less than that in methanol or ethanol. In the case of solutions of hydrogen iodide in isoamyl and isobutyl alcohols a yellow color was noted, indicating decomposition of the acid. Although the data are not satisfactory for the determination of Λ_0's and K_i's, they are nevertheless quite useful in ascertaining the relative strengths of the acids in the alcohols.

In n-propyl alcohol the acids are somewhat weaker than in corresponding ethanol solutions. Limiting conductances of 46.6 (for hydrogen chloride) and 47.2 (for hydrogen bromide) were estimated empirically by Goldschmidt and Thomas (79) from plots of $\Lambda-\sqrt[3]{c}$ and should be regarded as of qualitative significance only.

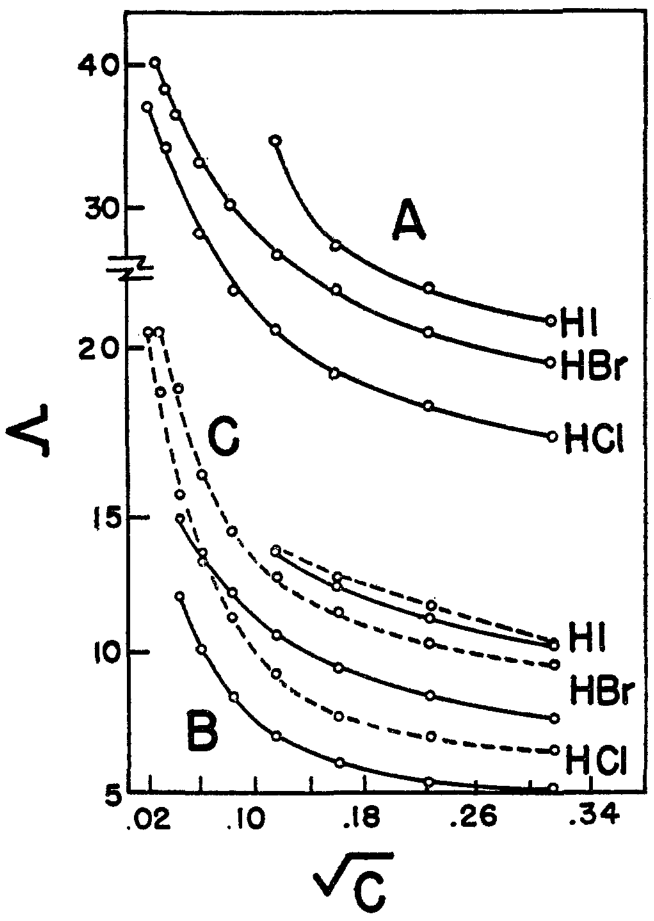


FIG. 2. Hydrogen halides in alcohols. A: *n*-Propyl alcohol (79). B: Isobutyl alcohol (75). C: *n*-Butyl alcohol (77).

The phoreograms for the three acids in isobutyl alcohol and *n*-butyl alcohol are typical of weak electrolytes, i.e., sharp tail-up at low concentrations. A detailed analysis of the conductances in terms of weak electrolyte concepts awaits further measurements at lower concentrations. The limited measurements for hydrogen iodide in isoamyl alcohol are only of interest insofar as they show an anomalous increase in conductance with concentration.

The phoreograms for hydrogen chloride in isoamyl alcohol and isoamyl alcohol–benzene mixtures (9) (figure 3) show pronounced minima and an anomalous increase in conductance with concentration at higher concentrations. In addition the minimum is displaced to higher concentrations with increasing dielectric constant in accordance with the behavior predicted by ion-pair (10) and triple-ion theories (66). Quantitative treatment of the data in accord with these concepts has not been successful.

On comparison of the results for the alcohols, several factors are noted: (*1*) the conductivities of the acids increase in the order HCl < HBr < HI in individual alcohols; (*2*) the conductivities of the individual acids decrease as the number of carbon atoms in the alkyl group increases. For example, using the data of Goldschmidt and coworkers for hydrogen chloride, the equivalent conductance of a 3.91×10^{-4} N solution decreases as follows: Λ, 187.9 ($n = 1$); 76.9 ($n = 2$); 37.41 ($n = 3$); 20.80 ($n = 4$) in the series $C_nH_{2n+1}OH$. The decrease in conductance with increasing number of carbon atoms is due largely to the higher viscosities and lower dielectric constants of the more complex alcohols. Furthermore, there is evidence that the basicities of the alcohols decrease with the increasing number of carbon atoms (122), and this would tend to minimize the ionogenic displacement equilibrium: $ROH + HX \rightleftharpoons ROH_2^+ + X^-$.

(*3*) Phoreograms of the acids in alcohols tend toward minima with increasing acid concentration. This effect becomes more noticeable with decreasing dielectric constants of the alcohols, and in the case of isoamyl alcohol and isoamyl alcohol–benzene mixtures (9) has been observed experimentally. Although the minima can be understood qualitatively in terms of the formation of ion aggregates, further work is required before a good understanding of these solutions is possible.

Conductivity measurements of acidified alcohol solutions (particularly at high acid concentration) are often complicated by the presence of side reactions, two of the most important being (*1*) esterification of trace amounts of organic acid impurities (HX acting as catalyst):

$$RCOOH + ROH + HX \rightleftharpoons RCOOR + HX + H_2O$$

and (*2*) formation of alkyl halides:

$$ROH + HX \rightleftharpoons RX + H_2O$$

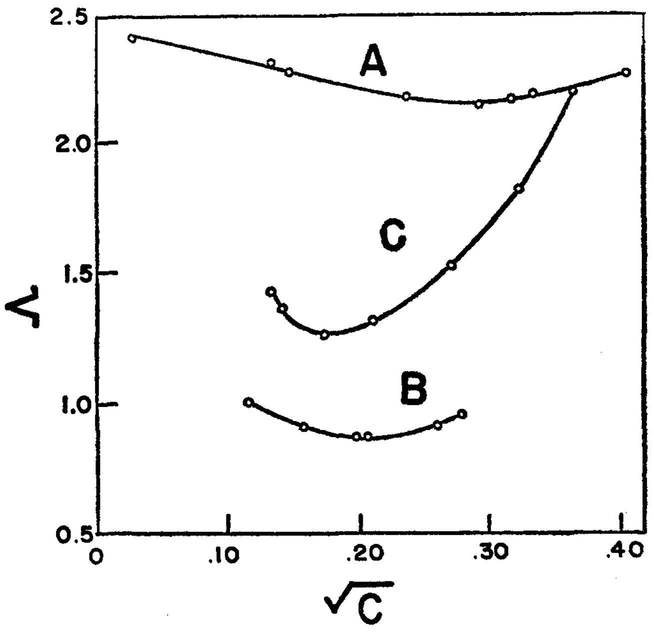


FIG. 3. Hydrogen chloride in isoamyl alcohol-benzene mixtures (9). A: Pure isoamyl alcohol. B: 20 per cent benzene + isoamyl alcohol. C: 40 per cent benzene + isoamyl alcohol.

both with the formation of water as one of the reaction products.

Numerous investigations have been reported on the kinetics of esterification (75, 76, 79) (see reference 96 for a comprehensive discussion) and the formation of alkyl halides (6, 72, 73, 81, 89, 185) in acidified alcohols. It should be noted that esterification can be minimized by exhaustive purification of the solvent. Relative to the second reaction above, the following points should be noted: (*a*) the rate of formation of alkyl halides from alcohols increases in the order primary < secondary < tertiary (21, 57); (*b*) solutions of hydrogen iodide are most reactive, while those of hydrogen chloride are most stable (57, 73) (hydrogen iodide can also decompose photochemically); (*c*) acidified solutions of primary alcohols react very slowly at room temperature in accord with relatively high values for the energies of activation (25–30 kcal.) (89), e.g., the formation of alkyl chlorides at 20°C. is incomplete even after a period of several months (73, 185). The rate of alkyl halide formation increases markedly with increasing temperatures (72, 73). Smith (185) has observed that the hydrogen chloride concentration of a 5×10^{-3} *N* methanol solution decreases by 2 per cent after a period of 100 hr. at 30°C.; at 50°C. the hydrogen chloride concentration decreased by 16 per cent for the same period.

The extent of reaction for a large number of alcohols with hydrogen chloride and hydrogen bromide has been measured (72, 73), and the interactions of alcohols with hydrogen halides have been reviewed by Gerrard, Madden, and Tolcher (73).

2. Aldehydes and ketones

Solvents with a carbonyl polar group are usually weak donors and as a consequence acid–base interactions occur to a slight extent only. Conductance results for the hydrohalide acids in aldehydes and ketones (25, 37, 106, 177) (shown in figure 4) are limited and of qualitative nature only. Measurements are complicated by side reactions, e.g., aldol condensation, and stable electrical resistances are generally uncommon, e.g., the conductivity of hydrogen chloride increases with time in cinnamaldehyde (177) and acetone (132). From figure 4 it is apparent that hydrogen chloride is an extremely poor conductor in all of these solvents. The questionable accuracy and the occurrence of chemical reactions preclude any meaningful analysis of the data.

Relative to the acetone–hydrogen chloride system the following points are to be noted. Sackur (177) reported no evidence for a chemical reaction in the latter system, although his results were in poor agreement with the earlier work of Kahlenberg and Lincoln (106). In more recent publications, Kane (109) and Everett and Rasmussen (45) were unable to obtain reproducible conductances and e.m.f. measurements at 25°C. Unpublished data of Kane (109) showed that hydrogen chloride is a very weak electrolyte in acetone with a K_i value of the order of 10^{-8}. Aged solutions attained a yellowish color and characteristic odor, indicating some chemical reaction. Dorofeeva and Kudra (37) found that the specific conductance passed through a minimum at 0.087 *M* hydrogen chloride and a maximum at 1.32 *M* hydrogen chloride in acetone. In addition, two decomposition potentials were observed in polarographic current–voltage curves and were attributed to the formation of solvated hydrogen chloride species. The presence of chemical reactions was not discussed by these authors.

Maass, Miller, and Danyluk (132) confirmed that fresh solutions of hydrogen chloride are unstable at room temperature with the conductivity showing a marked increase with time and the solutions becoming a deep brown in color. By contrast, solutions prepared at −75°C. are quite stable up to −20°C. and do not show any conductance or color change with time.

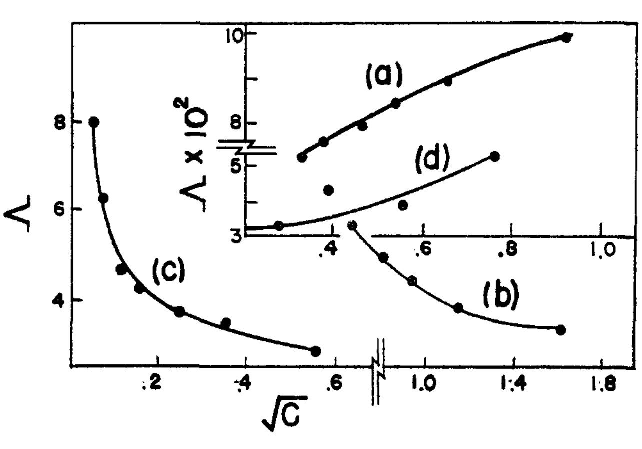
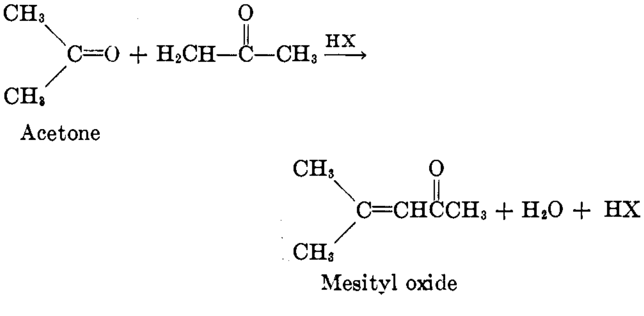


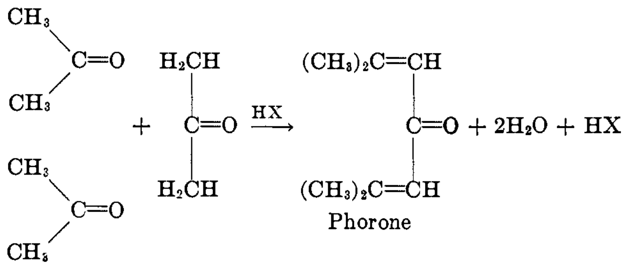
FIG. 4. Hydrogen chloride in aldehydes and ketones. (a) Cinnamaldehyde (177). (b) Benzaldehyde (177). (c) Acetone (177). (d) Acetaldehyde (25).

The unstable nature may be associated with an acid-catalyzed condensation of acetone to mesityl oxide and phorone with two and three molecules of acetone, respectively (40) (*cf.* Fieser and Fieser (52) and Karrer (110)). Thus:



$$(CH_3)_2C{=}O + H_2CH{-}\overset{\overset{O}{\|}}{C}{-}CH_3 \xrightarrow{HX} (CH_3)_2C{=}CH\overset{\overset{O}{\|}}{C}CH_3 + H_2O + HX$$

and



Phorone

Colonge (26) investigated a number of ketones in the presence of hydrogen chloride and confirmed their condensation at 25°C. An unstable β-chloroketone intermediate which is readily destroyed by water or alkaline solutions was isolated in several systems.

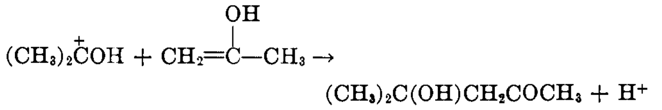
The kinetics of the acid-catalyzed condensation of ketones are not known with any degree of certainty. The following processes seem to contribute to the reaction mechanism (96). An acid–base interaction converting the carbonyl group to its conjugate acid occurs, e.g., for acetone:

$$(CH_3)_2C{=}O + H^+ \rightleftharpoons [(CH_3)_2C{=}OH]^+$$

and the conjugate acid exists in the tautomeric forms,

$$[(CH_3)_2C{=}OH]^+ \longleftrightarrow [(CH_3)_2\overset{+}{C}OH]$$

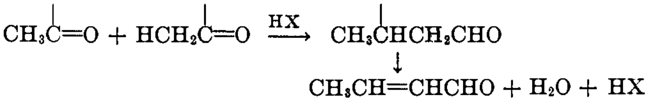
i.e., the oxonium and carbonium ions. The carbonium ion is strongly electrophilic and may interact with the enolic species:



$$(CH_3)_2\overset{+}{C}OH + CH_2{=}\overset{OH}{\overset{|}{C}}{-}CH_3 \rightarrow (CH_3)_2C(OH)CH_2COCH_3 + H^+$$

forming the ketol, which in turn undergoes dehydration to mesityl oxide. Thus the conductance increase with time observed in acetone–hydrogen chloride solutions (128, 132) may be understood as due to the formation of H_3O^+ ions by this reaction. Ion-pairs of the type $[(CH_3)_2C{=}OH]^+X^-$ and $[(CH_3)_2\overset{+}{C}OH]X^-$ are undoubtedly important in the condensation processes (as evidenced by the isolation of β-chloroketones) and must be considered in any complete account of the interactions in this system.

Acidified solutions of aldehydes undergo similar condensation reactions. Thus acetaldehyde condenses to form aldol and crotonaldehyde (52):



$$CH_3\overset{H}{\overset{|}{C}}{=}O + HCH_2\overset{H}{\overset{|}{C}}{=}O \xrightarrow{HX} CH_3\overset{OH}{\overset{|}{C}}HCH_2CHO \downarrow CH_3CH{=}CHCHO + H_2O + HX$$

Crotonaldehyde

Acetaldehyde also polymerizes to the trimer, paraldehyde, under the influence of an acid catalyst (52). The anomalous increase in conductance with concentration occurring in acetaldehyde (25), paraldehyde (25), and cinnamaldehyde (177) solutions may be associated in part with the condensation reaction.

Conductance data for hydrogen halides in aldehydes or ketones seem to be limited to hydrogen chloride. Measurements for hydrogen bromide–acetone solutions are in progress and results (128) indicate a behavior similar to that of hydrogen chloride.

Sackur (177), as early as 1902, attributed the low conductivities in aldehydes and ketones to the weak basic properties of the carbonyl group. He suggested the dissociation of solvent–solute addition compounds to account for the decrease in conductivity with dilution in cinnamaldehyde–hydrogen chloride solutions, with the free solvent and the free acid assumed to be nonionic. The formation of addition compounds between hydrohalide acids and compounds with the carbonyl group is now well known (129, 143), and the existence of ions of the type $[RR'C{=}O{-}H]^+$ in solution must be considered in any assessment of conductance results.

The donor properties of the carbonyl group have been investigated recently by infrared techniques. Cook (29) has noted a linear correlation, given by $\nu_{HCl} = 179.43\ I.P. + 807$, between the ionization potential (I.P.) of compounds with the carbonyl group and the variation of ν_{HCl}, the fundamental stretching frequency of hydrogen chloride.

3. Ethers

Although solvents with ether links, R—O—R′, are potentially interesting media for hydrogen halides because of the donor properties of the oxygen lone-pair electrons, conductance measurements have been reported in one system only, i.e., diethyl ether ($D.C._{20°} = 4.33$) at 18°C. Hydrogen chloride was found to be an extremely poor conductor in the latter solvent (38, 150) with equivalent conductances much less than 1 in the range investigated, 0.02–6.3 equiv. liter^{-1}. Mounajed (150) attributed the minimum in the phoreogram shown in figure 5 to a combination of H^+ and Cl^- with undissociated hydrogen chloride. Although the precise nature of the interactions was not discussed, it is not unlikely that ions of the type H_2Cl^+ and HCl_2^- exist in ether solutions at high concentration. The polarographic curve for ethyl ether–hydrogen chloride shows only one decomposition potential (2.16–2.18 volts) and has been attributed (38) to the discharge of a hydrogen atom from unionized $(C_2H_5)_2O{\cdot}HCl$. The potential dropped to 1 volt after several days; according to Dorofeeva and Kudra (38) this effect was due to the formation of H_2O and H_3O^+ ions.

The conductivity of freshly prepared solutions of hydrogen chloride in ether increased slowly with time; e.g., Λ for a 0.02 N solution increased from 0.00588

$\text{ohm}^{-1}\text{cm.}^2$ to 0.0853 $\text{ohm}^{-1}\text{cm.}^2$ over a period of one month. Mounajed attributed this effect to the reaction:

$$(C_2H_5)_2O + 2HCl \rightarrow 2C_2H_5Cl + H_2O$$

the conductance increase resulting from the formation of small amounts of water. No kinetic evidence was cited. In view of the relatively dilute nature of the solutions, it is more likely that the ether is cleaved to ethyl chloride and ethanol.

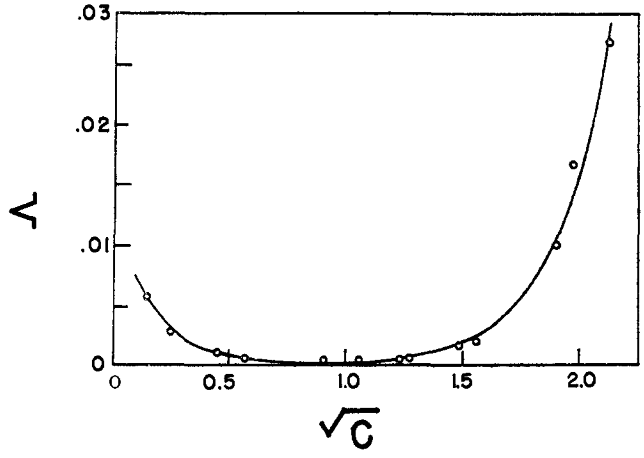


FIG. 5. Hydrogen chloride in diethyl ether (150).

The cleavage of ethers to halides and alcohols

$$ROR' + HX \rightarrow ROH + R'X$$

has been reviewed recently by Burwell (18). Ethers with a methoxy group are split most readily to methyl halide and alcohol (18). Of the hydrogen halides, hydrogen iodide is the most effective reagent and is used in the Zeisel method (208) for methoxy groups. In the cleavage of ethers, oxonium-salt formation $[RR'OH]^+$ is generally assumed as an intermediate in acidic media (18). The role of ion-pairs, $[RR'OH]^+X^-$, in the cleavage is not fully understood. The electrochemical properties of ether–hydrogen halide complexes (table 2) are therefore of considerable interest. Conductance measurements under conditions where chemical reactions are minimized (low temperatures) are essential to further understanding.

A number of conductance measurements have been reported at −89°C. and −100°C. for methyl and ethyl ether–hydrogen chloride (130) and methyl and ethyl ether–hydrogen bromide systems (128) over the concentration range 0–100 per cent acid. These were concerned mainly in correlating the conductivity change with the nature of the binary freezing-point curves. Of particular significance were the observations that conductivities of ether–HX mixtures were much higher than those of the pure components. For example, the specific conductance of a 1:1 ethyl ether–hydrogen bromide mixture at its melting point, −40°C., was 4.5×10^{-3} $\text{ohm}^{-1}\text{cm.}^{-1}$, while that of pure hydrogen bromide at its melting point was $<10^{-6}$ $\text{ohm}^{-1}\text{cm.}^{-1}$ The molecular complexes accordingly possess a fair amount of ionic character.

4. Pyridinic compounds

Pyridinic solvents, in accord with the lone-pair electrons and the low ionization potentials (table 1), possess marked basic properties. Interactions with hydrogen halides occur readily in these systems, and relatively stable compounds (predominantly ionic) are isolable in most cases (table 2).

The conductivities of hydrogen halides (as pyridinium halides) in pyridine ($\text{D.C.}_{25°}$ = 12.10) have been reported by a number of authors (2, 20, 31, 174, 200) and are shown in figure 6. Pyridinium chloride ($C_5H_5NH^+Cl^-$) is an extremely weak electrolyte in pyridine (2) at 25°C. with Λ values slightly greater than 1. Using an assumed value of $\Lambda_0 = 93$ [based on the limiting conductances of the pyridinium (49.6) and chloride ions (43) (table 4)] and activity coefficients calculated by the Gronwall, La Mer, and Sandved extension (84), Angerstein (2) evaluated the thermodynamic ionization constant (K_i) for pyridinium chloride as 7.15×10^{-7} from conductance and e.m.f. data for this electrolyte. The preceding method requires a knowledge of accurate limiting mobilities, and its utility is severely limited in the majority of nonaqueous solvents. The above value of Λ_0 does not seem in accord with the conductance data for pyridinium iodide solutions (*cf.* below).

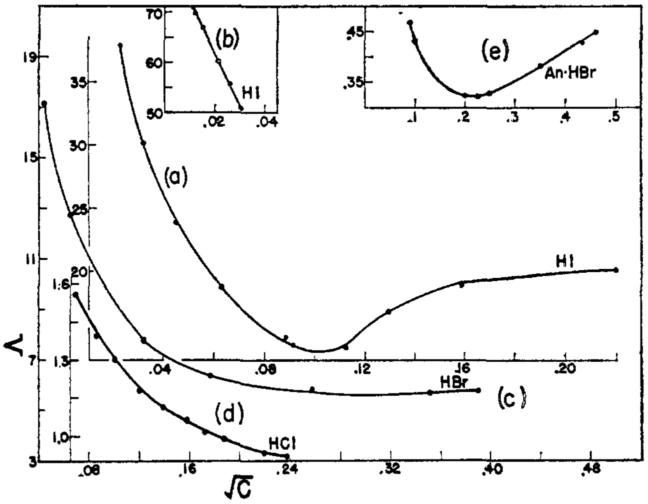


FIG. 6. Hydrogen halides in pyridine and quinoline. (a) Pyridinium iodide in pyridine (200). (b) Pyridinium iodide in pyridine (31). (c) Pyridinium bromide in pyridine (174). (d) Pyridinium chloride in pyridine (2). (e) Aniline hydrobromide in quinoline (200).

Sachanov (174) measured the conductivity of pyridinium bromide ($C_5H_5NH^+Br^-$) in pyridine at 25°C., but was not able to evaluate Λ_0 and K_i. Although the phoreogram for this salt passes through a shallow minimum at 0.12 equiv. liter^{-1}, a triple-ion plot of $\Lambda\sqrt{c}$

versus c does not yield a straight line, as predicted by theory (66).

Included in figure 6 are two sets of conductance data for pyridinium iodide in pyridine at 25°C. Agreement between the more extensive measurements of Walden (200) and those of Davies (31) is not satisfactory. The latter estimated values of Λ_0 (86.7) and K_i (5.9×10^{-4}) by the approximation method of Fuoss and Kraus; Walden's Λ_0 value of 75.0 was extrapolated graphically. The results of Davies' analysis seem more reliable, since the measurements were extended to lower concentrations. The presence of a well-defined minimum at 0.0125 equiv. liter^{-1} in the phoreogram for pyridinium iodide is of interest. As in the case of the hydrobromide, the data did not fit a triple-ion plot.

Thus, from the available data the strengths of the acids increase in the order HCl < HBr < HI and pyridine acts as a differentiating solvent. Considerable association into ion-pairs and triplets would be expected in a solvent of low dielectric constant, such as pyridine. The inability to fit the data for hydrogen bromide and hydrogen iodide in terms of a triple-ion plot ($\Lambda\sqrt{c}$ versus c) is therefore somewhat unexpected and warrants further investigation. It appears that ions of the type $C_5H_5NH^+HX_2^-$ may account for the anomalous increase in conductance at higher concentrations, and in this respect it should be noted that compounds of the composition $C_5H_5N \cdot 2HX$ have been isolated for hydrogen chloride (43, 44) and hydrogen bromide (112) (table 2).

Some semiquantitative measurements have also been reported (200) for aniline hydrobromide ($C_6H_5NH_3^+Br^-$) in quinoline (D.C. = 8.9) (figure 6), but other than indicating the extremely poor conducting properties of the latter solutions and the anomalous nature of the phoreogram they seem of limited value.

5. *Amines*

The solvent properties of amines are somewhat similar to those of pyridinic compounds. Amines are markedly basic and form hydrohalide salts readily with acids. Amine salts are analogous to ammonium halides and are formed by passing the hydrohalide gas through solutions of the amines in ether. The unshared lone-pair electrons on the nitrogen are donated to the acid, and scission of the H—X bond to form the salt follows; i.e.,

$$RNH_2 + HX \rightleftharpoons RNH_2 \rightarrow HX$$

$$RNH_2 \rightarrow HX \rightleftharpoons RNH_3^+X^-$$

The relative basicities of amines have been discussed in recent papers (14, 82, 193) and have been reviewed in several books (52, 155). Because of their low dielectric constants, amines are poor solvent media for salts and considerable ionic association will occur in the solutions.

The most extensive measurements in amines are those of Hlasko (92), who reported conductivities for four aniline hydrohalides, $C_6H_5NH_2 \cdot HX$ (X = F, Cl, Br, I) in aniline ($D.C._{25°}$ = 6.89) at 25°C. The results are illustrated in figure 7 with the exception of the data for X = F. The conductances for the latter are less than for X = Cl in this series. The four salts are all poor conductors with equivalent conductances considerably less than 1, except in the most concentrated hydrobromide and hydroiodide solutions. Of the four salts, aniline hydroiodide is the best conductor while aniline hydrofluoride is the poorest; aniline is thus a differentiating solvent for the acids.

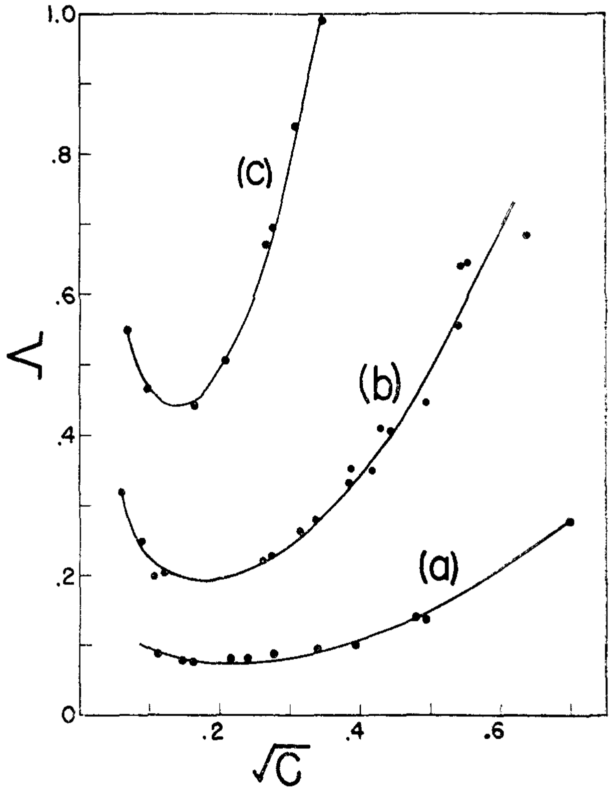


FIG. 7. Hydrogen halides in aniline at 25°C. (92). (a) Hydrogen chloride. (b) Hydrogen bromide. (c) Hydrogen iodide.

The minima in the phoreograms occur in approximately the same concentration range, i.e., 10^{-2} to 2.5×10^{-2} equiv. liter^{-1}. An analysis of the data in terms of triple-ion theory was not successful however, and the exact nature of the ionic species at higher concentrations in these solutions is in considerable doubt. Maxima have also been observed in several phoreograms at high concentrations, but an interpretation in terms of ion quadruples etc. is not obvious (84).

The values for the ionization constants calculated by Hlasko (92) for the four salts, using the Ostwald dilution law,

$$K = \Lambda^2 c / \Lambda_0(\Lambda_0 - \Lambda) \qquad (1)$$

where Λ_0 was estimated by Walden's rule, are incorrect, since recalculation shows the data do not in fact obey this relationship. It is doubtful that accurate determinations of Λ_0 and K_i are possible in the above systems, because of the very low conductivities of the dilute solutions, e.g., the resistance of a 10^{-2} equiv. liter^{-1} solution of aniline hydrochloride is of the same order as that of the pure solvent. Measurements at concentrations where the dilution law holds ($<10^{-4}$ N) are not experimentally feasible.

Agreement between the results of Hlasko and those of other investigators (Hodgson and Marsden (93, 94) for hydrogen chloride and hydrogen iodide; Pearce (162) for hydrogen chloride and hydrogen bromide; Pound (167) for hydrogen chloride; Sackur (177) for hydrogen chloride; Walden (200)) is relatively good (within 5 per cent in some cases) considering the difficulties in measurement. Pearce (162) has also reported conductivities for aniline hydrochloride and aniline hydrobromide in aniline at 0°C. and 35°C. Both solutes show an increase in conductances with an increase in temperature, and their phoreograms exhibit minima in the same concentration range as at 25°C.

Hodgson and Marsden (94) attempted to interpret the conductance behavior of aniline hydrohalides in aniline by assuming that a significant amount of the salt existed in the form of an undissociated solvated complex in dilute solutions. Equilibria of the following type were postulated in solution:

$$RNH_2 \cdot HX \rightleftharpoons RNH_3^+ + X^- \qquad K_1$$

$$RNH_2 \cdot HX + RNH_2 \rightleftharpoons (RNH_2)_2 \cdot HX \qquad K_2$$

$$(RNH_2)_2 \cdot HX \rightleftharpoons (RNH_2)_2H^+ + X^- \qquad K_3$$

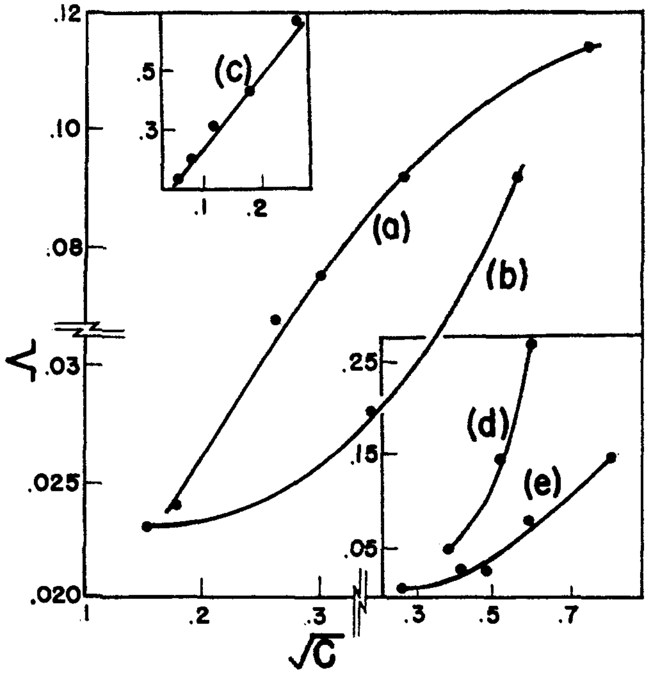


FIG. 8. Hydrogen halides in *o*-toluidine at 25°C. (a) Toluidine hydrochloride (177). (b) Toluidine hydrobromide (176). (c) Toluidine hydroiodide (176). (d) Pyridine hydrobromide (200). (e) Aniline hydrobromide (200).

where $(RNH_2)_2 \cdot HX$ is the solvated complex. A series of expressions were derived relating the measured molar conductivity to Λ_0, the total concentration of solute, C, and constants $K = K_3/K_1^{1/2}$ and $\alpha = K_1K_2/(1 - K_2)$. The values for the equilibrium constants, K_1, 0.36; K_2, 0.10; K_3, 0.091, for the aniline hydroiodide salt seem improbably high. The assumption that the Kohlrausch law is valid for the entire concentration range in the above does not seem justified.

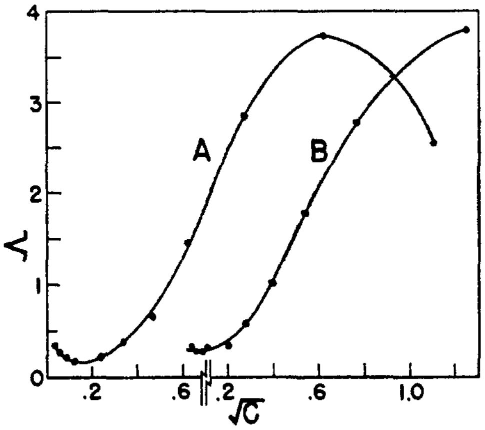


FIG. 9. Hydrogen chloride in (A) dimethylamine hydrochloride (42) and (B) ethylamine hydrochloride (42).

In *o*-toluidine (D.C.$_{18°}$ = 5.95) conductance measurements for the three acids hydrogen chloride (177), hydrogen bromide (78, 176) and hydrogen iodide (176) (in the form of the *o*-toluidine salts) indicate that they are very weak electrolytes with properties similar to those in analogous solutions in aniline. The phoreograms are shown in figure 8. A limited number of measurements have also been reported for pyridine and aniline hydrobromides (200) in *o*-toluidine. A distinguishing feature in all of the above cases is the decrease in conductance with dilution; a reversal of this undoubtedly occurs at still lower concentrations.

Sachanov (176) noted that the data for *o*-toluidine hydrobromide and hydroiodide fit an empirical equation of the form $\Lambda V^n = K$, where V = dilution and n and K are constants; e.g., $n = 0.23$ and $K = 0.054$ for the hydrobromide salt.

Conductance measurements have been reported by Elsey (42) for hydrogen chloride, over a considerable concentration range, in ethylamine (D.C.$_{100°}$ = 4.3 (gas)) and dimethylamine (D.C.$_{103°}$ = 3.3 (gas)) at −33.5°C. In both systems the phoreograms, as shown in figure 9, for hydrogen chloride (in the form of the respective salts) show minima and maxima. The data do not lend themselves for an estimate of the Λ_0's or K_i's nor can the data be interpreted adequately in terms of ion-aggregate concepts. The minimum in dimethylamine solutions occurs at a somewhat lower concentration, 4.7×10^{-3} N, than in ethylamine, 2.0×10^{-2} N.

6. *Nitriles*

Solvents containing the —C≡N polar group are weakly basic (194) with donor properties attributable to the lone-pair electrons on the nitrogen and the π electrons of the carbon–nitrogen triple bond in the cyano group. The formation of acid–base addition compounds in nitrile–hydrogen halide systems is well established (100, 154). For example, the complexes formed between hydrogen chloride, hydrogen bromide, hydrogen iodide and acetonitrile have been characterized by chemical analysis (100), freezing-point measurements (154), and infrared spectra both in the solid state and in solution (100). Solid substrates corresponding to the empirical formula $CH_3CN \cdot 2HX$ were isolated for the three acids; the structure of $CH_3CN \cdot 2HCl$ was shown to be essentially that of a nitrilium salt, $[CH_3CNH]^+ \cdot HCl_2^-$, while the structures of the compounds formed from hydrogen bromide and hydrogen iodide were of the imino hydrohalide type, $CH_3C(X){=}NH_2^+X^-$ (100). Since the dielectric constants of nitriles (e.g., $CH_3CN_{25°} = 37.5$) are somewhat higher than those of the analogous alcohols, their potentialities as solvents for ionogens and ionophores are of considerable interest.

Conductivity data for hydrogen halides in nitriles are meagre, the most extensive being those for acetonitrile–hydrogen chloride solutions. Pleskov (165) reported that hydrogen chloride is a strong electrolyte in acetonitrile ($D.C._{25°} = 37.5$) with little or no ionic association. This has not been confirmed in more recent investigations (99, 100, 101). Freshly prepared solutions of hydrogen chloride show marked increases in conductance with time (99) and "stabilized" equivalent conductances (101) are considerably lower than Pleskov's values, differing by more than a hundredfold, (see figure 10). Although reproducibility in measurements was less than desirable in the latter work, the phoreogram was shown to pass through a shallow minimum at approximately 5 × 10^{-2} equiv. liter^{-1}. Comparison of the phoreogram for stabilized solutions with that of freshly prepared solutions (figure 10 (extrapolated to zero time)) shows that the two curves are basically similar, apart from the lower conductivities of the zero-time solutions. This suggests that the ions formed during the conductance equilibration process are identical to those present at zero time. Polarographic measurements (24, 196) are in accord with the weak acidic nature of hydrogen chloride in acetonitrile. There is insufficient information in the Pleskov paper to resolve the disagreement of his results with the above, and no explanation can be offered accordingly.

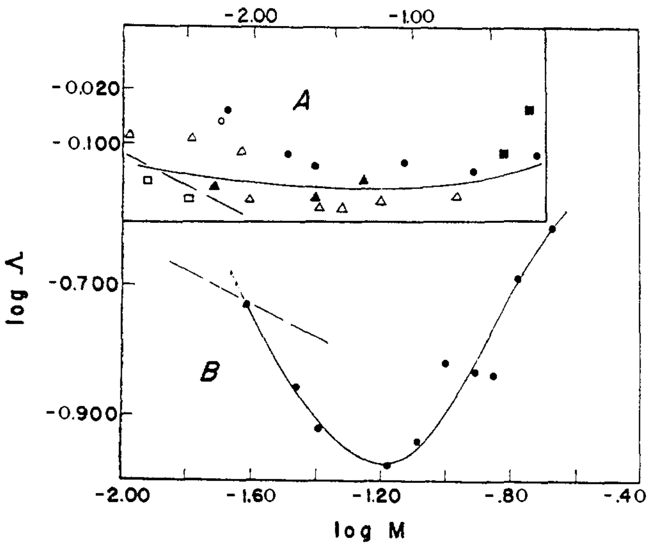


FIG. 10. Conductance-concentration variation: A, equilibrated CH_3CN-HCl; B, initial (zero-time) solutions (101).

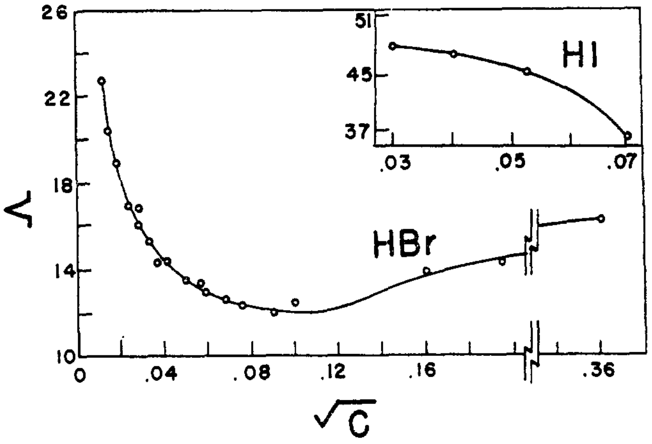


FIG. 11. Hydrogen halides in acetonitrile at 25°C. (101).

Hydrogen bromide and hydrogen iodide also are weak electrolytes in acetonitrile (101) (figure 11). Their conductivities, however, are considerably greater than that of hydrogen chloride, increasing in the ratio 1:20:60 at 10^{-3} *N*. A minimum is noted for the hydrogen bromide phoreogram at approximately 1.0–1.2 × 10^{-2} equiv. liter^{-1}.

Solutions of both hydrogen bromide and hydrogen iodide in acetonitrile show changes in conductivity with time, an increase being observed in the former and a decrease followed by an increase for the latter. The magnitudes of the changes are considerably less than for comparable solutions of hydrogen chloride and "equilibration" is achieved more rapidly.

Limiting conductances and K_i could not be evaluated for any of the hydrogen halides by the usual weak electrolyte methods nor was it possible to explain the minima in the conductance curves in terms of ionic association leading to triple-ion aggregates.

The conductances for both hydrogen chloride and hydrogen bromide were found to fit an empirical equation of the form:

$$\Lambda = A + Bm^{-1/2}$$

Constants A and B were evaluated from the linear plots of Λ versus $m^{-1/2}$. Inspection of the results for other ionogenic solutions (see table 8) shows that this equation applies to other solvent systems as well, i.e., it seems general in nature.

A qualitative interpretation of the conductivity results in acetonitrile has been given (99, 101) in terms of donor–acceptor interactions of the following type:

$$CH_3CN + HX \rightleftharpoons CH_3CN{\cdot}HX$$

$$CH_3CN{\cdot}HX \rightleftharpoons CH_3CNH^+X^-$$

$$\text{(Outer complex)} \quad \text{(Inner complex)}$$

$$CH_3CNH^+X^- \rightleftharpoons CH_3CNH^+ + X^-_{solv}$$

where acetonitrile acts as onium donor and HX as σ_D dissociative acceptor (Mulliken (152)). 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 (above) is followed by the ionization of the "inner" complex (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 (87), i.e.:

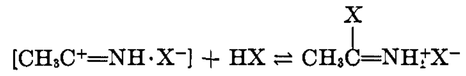
$$HX + X^-_{solv} \rightleftharpoons HX^-_{2\,solv}$$

The overall interactions would be equivalent to the formation of nitrilium type salts, of the 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

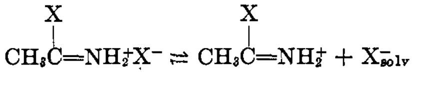
$$[CH_3C{\equiv}NH^+X^- \rightleftharpoons CH_3C^+{=}NH{\cdot}X^-]$$

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



$$[CH_3C^+{=}NH{\cdot}X^-] + HX \rightleftharpoons CH_3\overset{\overset{\textstyle X}{|}}{C}{=}NH_2^+X^-$$

and consequent ionization of the imino hydrohalide



$$CH_3\overset{\overset{\textstyle X}{|}}{C}{=}NH_2^+X^- \rightleftharpoons CH_3\overset{\overset{\textstyle X}{|}}{C}{=}NH_2^+ + X^-_{solv}$$

The increased polarizabilities of hydrogen bromide and hydrogen iodide favor an enhancement of the imino-type interactions over that in the acetonitrile–hydrogen chloride system.

At low acid concentrations ions of the types CH_3CNH^+ and X^- predominate and phoreograms exhibit the characteristics of a weak electrolyte; at high acid concentrations more complex ionic species, e.g., HX_2^- and $[CH_3C(X){=}NH_2]^+$, are present in appreciable concentration and an anomalous conductance increase with acid concentration results. In summary, it appears that at least two processes occur in these solutions whereby free ions are produced. The first (practically instantaneously) involves the direct transfer of protons from HX to CH_3CN to form the ions CH_3CNH^+ and X^-, which exist as associated pairs and free ions. This may account for the conductance at time zero. The second is the chemical interaction series in which the slowness of the second step (formation of imino hydrohalide) seems to determine the measurable (low) rate of increase in conductance, since the other two steps attain equilibrium almost instantaneously.

The conductivities of the addition compounds $CH_3CN{\cdot}2HCl$ and $CH_3CN{\cdot}2HBr$ have also been measured in acetonitrile (100) and are illustrated in figure 12. The conductances are quite similar in magnitude and variation to those for the individual acids. The agreement of the limiting slope for $CH_3CN{\cdot}2HCl$ with that predicted theoretically for ion-pair formation, i.e., $-\frac{1}{2}$, may be of significance. The slopes of log Λ–log c plots for hydrogen bromide and $CH_3CN{\cdot}2HBr$ approach limiting values of $-\frac{1}{3}$.

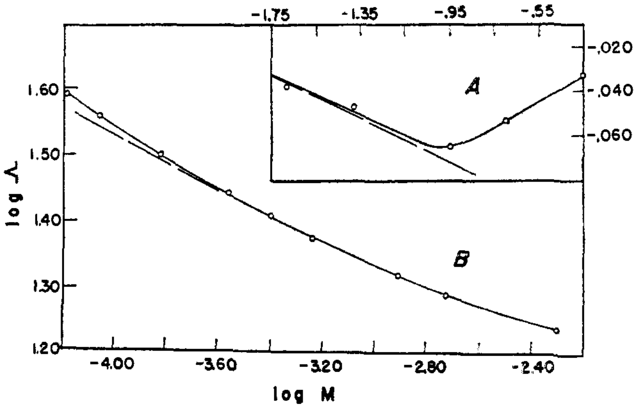


FIG. 12. $CH_3CN{\cdot}2HX$ in acetonitrile at 25°C. (100). A: $CH_3CN{\cdot}2HCl$. B: $CH_3CN{\cdot}2HBr$.

Except for some preliminary measurements in propionitrile and benzonitrile (102) which indicate a behavior for hydrogen chloride similar to that in acetonitrile, no conductances have been reported in nitriles other than acetonitrile. The conductivity of hydrogen chloride in hydrogen cyanide also increases rapidly with time, but the measurements are only qualitative (107).

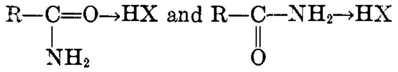
Relative to the electrical conductance of hydrogen halides, the hydrolysis of nitriles to amides and carboxylic acids warrants consideration (125, 144, 147, 168, 169). Rabinowitch and Winkler investigated the hydrolysis of acetonitrile (168) and propionitrile (169) in aqueous concentrated acidic media (hydrochloric and hydrobromic acids). The reaction:

$$RCN \xrightarrow[k_1]{H_2O} RCONH_2 \xrightarrow[k_2]{H_2O} RCOOH + NH_3$$

was shown to be a consecutive irreversible and unimolecular process. The rate increases with increasing acid concentrations. In the concentration range less than 4 N, the first step is rate determining, i. e., $k_1 \ll k_2$, whereas at extremely high concentrations (greater than 11 N), the second step seems to be rate determining. In a 1 N aqueous solution of hydrochloric acid the energy of activation for the hydrolysis was found to be 26.5 kcal./mol. At room temperatures the hydrolysis of acetonitrile proceeds very slowly, and was found incomplete even after a period of several months (147). Hydrogen bromide was less efficient than hydrogen chloride as catalyst in this process (125, 144). Relative to measurements in anhydrous systems, a qualitative observation (99, 101) was reported that $CH_3CONH_2 \cdot HCl$ was found present after long standing at room temperature if water in trace amounts had been added initially to freshly prepared anhydrous solutions of hydrogen chloride in acetonitrile. Due precautions at all steps of the experimental measurements in anhydrous solutions are essential to ensure that the possibility of side reactions such as hydrolyses is reduced to a minimum. A need exists for observations, both qualitative and quantitative, on the influence of trace amounts of water in anhydrous systems generally relative to such measurements.

7. *Amides*

Amides are in general polar solvents with relatively high dielectric constants in comparison with other organic compounds (e.g., formamide, $D.C._{20°} = 111.5$). They are accordingly good ionizing media for electrolytes, as is seen by conductivity measurements. Amides have two functional groups which can donate electrons, i.e., C=O and —NH_2. Accordingly complexes of the types



$$R-\underset{NH_2}{\underset{|}{C}}=O\rightarrow HX \quad \text{and} \quad R-\underset{O}{\underset{\|}{C}}-NH_2\rightarrow HX$$

are probable. Recent spectroscopic measurements (29) are not in accord with the general view that salts of the type $RCONH_3^+X^-$ predominate (96) and act as intermediates in hydrolysis reactions. Thus the shift of the fundamental absorption band, $\nu_{C=O}$, in amides to longer wavelengths is understood by the interaction between the proton and the carbonyl group.

Dawson, Newell, and McCreary (33) have reported measurements for hydrogen chloride in formamide ($D.C._{20°} = 111.5$) at 3°, 20°, and 40°C. The phoreograms for hydrogen chloride are shown in figure 13. The following values were obtained by extrapolations: Λ_0 at 3°C. = 14.41; Λ_0 at 20°C. = 24.50; Λ_0 at 40°C. = 39.40. The conductance curves approached the theoretical curves from above, and it was concluded that ionic association did not occur in these solutions. Since the data were for moderately concentrated solutions, 5.38×10^{-2} to 45.54×10^{-2} equiv. liter^{-1}, over a relatively small concentration range, the applicability of the Onsager equation may be fortuitous. The mobility of the solvated proton was found to be less than that of potassium ion in formamide. The possibility of solvent–solute addition compounds such as xHCONH$_2$–yHCl in these solutions seems not improbable.

Conductivity measurements for the addition compounds $HCONH_2 \cdot 3HCl$ and $2HCONH_2 \cdot 3HBr$ in formamide (figure 13) had been reported earlier by Röhler (171) but the data are too limited for adequate interpretation.

Equivalent conductance measurements have recently been recorded for hydrogen chloride and hydrogen bromide in acetamide ($D.C._{94°} = 60.6$) at 94°C. by Jander and Winkler (98). Limiting equivalent conductances, 34.24 (HCl) and 34.59 (HBr), were determined using the Shedlovsky modification of the Onsager equation (181). The measurements were for relatively high concentrations and small range (0.03–0.15 equiv. kg.$^{-1}$) and the validity of the constants obtained by the extrapolations may be questioned accordingly. The addition compounds

$$2CH_3CONH_2 \cdot HBr \text{ and } 2CH_3CONH_2 \cdot HCl$$

were confirmed by Jander and Winkler (97) without discussions relative to the ionization processes of these in acetamide. The well-characterized 1:1 compound, $CH_3CONH_2 \cdot HCl$ (108), was apparently not noted by these investigators.

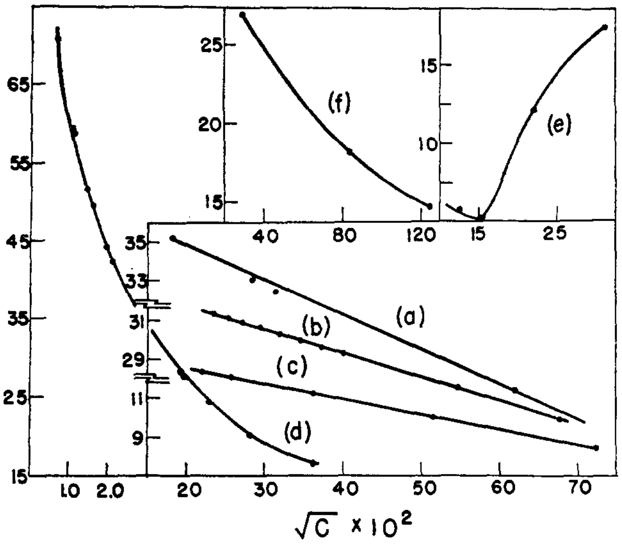


FIG. 13. Hydrogen halides in amides. (a, b, c) Hydrogen chloride in formamide at 40°, 20°, and 3°C., respectively (33). (d) Hydrogen chloride in N,N-dimethylformamide at 20°C. (191). (e) $HCONH_2 \cdot 3HCl$ in formamide (171). (f) $2HCONH_2 \cdot 3HBr$ in formamide (171).

Rochow and Thomas (191), Dawson, Golben, Leader, and Zimmerman (32), and Sears, Wolford, and Dawson

(179) have shown that hydrogen chloride is a weak electrolyte in N,N-dimethylformamide (D.C.$_{20°}$ = 38.3) at 20°C. (figure 13). The values for Λ_0 and K_i, 79.3 and 2.83×10^{-4}, respectively, were estimated by Rochow and Thomas from an Ostwald law graphical plot. Dawson and coworkers, by extrapolation of the phoreogram, reported a value of 70 for Λ_0. Reëvaluation of the Dawson data, using the Ostwald law, yields 65.3 and 6.55×10^{-4} for these parameters. Some of the difficulties in attaining reproducible measurements in the preceding system have been discussed by Rochow and Thomas. Discrepancies in conductivities were attributed to the presence of small amounts of water and/or basic impurities.

Sears, Wolford, and Dawson (179) have measured the conductivity of hydrogen bromide in N,N-dimethylformamide at 25°C. Although hydrogen bromide is a much stronger acid than hydrogen chloride it shows incomplete dissociation; e.g., the calculated value for the Onsager slope is −163, while the observed value is −313. The limiting equivalent conductance and K_i, by the Fuoss–Shedlovsky method for weak electrolytes, were found to be 88.7 and 1.7×10^{-4}, respectively. The limiting mobility of the protonated dimethylformamide cation was of the same order of magnitude as that of other cations.

Relative to conductivity data in amides it should be noted that these solvents are subject to hydrolysis by acids in the presence of water, much in the manner as for nitriles, i.e.,

$$RCONH_2 \xrightarrow[HX]{H_2O} RCOOH + NH_3 + HX$$

The reaction mechanisms are discussed in detail elsewhere (88, 96) and need not be reviewed here. As elsewhere, utmost precautions to exclude water even in smallest amounts from these anhydrous systems would seem essential to ensure accurate conductance data.

B. ACIDIC SOLVENTS

1. *Carboxylic acids*

Equivalent conductances for hydrogen chloride and hydrogen bromide have been reported in acetic acid (D.C.$_{25°}$ = 6.15) at 25°C. by Kolthoff and Willmann (123) and are illustrated in figure 14. Both acids are very weak electrolytes in this solvent, with hydrogen chloride somewhat weaker than hydrogen bromide. A satisfactory determination of Λ_0 and K_i has not been achieved. Smith and Elliot (186) estimated, colorimetrically, K_i values of 5.1×10^{-10} and 1.9×10^{-7} for hydrogen chloride and hydrogen bromide, respectively. Shkodin and Izmailov (184) reported K_i values of 6.3×10^{-9} and 4.0×10^{-7} for hydrogen chloride and hydrogen bromide from e.m.f. and conductance data.

Formic acid (D.C.$_{25°}$ = 58.5) is a relatively good ionizing medium for hydrogen chloride, as shown by the conductance measurements of Schlesinger and Martin (178) (figure 14). Discrepancies between these measurements and earlier results of Zanninovich-Tessarin (207) may be attributed to an impure solvent in the latter. Values for Λ_0 and K_i of 80.0 and 0.041, using the Ostwald law, were reported by the former group (178). Because of the relatively high concentration range (8×10^{-3} to 0.3 equiv. liter^{-1}) and the scatter in the results, these values should be regarded as approximations only.

2. *Nitro compounds*

Although solvents with a nitro group are polar (e.g., nitrobenzene, D.C.$_{25°}$ = 34.82, and nitromethane, D.C.$_{25°}$ = 35.87) the weakly acidic properties of the nitro group limit their utility as ionizing media for the hydrogen halides. The three acids hydrogen chloride (4, 91, 177), hydrogen bromide (17, 91), and hydrogen iodide (200) are all poor conductors in nitrobenzene, as is apparent from the results at 18°C. illustrated in figure 15. The reproducibility of the measurements was poor, and conductance–time changes were noted in hydrogen iodide and hydrogen bromide solutions. Trace amounts of water increase the conductivity markedly (4) and most probably account for the irreproducibility noted above. Values for Λ_0 and K_i cannot be evaluated from the preceding results.

Hlasko and Michalski (91) reported measurements for hydrogen chloride in nitromethane at 25°C. but apart from the fact that the conductivities are very low, e.g., 0.233 ohm^{-1}cm.^{2} at 0.0909 N, the results seem of little significance. Later measurements (86) have confirmed the poor conductance of hydrogen chloride in nitromethane.

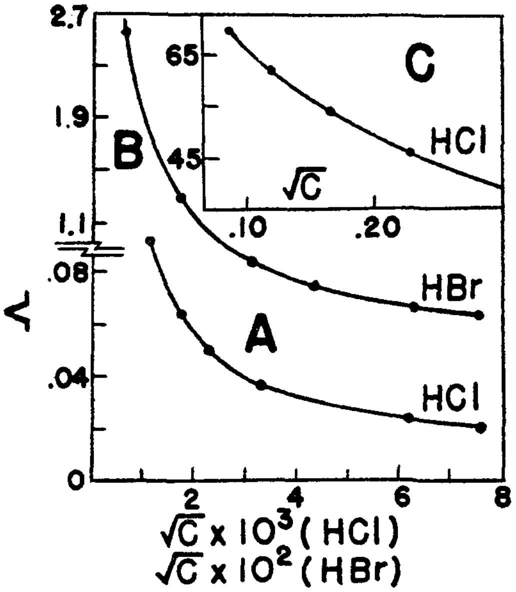


FIG. 14. Hydrogen halides in formic and acetic acids: A, B, in acetic acid (123); C, in formic acid (178).

C. APROTIC SOLVENTS

Conductance data for the halogen acids in aprotic solvents, i.e., those which do not exhibit acidic or basic properties, are noticeably lacking. Qualitative measurements have shown that hydrogen chloride is virtually unionized in benzene, xylene, and hexane (105). The slight increase in conductance observed when anhydrous acids are introduced into these solvents can be attributed to the presence of the last trace amounts of basic impurities, always so difficult to remove in the purification procedures. Thus 0.01 per cent water in the solvent is equivalent to approximately 0.005 mole per liter, and this concentration is comparable to solute concentrations in the dilute solution region.

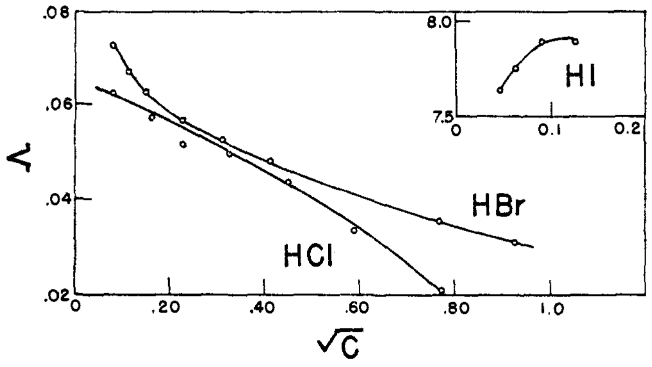


FIG. 15. Hydrogen halides in nitrobenzene (91, 200).

D. MISCELLANEOUS MEASUREMENTS

Conductance measurements have been recorded for organic compound–hydrogen halide systems using the anhydrous hydrogen halide as solvent. Steele, McIntosh, and Archibald in a classic work in 1906 (187) reported the conductivities of a wide variety of organic compounds ranging from alcohols to nitriles in anhydrous hydrogen chloride (−100°C.), hydrogen bromide (−83°C.), and hydrogen iodide (−50°C.). The formation of molecular compounds between the solute (organic molecule) and solvent molecules was proposed to account for the formation of ions and for the anomalous increase in conductivity noted with increasing solute concentration.

Fredenhagen and Cadenbach (53, 54) investigated the conductivities of aliphatic alcohols, carboxylic acids, ethers, and ketones in anhydrous hydrogen fluoride at −15°C. Equivalent conductances ranged from 150 ohm^{-1}cm.^{2} to 200 ohm^{-1}cm.^{2} Rather surprising was the observation that ethanol and 1-propanol had higher conductances than methanol. It appears that the rate-determining step for proton transfer is not as in alcoholic solutions (i.e., rotation of the ROH_2^+ ion). Measurements of the conductivities of aromatic hydrocarbons in anhydrous hydrogen fluoride have been reported by Klatt (118) and more recently by Kilpatrick and coworkers (117). The equilibrium constants:

$$K = \frac{[ArH^+][F^-]}{[Ar][HF]}$$

for a number of polymethylbenzenes were calculated from the equivalent conductances in the latter work, assuming that the degree of dissociation was given by $\alpha = \Lambda/\Lambda'$, where Λ' is the limiting conductance for hexamethylbenzene. The results from these conductance measurements and from distribution experiments are in qualitative agreement (135, 138).

VII. LIMITING CONDUCTANCES AND IONIZATION CONSTANTS

Accurate limiting equivalent conductances and ionization constants are essential to an understanding of the relative strength of electrolytes, the degree of ionization, and the interactions in ionic solutions. For solvents in a homologous series, the relative basicities can be gained from a knowledge of the ionization constants. A survey of the various procedures for evaluating Λ_0 and K_i, with special reference to the problem of the hydrogen halides in organic solvents, is of interest.

For incomplete dissociation (assuming $\alpha = \Lambda/\Lambda_0$ and the mass action law) good approximations may be gained from the Ostwald dilution law:

$$K = \frac{\Lambda^2 c}{\Lambda_0(\Lambda_0 - \Lambda)} \tag{1}$$

A convenient form of this equation is the expression:

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_0} + \frac{c\Lambda}{K(\Lambda_0)^2} \tag{2}$$

in which form it is readily apparent that a graph of $1/\Lambda$ against the specific conductance κ (since $\kappa = c\Lambda/1000$) gives Λ_0 and K_i directly from the intercept and slope of the straight line. The system hydrogen chloride–dimethylformamide (191) has been interpreted by this method.

Deviations from the Ostwald law behavior are the rule rather than the exception, since the effect of ionic interactions on the mobilities of the ions is assumed negligible and the activity coefficient of each ionic species is taken as unity. The Fuoss–Kraus equation (65), developed from the Onsager limiting equation (84) modified for incomplete dissociation, gives the expression for α as:

$$\alpha = \frac{\Lambda}{\Lambda_0 F(z)} \tag{3}$$

where $z = A\sqrt{\Lambda c}\,(\Lambda_0)^{-3/2}$, A is a constant, and F is a function of z. Combined with the thermodynamic ionization constant:

$$K_i = \frac{c\alpha^2 f_\pm^2}{(1 - \alpha)} \tag{4}$$

the dilution law, corrected for long-range interionic effects, becomes:

$$\frac{F(z)}{\Lambda} = \frac{1}{\Lambda_0} + \frac{[c\Lambda f_{\pm}^2/F(z)]}{K_i(\Lambda_0)^2} \tag{5}$$

where the mean molar ionic activity coefficient, $f_{\pm}$, is calculated by the Debye–Hückel law. A graph of $F(z)/\Lambda$ against $c\Lambda f_{\pm}^2/F(z)$ is used to obtain the values of Λ_0 and K_i most readily. The values of $F(z)$ have been conveniently tabulated as interpolation tables by Fuoss (60). The conductances of ionophores in many systems and of the hydrogen halides in certain nonaqueous solvents, e.g., hydrogen chloride in ethanol and methanol (161) and hydrogen iodide in pyridine (31), have been treated by this method.

The Shedlovsky equation (182) for weak electrolytes, also derived from the Onsager limiting equation and the thermodynamic ionization constant, has the form:

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_0} + \frac{[c\Lambda f_{\pm}^2 S(z)]}{K_i(\Lambda_0)^2} \tag{6}$$

where

$$S(z) = 1 + z + \frac{z^2}{2} + \ldots$$

and z is defined as in the Fuoss–Kraus expression. This equation has been found better for estimates of Λ_0 and K_i, particularly in the range of values $10^{-3} \leq K_i \leq 1$. The limiting mobility of hydrogen chloride in methanol (183) was obtained by the Shedlovsky method. Recalculation of the data for hydrogen chloride in ethanol by this method would undoubtedly give improved values. The two extrapolation procedures have been critically discussed by Fuoss and Shedlovsky (69).

Of the nonaqueous solvents listed in the preceding section, the alcohols appear the best ionizing media for hydrogen halides. The limiting equivalent conductances are highest in these solvents. A summary of these results is given in table 4(a).

Limiting conductance data in solvents other than alcohols are scarce and where estimates have been made, the results are frequently of doubtful accuracy, e.g., the values for formic acid and acetic acid are obviously low. The spread in the values for Λ_0 (up to 5 per cent) in methyl and ethyl alcohols for which a number of independent investigations have been reported serves to stress the difficulties encountered in nonaqueous solutions.

Inspection of table IV(b) shows that the proton has an abnormal mobility in alcohol solutions; e.g., $\lambda_{0_{\mathrm{H}^+}} = 142.0$ (methanol); $\lambda_{0_{\mathrm{H}^+}} = 53.6$ (ethanol), although not as high as in water. A rough estimate of the excess proton mobilities in alcohols is possible from:

$$\lambda_{0_{\mathrm{H}^+\,(\mathrm{excess})}} = \Lambda_{0_{\mathrm{HX}}} - \Lambda_{0_{\mathrm{BX}}}$$

where BX is a strong electrolyte and the radii of B^+ and the solvated proton (28, 188) are similar. In table 5 a summary of excess proton conductances in methanol and ethanol thus estimated is given. The excess constitutes about 65 per cent of the total hydrogen–ion conductance in methanol and ethanol and over 80 per cent in water.

Conway, Bockris, and Linton (28) have recently given a comprehensive discussion of abnormal proton mobilities in water and aliphatic alcohols. It was proposed that the rate-determining step in proton conductance in alcoholic media is the rotation of hydrogen-bonded alcohol molecules near the alkoxonium ion (ROH_2^+). The decreasing contributions to the anomalous conductivity with increasing length of the alkyl chain may be understood on the basis of a slow rotation step.

By contrast the proton does not show abnormal mobilities in nonhydroxylic solvents and limiting ionic mobilities are of the same order as those of other cations; e.g., $\Lambda_{0_{\mathrm{HCl}}} = 24.10$ and $\Lambda_{0_{\mathrm{NH_4Cl}}} = 28.30$ (33) in formamide at 20°C. Minimization of possibilities of proton transfer by hydrogen-bonded chains undoubtedly accounts for this change in mobility in large part.

The limiting ionic conductances of the halide ions increase in the order $\mathrm{Cl}^- < \mathrm{Br}^- < \mathrm{I}^-$ in the solvents for which data are available. This is not unexpected in view of the greater polarizabilities of the larger anions.

The effect of temperature upon the limiting conductances (*cf.* table 4(a, b)) has not been widely investigated. The results reported for methanol and ethanol appear to be the only reliable data. In each case the limiting conductance shows a positive temperature dependence. This may be attributed in part to corresponding changes of viscosity; in alcohols the temperature dependence of the rate of the proton-transfer process also undoubtedly contributes.

Correlation of the limiting conductances of the acids in various solvents empirically, i.e., Walden product, has not been too successful, with the exception of the alcohols where a constancy is approached. The latter results are summarized in table 6. The simple modification of the Walden product relating the conductances and the dielectric constants of the solvents $\Lambda_0\eta_0/D$, according to van Rysselberghe (195), does not seem to apply for solutions of the hydrogen halides in organic solvents. The conditions under which the preceding are obeyed, i.e., large symmetrical ions with low surface charge density and minimum solvation effects, are apparently not fulfilled in these solutions. The recent calculations by Fuoss (63a) on the dependence of the Walden product on dielectric constant show that the calculated size of the ionic species depends on the nature of the solvent. The deviation of the Walden product from constancy is understood as due to an increase in viscosity attributed to the electrostatic coupling between the moving ions and the solvent dipoles. Insufficient data are available to evaluate this approach in the hydrogen halide–organic solvent systems.

A summary of the ionization constants is given in

TABLE 4

Limiting equivalent and ionic conductances of hydrogen halides in organic solvents

(a) Limiting Equivalent Conductances

Temperature	HCl	HBr	HI	References
		Methanol		
°*C.*				
25	202.5	212.3	221.8	(90)
	196.7			(192)
	198.5			(183)
	193.2			(85, 161)
	192.3			(172)
	204.3	206.6	212.2	(76)
15	173.0			(161)
4	150.4			(161)
		Ethanol		
25	81.7			(161)
	82.46			(41)
	83.8			(85)
	84.25			(8)
	84.7			(192)
	89.1	88.9	93.2	(76)
15	67.30			(161)
4	53.25			(161)
		1-Propanol		
25	46.6	47.2		(79)
		Pyridine		
25	93*		86.7	(2, 31)
		Formamide		
40	39.40			(33)
20	24.50			(33)
3	14.41			(33)
		N,N-Dimethylformamide		
°*C.*				
25	79.3	88.7		(191, 179)
	70			(32)
	65.3			(32, recalculated)
		Formic acid		
25	80.0			(178)
		Acetic acid		
25	1.54			(123)

(b) Limiting Ionic Conductances

Temperature	H^+	Cl^-	Br^-	I^-	References
			Methanol		
°*C.*					
25	141.8	51.27	56.4		(161)
	142.0	51.2			(85)
4	113.2	37.12	41.85		(161)
			Ethanol		
25	63.3	21.4			(192)
	57.40			28.80	(161)
	59.5	24.3			(85)
	64.5	24.5			(76)
4	37.24	16.01		19.30	(161)

* Estimated from limiting ionic mobilities.

table 7. The most accurate values are those for hydrogen chloride in methanol and ethanol at 25°C. The disagreement apparent in the values for any one system may originate in part from the computational methods used; e.g., K_i values for hydrogen chloride in methanol are 0.059, using the Shedlovsky extrapolation, and 0.118 using the Fuoss and Kraus equation. Reëvaluation of the ionization constants for hydrogen chloride in methanol in the light of the more recent concepts (62) would be of interest.

The ionization constants indicate that the basicities of the alcohols decrease in the series $C_nH_{2n+1}OH$ as n

TABLE 5

Excess proton conductance in alcohols

Alcohol	$\Lambda_{0_{HX}}$	$\Lambda_{0_{BX}}$	Excess Proton Conductance $\lambda_+ = \Lambda_{0_{HX}} - \Lambda_{0_{BX}}$
Methanol (25°C.).....	193.2 (HCl)	104.9 (KCl)	88.3
(15°C.).....	173.0 (HCl)	90.7 (KCl)	82.3
(4°C.).....	150.4 (HCl)	76.5 (KCl)	73.9
Ethanol (25°C.).....	81.7 (HCl)	42.5 (NaCl)	39.2
(40°C.).....	53.3 (HCl)	31.0 (KCl)*	22.3

* Estimated.

TABLE 6

Walden's rule in organic solvent–hydrogen halide systems

Solvent	Temperature	$\Lambda_0\eta_0$		
		HCl	HBr	HI
	°*C.*			
Methanol..............	25	1.081	1.125	1.155
Ethanol...............	25	0.908	0.958	1.005
1-Propanol............	25	0.934	0.946	
Formic acid...........	25	1.573		
Acetic acid...........	25	2.02×10^{-2}		
N,N-Dimethylformamide.	20	0.698		
Formamide.............	20	0.809		

increases. Colorimetric measurements by Kolthoff and Guss (122) are in accord with this generalisation.

It is of interest to note that K_i for hydrogen chloride in methanol has a positive temperature gradient in the range 4–25°C. (161), while K_i in ethanol has a negative temperature gradient. Although it is possible, in principle, to determine the thermodynamic quantities ΔH_i, ΔF, and ΔS knowing the variation of K_i with temperature, the experimental limitations of the conductance techniques limit the use of such measurements for this purpose. Some of the problems in the use of the A.C. conductance technique for thermodynamic data have been discussed by Feates, Ives, and Pryor (50). The mean heats of ionization reported by Ogston (161) for hydrogen chloride, i.e.,

Alcohol	15-25°C.	4-15°C.
	cal.	*cal.*
Methyl alcohol	−1100	−1560
Ethyl alcohol	+4500	+6700

should be regarded as approximate values, since the values of K_i are not precisely known and the results are based on measurements for a rather limited temperature range.

Attempts to estimate ionization constants for the acids in other nonaqueous solvents have been largely unsuccessful owing to lack of precise data at low concentration; e.g., $<10^{-4}$ equiv. liter^{-1}. Difficulties are encountered in the interpretation of conductance data in terms of the Ostwald law and its modifications: e.g., hydrogen chloride and hydrogen bromide in acetonitrile, aniline, and pyridine. The values of K_i for hydrogen chloride and hydrogen bromide in solvents other than alcohols are thus qualitative only. Further conductance studies, particularly at low concentrations, are required to meet the need for data in this field.

VIII. EQUIVALENT CONDUCTANCE–CONCENTRATION VARIATION

The phoreograms for halogen acids in nonaqueous solutions are of considerable interest, since "anomalies" are exhibited in the majority of cases. In the "anomalous" systems the equivalent conductance decreases with dilution initially until it reaches a minimum value and then it increases rapidly with further dilution. In some cases the phoreograms show maxima in the more concentrated regions, e.g., aniline hydrohalides in aniline. This behavior is not unique, having been observed in many systems, particularly for ionophores in solvents of low dielectric constant (64).

Early attempts to account for the variation in conductance with dilution, such as those made by Archibald, McIntosh, and Steele (187) and Sachanov (175), were based on the law of mass action and a series of simultaneous equilibria, one of which at least was ionization. Thus it was assumed that a prerequisite of ionization was the initial formation of an electrolyte type of compound or a complex between solvent–solute or solute–solute molecules. The conductivity thus depended upon the manner in which the degree of ionization of the "electrolyte compound" responded to mass action effects and solute concentration. Sachanov attributed minima in the phoreograms to the series of simultaneous equilibria:

$$AB \rightleftharpoons A^+ + B^-$$

$$[AB]_m \rightleftharpoons mAB$$

TABLE 7

Ionization constants in organic solvents

Temperature	HCl	Reference
	Methanol	
°C.		
25	0.059 0.118	(183) (161)
15	0.112	(161)
4	0.102	(161)
	Ethanol	
25	8.23 × 10^{-3} 0.0112 0.0113	(41) (161) (8)
15	0.0147	(161)
4	0.0232	(161)

Temperature	HCl	HBr	References
	Pyridine		
°C.			
25	7.15 × 10^{-7}		(2)
	N,N-Dimethylformamide		
25 20	2.83 × 10^{-4} 6.55 × 10^{-4}	1.7 × 10^{-2}	(191, 179) (32)*
	Formic acid		
25	0.041		(178)
	Acetic acid		
25	5.1 × 10^{-10}	1.9 × 10^{-10}	(186)

* Recalculated.

and

$$[AB]_m \rightleftharpoons [A_mB_{m-1}]^+ + B^-$$

An increase in conductance with dilution follows from the dissociation of AB into simple ions, while a decrease in conductance with dilution results from the third equilibrium, i.e., association of a solute–solute molecular type complex. The minimum occurred in the phoreogram at the point where contributions due to the two effects were equal. These concepts did not gain acceptance, partly because the evaluation of ionization constants did not follow too readily and in large part because with the advent of the Debye–Hückel theory such studies were overshadowed by the striking successes of that theory relative to properties of strong electrolytes.

A quantitative explanation of minima and maxima in phoreograms for ionophores in solvents of low dielectric constant has been developed by Fuoss and Kraus (66). The formation of higher ionic aggregates, i.e., triple ions and ion quadrupoles, is assumed with increasing concentration. An increase in conductance follows with the formation of triple ions by coulombic interaction between the ionic species and ion-pairs, viz:

$$[A^+B^-]^0 + A^- \rightleftharpoons [A^+B^-A^+]^+$$

and

$$[A^+B^-]^0 + B^- \rightleftharpoons [B^-A^+B^-]^-$$

In this treatment the dissociation constant, K_3, of triple ions is evaluated from the theoretical expression:

$$K_3^{-1} = \frac{2\pi N a_3^3}{1000} I(\mathrm{b}_3) \tag{7}$$

where N = Avogadro's number, a_3 = the distance of closest approach for triple ions, and $I(b_3)$ is a complex function, the values of which have been tabulated (84) for ready reference. The variation of equivalent conductance for systems where the formation of triple ions occurs is given by the equation:

$$\Lambda = \sqrt{\frac{K}{c}}\,\Lambda_0 + \frac{\sqrt{Kc}}{k}\,\Lambda_{0_3} \tag{8}$$

which is the expression for a curve with a minimum. In equation 8 K and k are the equilibrium constants for ion-pairs and triple ions and Λ_0 and Λ_{0_3} have the usual significance. Accordingly, a graph of $\Lambda c^{1/2}$ against c should yield a straight line where interactions such as those above predominate. Ample experimental verification of the triple-ion theory is reported in the literature (66). Further interactions between triple-ion species and simple ions have been discussed to account for additional inflections in conductance curves (67).

In systems where the solute molecules are ionogens, both the ion-pair and triple-ion theories are frequently insufficient to describe the conductance–concentration dependence. This is illustrated by the hydrogen halide–nonaqueous solvent systems. Plots of $\Lambda c^{1/2}$ versus c yield curves with increasing positive slopes in most cases, e.g., hydrogen bromide in acetonitrile and hydrogen bromide and hydrogen iodide in pyridine. The limitations undoubtedly may be attributed in part to the fundamental assumption in these ion-aggregate theories that potential energies of the interacting ionic species result from electrostatic coulombic forces only. Kraus (124) has reviewed this problem for a variety of systems where hydrogen bonding and acid–base equilibria are complicating factors.

Modifications of the Fuoss–Kraus conductance expression for weak electrolytes (equation 5) have been proposed by Witschonke and Kraus (206) to account for interactions not governed by coulombic forces. Thus in nonbasic solvents, e.g., nitrobenzene, equilibria of the following types are possible

$$\mathrm{BHA} \overset{\gamma}{\rightleftharpoons} \mathrm{BH^+} + \mathrm{A^-}$$

$$\mathrm{BHA} \overset{x}{\rightleftharpoons} \mathrm{B} + \mathrm{HA}$$

for donor–acceptor electrolytes, e.g., anilinium picrate. Equilibrium constants for the ionization and dissociation to free acid and base, respectively, are given by

$$K = \frac{c\gamma^2 f_\pm^2}{(1-\gamma-x)} \text{ and } k = \frac{cx^2}{(1-\gamma-x)}$$

respectively; the activity coefficient $f_\pm$ is obtained from the Debye–Hückel limiting law. The Fuoss–Kraus equation then has the modified form:

$$\frac{1}{f_\pm}\left(\frac{F(z)}{\Lambda} - \frac{1}{\Lambda_0}\right) = \frac{c\Lambda f_\pm}{F(z)}\,\frac{1}{K\Lambda_0^2} + \frac{1}{\Lambda_0}\sqrt{\frac{k}{K}} \tag{9}$$

where $F(z)$ is the same as before. A graph of

$$\frac{1}{f_\pm}\left(\frac{F(z)}{\Lambda_0} - \frac{1}{\Lambda}\right)$$

against $c\Lambda f_\pm/F(z)$ yields a straight line from which the true values of Λ_0, K, and k are readily calculated. The data for several picrates in nitrobenzene were treated with success by this theory (206), and the method can be extended, in principle, to systems of hydrohalide salts in nonbasic solvents, e.g., nitromethane and nitrobenzene.

French and Roe (55) recently proposed modifications of the Fuoss and Kraus ion-aggregate theory for the case of formation of unilateral triple ions, such as, for example, $\mathrm{Pi^-H^+Pi^-}$ in picric acid solutions (55, 56). Assuming the simultaneous equilibria for ion-pairs and unilateral triple ions in these solutions:

$$\mathrm{H^+\,Pi^-} \rightleftharpoons \mathrm{H^+} + \mathrm{Pi^-} \qquad K_1$$

$$\mathrm{Pi^-H^+Pi^-} \rightleftharpoons \mathrm{Pi^-} + \mathrm{H^+Pi^-} \qquad K_2$$

it follows that the equivalent conductance will be given by:

$$\Lambda[c(K_2 + c)]^{1/2} = \Lambda_0(K_1K_2)^{1/2} + \Lambda_{0_3}\left(\frac{K_1}{K_2}\right)c \tag{10}$$

where K_1 and K_2 are the dissociation constants for ion-pairs and unilateral triple ions, and Λ_0 and Λ_{0_3} have the usual meaning. The constants in equation 10 are evaluated from the slope and intercept of the linear plot of $\Lambda[c(K_2 + c)]^{1/2}$ versus c; K_2 is found by graphical approximation.

Unilateral triple ions of the type $[X^- - - HX]^-$, stabilized by hydrogen bonding between an undissociated acid molecule and the anion, may be expected in concentrated hydrogen halide solutions if solute–solute interactions are favored. Experimentally the existence of bihalide ions, HF_2^- (30), HCl_2^- (87, 198), and HBr_2^- (112), in various media has been confirmed, and in one instance the mobility of the HCl_2^- ion has been estimated (87). Tests of the concept of the unilateral triple ion with the conductance data for hydrogen halide–nonaqueous solvent systems show that, in general, the properties of these solutions cannot be explained in this manner. For example, in the hydrogen bromide–acetonitrile system a straight line is obtained for the graph of $\Lambda[c(K_2 + c)]^{1/2}$ versus c (as predicted by equation 10) for all values of $K_2 \geqslant 10^{-4}$, obviating an unequivocal determination of K_2 and the constants in this expression.

TABLE 8

Values of constants A and B in empirical equation $\Lambda = A + Bm^{-1/2}$

Solvent	Temperature		A	B	Concentration Range	Reference
	°C.					
Acetonitrile	25	HCl	0.69	4×10^{-3}	$10^{-4} < m < 4 \times 10^{-2}$	(101)
		HCl	0.76	-4×10^{-3}	$10^{-2} < m < 0.7$	(101)
		HBr	10.2	0.165	$10^{-4} < m < 1.2 \times 10^{-2}$	(101)
		HBr	17.7	−0.63	$1.2 \times 10^{-2} < m < 0.1$	(101)
Acetone	25	HCl	2.7	0.255	$2.45 \times 10^{-3} < m < 0.3$	(177)
Pyridine	25	HCl	0.64	6.5×10^{-2}	5×10^{-3} to 5.5×10^{-2}	(2)
		HBr	2.7	0.65	$m < 5 \times 10^{-2}$	(174)
Acetic acid	25	HCl	3.6×10^{-3}	9.8×10^{-4}	$m < 10^{-2}$	(123)

While the hydrogen halide species are 1:1 electrolytes, it appears that in anhydrous organic solutions the situation may arise not infrequently where there may be at least two processes occurring whereby free ions are produced (*cf.* the case of $HX–CH_3CN$). Thus consideration of both mass action effects according to the earlier concepts (175, 187) and the ion-aggregate equations based on modern concepts of ionic interactions (above) may be important to an understanding of the conductances of the hydrogen halides in these solutions.

IX. Empirical Conductance Equations

It has been possible to represent the experimental conductance data for solutions of halogen acids in several nonaqueous organic solvents by an empirical equation of the form:

$$\Lambda = A + Bm^{-1/2}$$

where m is the molarity (see page 221). The constants A and B are evaluated from the linear plots of $\Lambda m^{1/2}$ versus $m^{1/2}$ (or Λ versus $m^{-1/2}$). A summary of the values for these parameters found for four solvent systems is given in table 8. In each of the systems interactions between the ionogenic solute and the polar solvent may lead to compound formation. Additional data are needed to explore the applicability of this empirical equation more generally. The apparent linear relation between $\Lambda m^{1/2}$ and $m^{1/2}$ is at present without theoretical justification.

X. Charge-transfer Concepts

From the preceding discussion and the compilation of conductance data it is apparent that hydrogen halides frequently exhibit a highly individual behavior in nonaqueous solvents. This is attributed not only to the chemical properties of the solvent but also to the ionogenic nature of the acids.

The predominantly covalent character of the bonds in hydrogen chloride, hydrogen bromide, and hydrogen iodide is well established by their low conductivities (187) and partial ionic character (per cent ionic character: HF, 60; HCl, 17; HBr, 11; HI, 5) (149). Thus, ionization of the acids seems dependent upon the extent of their interaction with solvent molecules and can be expressed by the ionogenic displacement equilibrium:

$$HX + D \rightleftharpoons DH^+ + X^-_{solv}$$

i.e., an acid–base type of equilibrium.

The concept of solvent–solute interaction in electrolytic solutions is not new. It was the subject of active controversy between ionists and proponents of solvate theories in the early 1900's. In 1918 Kendall (114), in support of solvent–solute interactions, stated "... there are two phenomena which proceed in parallel for *acids* and *bases* of all strengths in aqueous solution; ionization and combination with the solvent." He concluded by proposing the hypothesis that "... ionization is preceded by combination between solvent and solute (acid or base) and is, indeed a consequence of such combinations." Kendall developed this hypothesis extensively in subsequent papers (115, 116) but interpretation of the factors contributing to solute–solvent interaction rested on vague unsaturation valence forces as dictated by the limited knowledge of chemical bonds in that period.

At the present time a satisfactory theoretical account for the electrolytic properties of ionogens is still to be achieved. Modern concepts of electronic structure and bond forces give a better insight on the solute–solvent interactions, and consequently the ionization processes in such systems. Relative to this the charge-transfer (C-T) theory of Mulliken (151, 152) and its applicability to hydrogen halide–organic solvent systems is of interest.

The charge-transfer theory provides a quantum-mechanical explanation of interactions between electron donors and acceptors (bases and acids in the Lewis sense) and accounts for the existence of $n:m$ addition compounds in these systems in terms of a resonance between no-bond and dative-bond structures, i.e., $D \cdot HX \leftrightarrow DH^+X^-$.

According to charge-transfer concepts the hydrogen halides can be classified as σ dissociative acceptors (152) (given the notation d or $h\sigma_D$). The acceptor action results from the electronegative characteristics of the halogen and is usually accompanied by a diminution of the covalent character of the HX σ bond. The extent of dissociative interaction will depend upon the electron-donor ability of the base and to some extent on the approachability of the base.

In considering the neutral molecule bases Mulliken distinguishes two types of donor action: the relatively strong donor action of onium (n) bases resulting from nonbonding lone-pair electrons, e.g., lone-pair electrons on the nitrogen or oxygen of amines or oxy solvents; and the weak donor action of π bases which results from a bonding orbital, e.g., unsaturated hydrocarbons, $C{\equiv}N$ groups, $C{=}O$ groups.

On the basis of the charge-transfer theory ionization of hydrogen halides in organic solvents can occur in three steps. The first involves formation of an $n:m$ type addition compound between acid acceptor and donor (D) solvent molecules, i.e.,

$$n\mathrm{HX} + m\mathrm{D} \rightleftharpoons m\mathrm{D} \cdot n\mathrm{HX}$$

The addition compounds are generally of the 1:1 type, although in several instances, e.g., solvents with $C{=}O$, $C{\equiv}N$, or pyridinic groups, there is the additional possibility of compounds such as $D \cdot nHX$ ($n = 2, 3, \cdots$) resulting from the presence of both π and n (onium) type donor centers. The dative bond formed between solvent and solute varies from very loose associative hydrogen bonds, as in acetone–hydrogen chloride and acetonitrile–hydrogen chloride systems, to relatively strong covalent bonds as in pyridine hydrochloride (in this case the charge-transfer bond leads to formation of a covalent bond between the nitrogen and the hydrogen of the acid and the scission of the sigma bond; *cf.* below). The existence of hydrogen-bonded acid–solvent addition compounds in solution has been confirmed in many systems by spectroscopic measurements (100, 103, 104, 166) (*cf.* Section V).

The second step is the scission of the HX σ bond in the addition compound, with the resultant formation of a salt-like compound, e.g.,

$$\underset{\text{(Outer complex)}}{\mathrm{D \cdot HX}} \rightleftharpoons \underset{\text{(Inner complex)}}{\mathrm{DH^+X^-}}$$

Transition from an outer to an inner complex generally occurs very rapidly. However, in some systems, e.g., where both the electron donor and the electron acceptor are relatively weak, there may be a finite activation energy for the outer-inner transition and this would lead to a conductance increase with time, e.g., hydrogen chloride in acetonitrile, iodine in pyridine (153). One other point can be noted: the scission of the σ bond depends to a certain extent upon the polarizability of the HX molecule. Since the polarizabilities of the hydrogen halides increase in the order HCl < HBr < HI (114), hydroiodide addition compounds would be expected to possess the most ionic character, as is the case (*cf.* conductance data).

The final step is the ionization (electrolytic) of the inner complex in solution to yield solvated ions, e.g.:

$$\mathrm{DH^+X^-} \rightleftharpoons \mathrm{DH^+} + \mathrm{X^-_{solv}}$$

Thus the ionization of hydrogen halides in organic solvents as expressed above involves three processes. These are dependent upon the electron-donor ability of the base, the acceptor properties of the acid, and the dielectric constant of the media. Hence solvent molecules with available donor electrons and low ionization potentials will readily form ionic addition compounds with hydrogen halides. Electrolytic dissociation of these compounds is governed in turn by the dielectric properties of the solvent; e.g., pyridinium bromide is a much better conductor in pyridine (D.C. = 12.01) than in *o*-toluidine (D.C. = 5.95).

Solute–solvent interactions more complex than the above in these acidic systems, particularly when the solvent has appreciable basic and/or acidic properties, must be anticipated in any complete account of the conductances of the hydrogen halides in anhydrous polar organic solvents. Thus in CH_3CN–HX solutions ionic species such as $CH_3C(X){=}NH_2^+$ undoubtedly contribute. These processes, occurring simultaneously, lead to different chemical species which may contribute to the formation of free ions by ultimate ionizations. If the rate-determining step is sufficiently slow, such interactions would be evident as a conductance increase–time effect in the measurements. Systematic studies on the nature of the species, together with mass action effects, and the modern concepts of ion-aggregate theories seem essential where two or more simultaneous processes are feasible, and would lead to useful information in this field.

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