lations of the type described here are only accurate to ±0.15 eV.

Another argument supporting a bound excited anion state is our calculated value of the dipole moment of the radical. A recent discussion by Garrett[16b] suggests that such a large dipole moment must produce bound states. It is far above the critical dipole moment (1.625 D), and in the range (≥3.2 D) where nonionic polar molecules have been calculated by Jordan[9] to have positive electron affinities. In addition, the nodal nature of the 11a′ orbital, and similarities of the equilibrium geometries and the force-field matrices for the radical and the excited anion, suggest that the latter is well described as a radical binding a loose electron, thus strengthening the dipole argument. Finally, the optical transition from the anion ground state to this excited state is symmetry allowed, and suggests a substantial transition dipole moment. This is consistent with the experimental observation of a transition whose intensity is comparable to that associated with the photodetachment continuum cross section.

In conclusion, both the CI calculation on the anion and the calculated dipole moment of the neutral acetaldehyde enolate radical suggest that there is a Rydberg-like excited anion which may be bound. This state appears to be the most likely candidate to explain the resonances previously observed in electron photodetachment experiments.

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The Nature of Hydrofluoric Acid. A Spectroscopic Study of the Proton-Transfer Complex $H_3O^+\cdot F^-$

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Abstract: Further spectroscopic measurements confirm the $H_3O^+\cdot F^-$ ion pair or proton-transfer complex as a predominant species in aqueous hydrofluoric acid. This complex owes its remarkable stability to a very strong hydrogen bond, mostly electrostatic. Being ionic, yet electrically neutral, it can account both for the essentially complete ionization of HF in water and the apparent weakness of the dilute acid. The ionization process may be represented by the double equilibrium $H_2O + HF \rightleftharpoons [H_3O^+\cdot F^-] \rightleftharpoons H_3O^+ + F^-$. The concentration of the various species cannot be determined from the spectroscopic data. However, the first equilibrium certainly lies well to the right, and cryoscopic data point to a value of about 15% for the dissociation of the complex. Dissociation can also occur in another way in the concentrated acid: $[H_3O^+\cdot F^-] + HF \rightleftharpoons H_3O^+ + HF_2^-$. Both the HF_2^- and separate H_3O^+ ions take part in the proton-migration process, which accounts for the sharp rise in conductivity with concentration. Deuterium fluoride is less strongly associated and less extensively ionized in solution than its hydrogen counterpart. Proton-transfer complexes with oxonium ions are also formed by anhydrous HF in various organic solvents.

Introduction

The surprising weakness of dilute hydrofluoric acid, in marked contrast with the three other hydrohalic acids,[1] has presented a challenge to the theory of chemical bonding. Conventionally the ionization of HF in water has been represented as a two-step process:

$$H_2O + HF \rightleftharpoons H_3O^+ + F^- \qquad (1)$$

and

$$HF + F^- \rightleftharpoons HF_2^- \qquad (2)$$

The first step, with an equilibrium constant in the range 2.4–7.2 × 10^{-4},[2] implies a dissociation of only a few percent. This unexpected behavior has been variously attributed to the greater strength of the H–F bond than that of the other hydrogen halides,[3] the hypothetical dimer H_2F_2,[4] or the equilibrium between chain structures of ions and ring structures of neutral HF molecules.[2] However, the very hypothesis of weak ionization is untenable, as explained elsewhere,[5] because it conflicts with a number of experimental facts. Foremost among those is the infrared absorption spectrum of aqueous hydrofluoric acid,[6] which shows great resemblance to that of the three other hydrogen halides, but also some differences. It is the analysis of that spectrum[7] which has led to the concept of hydrogen-bonded ion pair, or proton-transfer complex $H_3O^+\cdot F^-$.[8] Such a complex should have characteristic vibrations similar to, but distinguishable from, those of separate H_3O^+ ions. With this in view we have studied the vibrational spectra of (a) the concentrated acid as a function of temperature, (b) solutions of the bifluoride ion, HF_2^-, an important species in this system, and (c) the completely deuterated acid to confirm our assignments and detect any isotope effect.

Experimental Section

The spectra were recorded with the same equipment and much the same technique as in previous studies.[6,9] In infrared some difficulty was encountered in reproducing exactly the spectra of the saturated acid because of the high partial pressure of HF. However, these minor variations, mainly in the relative intensity of the 1840- and 1645-cm^{-1} bands, do not affect significantly our interpretation of the results. The sample of deuterium fluoride prepared specially by Merck Sharp and Dohme (Montrêal) was of high isotopic purity. The saturated solution contained only 38 mol% of DF in D_2O. (Unless otherwise stated concentrations are given throughout in mol%.)

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[1] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 2nd ed., Interscience, New York, 1966, p 223.

[2] H. H. Hyman and J. J. Katz in "Non-Aqueous Solvent Systems", T. C. Waddington, Ed., Academic Press, New York, 1965, Chapter 2, p 62.

[3] L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, N.Y., 1960.

[4] R. P. Bell, "The Proton in Chemistry", 2nd ed., Cornell University Press, Ithaca, N.Y., 1973.

[5] P. A. Giguère, *J. Chem. Educ.*, **56**, 571 (1979).

[6] P. A. Giguère and S. Turrell, *Can. J. Chem.*, **54**, 3477 (1976).

[7] P. A. Giguère, *Chem. Phys. Lett.*, **41**, 598 (1976).

[8] The name proton-transfer complex seems more appropriate here in view of the partial covalent character, as opposed to the purely Coulombic ion pairs of ordinary electrolytes. Likewise, the formula $H_3O^+\cdot F^-$ represents adequately the ionic, yet in effect neutral, character of the new entity.

[9] P. A. Giguère and C. Madec, *Chem. Phys. Lett.*, **37**, 569 (1976).

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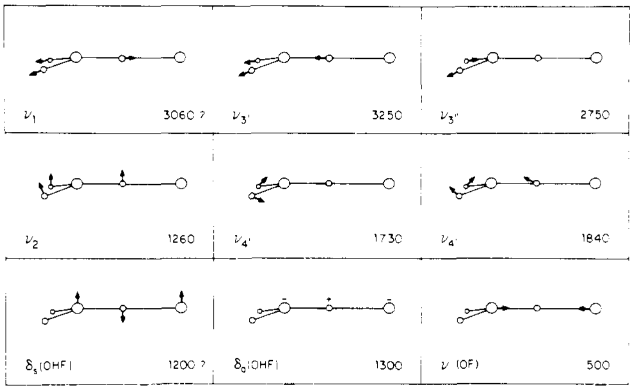

Figure 1. Normal modes of vibration of the $H_3O^+\cdot F^-$ proton-transfer complex with their approximate frequencies in cm^{-1}.

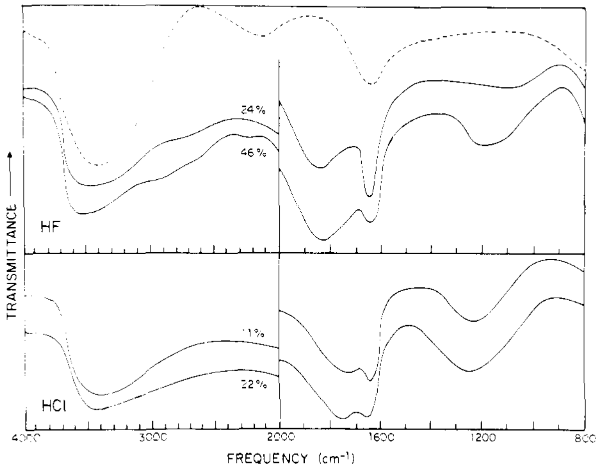

Figure 2. Comparative absorption in infrared of capillary films of concentrated hydrofluoric and hydrochloric acids. The various curves have been displaced along the ordinate for clarity. (Expanded ordinate scale (5×) below 2000 cm^{-1}.) ---, H_2O absorption.

Results

The vibrational spectra of hydrofluoric acid are still more difficult to decipher than those of the three other hydrohalic acids. Besides the well-known problems arising from overlapping of the broad bands of both H_2O and H_3O^+, and the strong "continuum" or sloping background, hydrofluoric acid presents some further complications, namely, (a) the variety of ionic and molecular species, (b) the strong molecular association of HF itself, which competes with H_2O in solvation, and (c) the near coincidence of the O–H and H–F stretching and bending frequencies. Therefore, interpretation of the spectra must be predicated partly on correlation with other physicochemical properties of the aqueous acid and with the spectra of HF in certain organic solvents. According to theory the $H_3O^+\cdot F^-$ complex should have nine fundamental vibrations depicted in Figure 1. For convenience the notation refers to the six fundamentals of the H_3O^+ unit, with degeneracy of the ν_3 and ν_4 modes removed under the lower symmetry (from C_{3v} to C_s), plus the three vibrations of the O–H···F bridge. The approximate frequencies of the latter are based on analogy with those of the HF_2^- ion. An important feature of this model is the large dipole moment, almost coincident with the O–H···F axis.

Vibrational Spectra. As usual with the spectra of strong acids the 3μ region is extensively overlapped (Figure 2). The maximum of the strong water band around 3450 cm^{-1}, which is gradually shifted to slightly lower frequencies in the other strong acids,[6] shifts in the opposite direction in hydrofluoric acid, and up to ca. 3525 cm^{-1} in the saturated acid, both in Raman and infrared spectra. In the latter a weak shoulder appears near 3610 cm^{-1}. As explained before[10] these frequencies are suitable for the H–F stretching of the $H_2O\cdot HF$ complex and the dimer $(HF)_2$. But there is no ambiguity about assignment of the broad shoulder centered at 2750 cm^{-1}, a frequency some 150 cm^{-1} lower than that of a degenerate ν_3 of separate H_3O^+ ions. By far the most characteristic feature of the infrared spectra is the broad band centered at 1840 cm^{-1}, assignement of which has led finally to the concept of a $H_3O^+\cdot F^-$ complex.[7] Its obvious resemblance to the 1730-cm^{-1} band of the other strong acids leaves little doubt as to its origin. This must be the highest frequency ever reported for an OH bending vibration. It represents a blue shift of some 110 cm^{-1} from the ν_4 frequency of separate H_3O^+ ions, and twice as much from that of the almost free ion, 1610 cm^{-1}.[11,12] Strong as it seems, that band is much weaker than that at 1730 cm^{-1} for the other acids relative to the H_2O band at 1645 cm^{-1}. This marked difference can be rationalized in terms of the associated dipole moment changes. Indeed, the derivative of the molecular dipole moment with respect to the HOH angle ($\delta\mu/\delta\alpha$) is expected to be smaller for the $H_3O^+\cdot F^-$ complex than for the separate H_3O^+ ion. For reasons already mentioned the relative intensity of that band could not be measured with any accuracy. Qualitatively, it seemed to increase regularly with acid concentration from the limit of detection, ca. 2%, up to saturation at 46%. Its frequency at the maximum also increases with concentration (from 1835 to 1845 cm^{-1}) due, no doubt, to replacement of H_2O by HF in solvation.

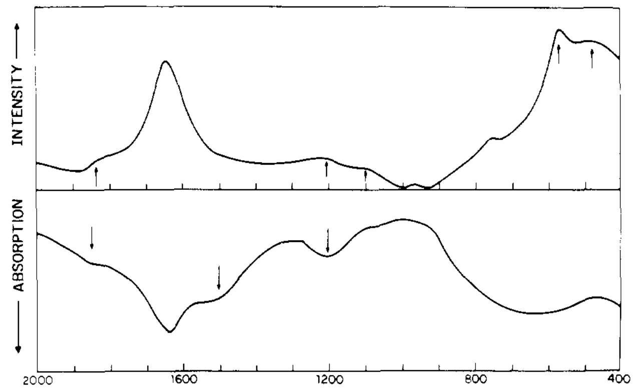

Figure 3. Infrared and Raman spectra of a 7% solution of KHF_2 in water.

Another striking difference between hydrofluoric acid and the three heavier hydrohalic acids is evident in the 1200-cm^{-1} region. Whereas in the latter the symmetric bending, ν_2, of H_3O^+ gives rise to a strong, clear-cut band centered at that frequency, by contrast in hydrofluoric acid, even up to 20% concentration, there is only a weak, continuous absorption evolving toward a vague maximum around 1000 cm^{-1}.[13] At higher concentrations a broad absorption of atypical contour gradually emerges between 1300 and 900 cm^{-1}. Again this singularity is consistent with the $H_3O^+\cdot F^-$ model from the dipole-moment viewpoint. Lastly, a Raman band at ca. 500 cm^{-1}, which shifts up to 525 cm^{-1} with acid concentration, is assigned tentatively to the H bond stretching of the proton-transfer complex.

HF_2^- Ion. In view of its remarkable stability the bifluoride ion is certainly a component of hydrofluoric acid, particularly at high concentrations. To help evaluate its role we have reexamined its vibrational spectra in aqueous solutions of KHF_2. Previous investigators[14,15] had reportedly detected its infrared band ν_3 around 1535–1550 cm^{-1} in hydrofluoric acid, but their published spectra were not convincing. The frequency at the maximum of that weak band cannot be determined accurately because of its location on

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(10) P. A. Giguère, C. Martel, and S. Turrell, *Chem. Phys. Lett.*, **56**, 231 (1978).

(11) B. Desbat and P. V. Huong, *Spectrochim. Acta, Part A*, **31**, 1109 (1976).

(12) J. P. Masson, J. P. Desmoulin, P. Charpin, and R. Bougon, *Inorg. Chem.*, **15**, 2529 (1976).

(13) As noted elsewhere[6] there was an error in the first reproduction of that region of the spectra.[7]

(14) L. H. Jones and R. A. Penneman, *J. Chem. Phys.*, **22**, 781 (1954).

(15) N. Zengin, *Commun. Fac. Sci. Univ. Ankara, Ser. A*, **11**, 1 (1961); *Chem. Abstr.*, **57**, 16008 (1962).

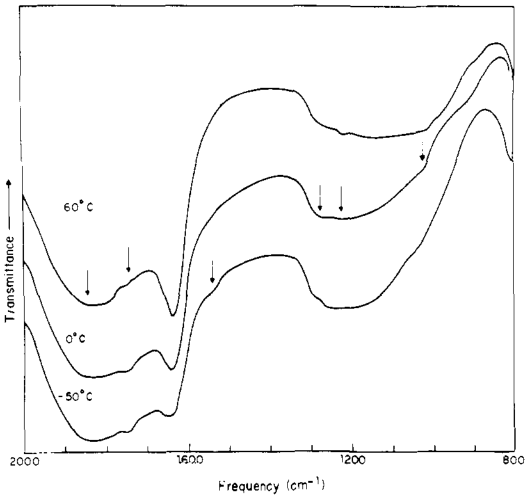

Figure 4. Effect of temperature on the IR spectrum of saturated solutions of hydrofluoric acid.

the slope of the strong ν_2 band of water (Figure 3), and its noticeable broadening toward low frequencies, a feature common to the H–X stretching bands of all proton-transfer systems.[10] The other characteristic frequency of HF_2^-, the bending ν_2 at ca. 1200 cm^{-1}, unfortunately coincides with that of other possible species, ionic and molecular. On its low-frequency side a couple of secondary maxima had been assigned tentatively to the polymer ion $H_2F_3^-$.[14] However, this now seems unlikely as the main band of that complex ion near 1770 cm^{-1} [16] is completely missing here. Furthermore, neither the fragility of that polymer ion nor the stoichiometry favors its presence in aqueous solution. More likely the two satellite bands near 1000 and 1150 cm^{-1} belong to the $H_3O^+{\cdot}F^-$ complex from hydrolysis. Support of this view may be seen in the weak absorption near 1840 cm^{-1}. These minor features are also visible in the Raman spectrum (Figure 3) besides the already mentioned O–H···F stretching band at 500 cm^{-1}. A fairly sharp peak on top of the latter at 570 cm^{-1} is of suitable frequency for the ν_1 vibration of HF_2^- by analogy with 600 cm^{-1} in the KHF_2 crystal.[17]

Temperature Effects. Early studies by Roth[18] had revealed a surprising increase of nearly 50% in the apparent dissociation constant of dilute hydrofluoric acid on cooling from 25 to 0 °C, in contrast with ordinary weak acids which show no measurable temperature effect. The present spectra (Figure 4) confirm and illustrate this peculiarity. Indeed, on cooling there is a marked increase of absorption in the 1200-cm^{-1} region and a concomitant decrease of the H_2O band at 1645 cm^{-1}. The former features a pair of secondary maxima at 1310 and 1200 cm^{-1}, while that at 1000 cm^{-1} nearly vanishes. As for the 1840-cm^{-1} band, although its overall intensity remains fairly constant, its contour evolves toward low frequencies and a small peak gradually emerges at 1730 cm^{-1}. The latter must arise from an increased concentration of separate H_3O^+ ions because the ν_4 mode of the $H_3O^+{\cdot}F^-$ complex, expected at the same frequency, is inactive in infrared. Likewise, the increase in HF_2^- ions is signaled by the appearance at −50 °C of its ν_3 band near 1550 cm^{-1}. Obviously the ionic species are favored at low temperature at the expense of the molecular ones in hydrofluoric acid. In contrast no appreciable temperature effect could be detected in the infrared spectrum of concentrated hydrochloric acid between −50 and 40 °C.

Deuterated Acid. In view of the fundamental importance of H bonding in acid–base equilibrium one may expect interesting observations on the D bond from a study of the deuterated acids. In the infrared spectrum of deuteriochloric acid (Figure 5) the characteristic bands of D_3O^+, ν_4 at 1300 cm^{-1}, and ν_2 at 900 cm^{-1}, show the expected isotope shift. However, they are definitely weaker and more diffuse than their hydrogen counterpart. This effect is somewhat exaggerated by the slight isotopic contamination of our sample (2–4% of HCl) responsible for some absorption at 1450 cm^{-1} (ν_2 of HDO) and the shoulder around 1020 cm^{-1} on the ν_2 band of D_3O^+. Likewise, the tiny peaks at 2900 and 2840 cm^{-1} are attributable to the hybrid species, HD_2O^+ and H_2DO^+, respectively. There was no such complication with the isotopically pure deuteriofluoric acid. Yet here also the ν_4'' band of the D_3OF complex at 1400 cm^{-1} is a lot weaker than its hydrogen counterpart with regard to the D_2O band at 1210 cm^{-1}. The most surprising difference, however, comes from the lack of any significant absorption in the 900-cm^{-1} region. Instead, one finds a fairly strong band centered at 730 cm^{-1}, the exact frequency of an absorption minimum in the spectrum of the deuteriochloric acid. The most plausible assignment here is to the O···D–F bending in the $D_2O{\cdot}DF$ complex. As well, the rather strong peak at 2640 cm^{-1} may be assigned to the D–F stretching of that complex. These are definite indications of a lesser degree of ionization of the isotopic acid, as explained below.

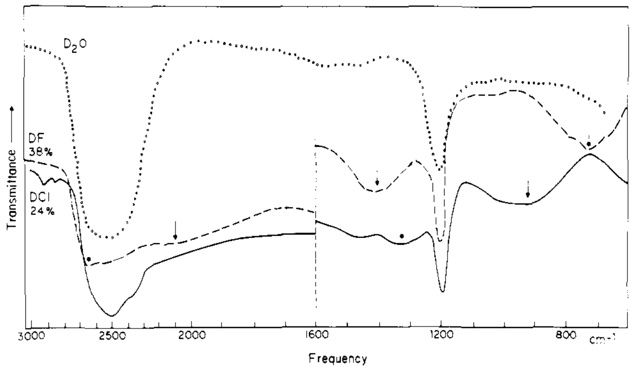

Figure 5. Infrared spectra of the deuterated acids. (Expanded ordinate below 1600 cm^{-1}.)

Discussion

The above results can be rationalized uniquely in terms of the $H_3O^+{\cdot}F^-$ complex as the predominant entity in hydrofluoric acid. Its remarkable stability comes from an exceptionally strong hydrogen bond, comparable to that in the HF_2^- ion. Pending further structural data, otherwise not readily obtainable,[19] the O–H···F distance may be estimated at 2.3 Å by analogy with the F···H···F distance in KHF_2, 2.26 Å.[20] As for the bridging O–H bond, it must be slightly longer than the 1.02 Å found by neutron diffraction in hydrated deuteriochloric acid.[21] The very strong hydrogen bonds in $H_3O^+{\cdot}F^-$ and HF_2^-, as well as those found recently in organic acid–fluoride complex anions, e.g., $AcOH{\cdot}F^-$,[22] form a separate class of chemical bonds, intermediate between the covalent and the ordinary hydrogen bonds. Their great strength—not to be confused with their dissociation energy—must be ascribed to the high electrostatic potential around the relatively small F^- anion. In addition, the strong Coulombic force in $H_3O^+{\cdot}F^-$ makes up in part for the contribution of resonance in the centrosymmetric HF_2^-.

Ionization Process. The $H_3O^+{\cdot}F^-$ concept demands reformulation of the complicated ionization of hydrogen fluoride in water. Tentatively it may be described by a double equilibrium:

$$H_2O + HF \rightleftharpoons [H_3O^+{\cdot}F^-] \rightleftharpoons H_3O^+ + F^- \qquad (3)$$

For reasons fundamental as well as practical the equilibrium constants cannot be estimated from the spectra. However, there

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(16) A. Azman, A. Ocvirk, D. Hadzi, P. A. Giguère, and M. Schneider, *Can. J. Chem.*, **45**, 1347 (1967).

(17) L. Couture-Mathieu and J. P. Mathieu, *C. R. Acad. Sci.*, **230**, 1054 (1950).

(18) A. W. Roth, *Justus Liebigs Ann. Chem.*, **542**, 35 (1939); *Chem. Abstr.*, **34**, 2685 (1940).

(19) Diffraction methods would be of little use here both because of the similar scattering power of O and F atoms and the interference of other species with neighboring interatomic distances.

(20) L. Helmholz and M. T. Rogers, *J. Am. Chem. Soc.*, **61**, 2590 (1939).

(21) R. Triolo and A. H. Narten, *J. Chem. Phys.*, **63**, 3624 (1975).

(22) J. Emsley, *J. Chem. Soc. A*, 2072 (1971).

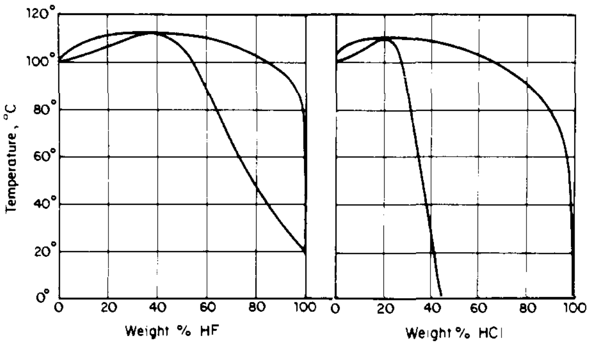

Figure 6. Boiling-point curves of the H_2O-HF and H_2O-HCl systems.

is no doubt that the first equilibrium lies well to the right. Incidentally, the accepted values of the dissociation constants of the three other hydrogen halides in water, and their evaluation from thermochemical cycles,[3,24,25] now appear fictitious, based as they are on properties of concentrated acids.[4] Instead, trace amounts of $H_3O^+{\cdot}X^-$ complexes can account for the finite values of these constants, p$K = -7$ for HCl, -9 for HBr, and -9.5 for HI,[1] as suggested elsewhere.[6] In solvents of lower dielectric power like liquid SO_2 they form mostly ion pairs.[9]

A further complication in hydrofluoric acid is the secondary dissociation mechanism for the complex at high concentrations:

$$[H_3O^+{\cdot}F^-] + HF^- \rightleftharpoons H_3O^+ + HF_2^- \qquad (4)$$

Although the bifluoride ion is quite stable, its concentration remains low because of the stoichiometry. It is noteworthy that the concentration of HF_2^- is strongly temperature dependent. As for the molecular complex $H_2O{\cdot}HF$, detected only in the concentrated acid, it exists also in the vapor[26] where its H bond (2.68 Å)[27] is slightly stronger than that in the $(HF)_2$ dimer (2.74 Å).[28]

Physicochemical Properties. The $H_3O^+{\cdot}F^-$ model can account satisfactorily for the anomalous behavior of hydrofluoric acid. First is the apparent weakness of the dilute acid as measured by electrical conductivity and indicators.[23] Then the sharp increase in acidity with concentration, revealed in particular by the Hammett acidity function H_0,[29] follows from the increase in separate H_3O^+ and HF_2^- ions, both capable of taking part in the proton-migration process. The latter ion is known to undergo hydrolysis presumably according to the equation

$$HF_2^- + H_2O \rightleftharpoons [H_3O^+{\cdot}F^-] + F^- \qquad (5)$$

Likewise, hydrolysis of the metal fluorides may be described thus:

$$2H_2O + F^- \rightleftharpoons [H_3O^+{\cdot}F^-] + OH^- \qquad (6)$$

The excess heat of neutralization of hydrofluoric acid, 3.3 kcal mol^{-1} over that of all strong acids, seems in conflict with the notion of a stable $H_3O^+{\cdot}F^-$ complex. It must be remembered, however, that, the latter being a neutral species, its heat of hydration is certainly much smaller than that of the two separate ions.

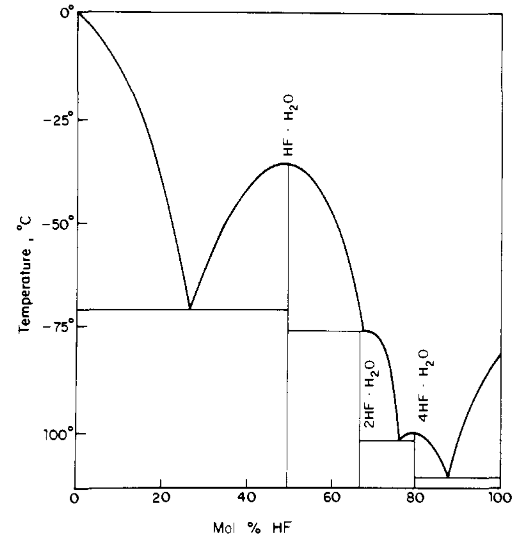

Figure 7. Phase diagram of the H_2O-HF system. In fact the three "hydrates" are ionic: $H_3O^+F^-$, $H_3O^+HF_2^-$, and $H_3O^+H_3F_4^-$.

Table I. Characteristic Frequencies (cm^{-1}) of Proton-Transfer Complexes Involving Oxonium Ions, from the Data of Huong and Couzi[33]

organic bases	ν_{O-H}	δ_{OHF}
$(Me_2N)_3PO^a$	2500	1900
$(Me_2N)_3PO^a$	2700	1800
Me_2NCOH^a	~2600	1950
Me_2NCOH^a		1850
Me_2CO	2600	1850
Me_2O	2600	1840
Et_2O	2700	1820
Me_2SO	~2700	1800
Me_2SH	~2650	1750
MeCN	~2900	~1700

[a] The double band may be due to protonation on either the N or the O atom.

Phase relationships, which usually do not reveal much about the nature of solutions, are very instructive in the present case. The large negative deviations from Raoult's law leading to an azeotrope in the boiling-point curve (Figure 6) confirm the ionic nature of the solute. On the contrary, the hypothesis of mostly undissociated HF predicted a lowering of the boiling point of HF solutions. In that connection the present results for the deuterated acid support other indications that the D_2O-DF system is less extensively ionized than its hydrogen counterpart.[29] Not only is pure DF more volatile than HF (bp 18.66 vs. 19.92 °C), the saturated solution (and also, presumably, the azeotrope) is much less concentrated.[30] This large isotope effect is a clear indication that the D···F bond is weaker than the H···F bond. It is unfortunate that so little information is available on this very interesting system. As for the phase diagram of the H_2O-HF system, it is characteristic that there is no solid phase containing more water than the monohydrate (Figure 7). The contrary is true for the three heavier hydrogen halide systems. The melting point of the monohydrate, -35.2 °C, is rather low because each F^- ion must accept three H bonds. Indeed, there are no ion pairs or complexes in that crystal as confirmed by its infrared spectrum, in particular the ν_2 and ν_4 bands of H_3O^+ at 1000 and 1700 cm^{-1}, as for the three other hydrogen halides.[31] It is noteworthy that in the low-temperature spectra (Figure 4) the sample, of nearly 1:1 composition, was considerably supercooled (down to -70 °C in one experiment).

Oxonium Ion Complexes. By analogy with $H_3O^+{\cdot}F^-$ one may expect similar proton-transfer complexes in solutions of anhydrous HF in certain classes of organic bases. A number of these have been studied previously in infrared, leading to conflicting interpretations. First, Adams and Katz[32] observed the characteristic OH bending band at ca. 1800 cm^{-1} in ethanol on the first addition of HF, and in diethyl ether, acetone, etc., at concentrations of 40%

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(23) H. R. Leech in "Mellor's Treatise on Inorganic Chemistry", Supplement 2, Part I, Longmans, London, 1956, Chapter I, Section 3.

(24) J. C. McCoubrey, *Trans. Faraday Soc.*, **51**, 743 (1955).

(25) R. T. Myers, *J. Chem. Educ.*, **53**, 17 (1976).

(26) R. K. Thomas, *Proc. R. Soc. London, Ser. A.*, 344, 579 (1975).

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(28) T. R. Dike, B. J. Howard, and W. A. Klemperer, *J. Chem. Phys.*, **56**, 2442 (1972).

(29) M. F. A. Dove and A. F. Clifford, "Chemistry in Nonaqueous Solvents", Vol. II, Part I, G. Jander, H. Spandau, and C. C. Addison, Eds., Pergamon Press, Oxford, 1971, p 207.

(30) The concentration of 38% shown in Figure 5 for the deuterated acid is only approximate owing to the great difficulty experienced in preventing evaporation of the sample on the AgCl or CaF_2 windows.

(31) C. C. Ferriso and D. F. Hornig, *J. Chem. Phys.*, **23**, 1464 (1955).

(32) R. M. Adams and J. J. Katz, *J. Mol. Spectrosc.*, **1**, 306 (1957).

J. Am. Chem. Soc. **1980**, *102*, 5477–5481

or thereabouts. Because of this concentration effect, presumably related to the dielectric constant of the medium, they assigned that band to an ionic species, not to oxonium ion, however, but erroneously to the hypothetical counterion HF_2^-. On the contrary Huong and Couzi,[33] who extended their measurements to many other solvents, concluded against proton transfer mainly on the basis of electrical conductivity[34] and Raman spectra.[35] Instead, they assigned the bands at about 1850 cm^{-1} to the overtone of the $O\cdots H-F$ bending in molecular complexes. But this also is untenable on the grounds both of intensity (overtones very much stronger than fundamentals) and frequency (large positive anharmonicities). Another objection they invoked had to do with the almost constant frequency of the 1850-cm^{-1} band in widely different organic bases. These objections can be dismissed in terms of proton-transfer complexes, $ROH^+ \cdot F^-$. The near invariance of the 1850-cm^{-1} frequency (Table I) is a consequence of the strong electrostatic character of the H bond in these complexes. There may also be some partial compensation of the mass effect of the substituent and the strength of the organic base. In fact, the weaker bases, such as acetonitrile and the mercaptans, may be only slightly protonated by HF, hence the lower bending frequency. Besides the OH (or XH) bending there is also the stretching frequency which, generally speaking, varies in the opposite direction.

The elaborate study of Huong and Couzi has yielded some other interesting observations. For instance, in a dilute solution of anhydrous HF (0.015 mol/L) and diethyl ether (0.01 mol/L) in carbon tetrachloride the following characteristic infrared bands appear side by side: (a) 3870 cm^{-1}, of monomeric HF (vs. 3961.64 cm^{-1} in the gas), (b) 3550 cm^{-1} of the dimer $(HF)_2$, (c) 3220 cm^{-1} of the molecular complex $H_2O \cdot HF$, and (d) 2700 and 1820 cm^{-1} of $Et_2OH^+ \cdot F^-$. Significantly, the latter pair of bands is missing in a 1:1 mixture of HF and ether in the same solvent. This confirms that the formation of proton-transfer complexes requires stabilization by solvation. Further evidence to that effect is the recent detection in a solid-argon matrix at 10 K of the $H_3O^+ \cdot NO_3^-$ complex stabilized by a slight excess (~6%) of water of hydration.[36]

In conclusion, although the above results provide compelling evidence for the new theory, many points remain to be elucidated. Further experimental data are clearly desirable on both the H_2O–HF and D_2O–DF systems. In that connection NMR spectroscopy would be particularly useful. Also desirable are quantum-chemical calculations on the stabilizing effect of solvation similar to those of Newton on the hydrates of H_3O^+[37] and of Morokuma on the $NH_4^+ \cdot F^-$ complex.[38]

Acknowledgments. The experimental work could be carried out thanks to a grant from the National Research Council of Canada.

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Luminescence Quenching in the Cluster Network of Perfluorosulfonate Membrane[1]

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Abstract: The effects of the morphology of a perfluorosulfonate membrane (Nafion 120) on the kinetics of quenching of excited states were studied. The charge transfer excited state of $Ru(bpy)_3^{2+}$ was used as a probe and its luminescence quenching by various metal cations and by methylviologen measured. Linear Stern–Volmer behavior was observed when the quenching rate constant was small. When the quenching rate constant approaches the diffusion-controlled limit, deviations from such behavior are observed. Under these conditions, the situation is very similar to nonhomogeneous quenching in micellar systems. A kinetic analysis of the decay curves similar to the one used for the latter systems was then adapted. This analysis can yield detailed information on the microstructure and interactions prevailing in the membrane. The possible implications of such membranes for energy conversion and storage systems are outlined.

Introduction

The photophysical and photochemical processes occurring in a system consisting of a molecule in an excited state and a quencher will often depend not only on the quenchee–quencher pair but also on their immediate environment. Thus, intensive studies have been directed at elucidating the effects of the hydrocarbon–water interface in micellar solutions on such processes.[2-5] In these micellar systems, both the hydrophobic interactions and the interfacial electrostatic interactions are utilized to enhance electron transfer and charge separation in model systems for solar energy conversion and storage. Effects similar to those observed in micellar solutions have been recently observed in ion-exchange resins[6] or polyelectrolytes.[7] In these studies, the thoroughly investigated metal-to-ligand charge transfer state of $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) was quenched by metal ions, such as Cu^{2+} or Fe^{3+}, in the presence of Sephadex-SP cation

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