ON THE ACIDITY OF HYDROGEN FLUORIDE

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SUMMARY

An explanation is proposed for the rapid increase in acidity in progressing from dilute solutions of HF in H_2O to solutions of greater concentration (ca. 10M). Anhydrous HF has been shown to be more acidic than generally believed and to require very small adventitious concentrations of F^- to become quite basic. Oxidation of I_2 is used to demonstrate the dependence of the nature of species in HF solution on the acidity or basicity of the medium.

INTRODUCTION

It is customary to comment in reviews and textbooks on the apparent paradox of hydrogen fluoride being very weakly acidic as a solute in dilute solution in water, with an acidity constant of about 6.5×10^{-4} at 25°C, whereas it is one of the most acidic solvents known — more acidic than has generally been believed according to recent work from Gillespie's group [1].

There are very few reports of systematic study of HF-H_2O mixtures other than for dilute solutions of one component in the other. Some measurements of the Hammett acidity function H_0 have been made over much of the composition range [2-5]; but there is not close agreement between the different studies, although they show the same general features. There is a rapid increase in the value of $-H_0$ over the first few mole % of HF in H_2O until a value of about 0 is reached, then a steady increase in $-H_0$ with increase in HF concentration until values of about 8 or 9 are reached at 95-98% and then another rapid increase as 100% HF is approached. Varying degrees of inflexion are reported in the $-H_0$ vs. concentration plot in the region of 50-80 mole % HF. For acidic HF, a value of H_0 of -15.3 was reported for 3M SbF_5 [6], a value now known to be far too low. [1]

MODERATELY CONCENTRATED SOLUTIONS OF HF IN H_2O

One current research interest at Melbourne centres on studies of reasonably concentrated solutions (up to 10 M) of HF in H_2O [7]. It has been established that, with increase in HF concentration, conductance increases, as does the H^+ activity as measured with the H_2 electrode. The activity of free F^- ion, reliably measured with the $[Pb(Hg):PbC\ell F:C\ell^-_{aq},F^-_{aq}]$ electrode [8], decreases markedly. It has long been stated that in aqueous solution HF_2^- is formed at the expense of F^- according to the equation:

$$F^- + HF \; \rightleftarrows \; HF_2^-$$
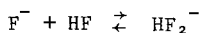
for which an equilibrium constant of about 4 (at 25°C) has been reported.

In the Melbourne work it is postulated that, in turn, $H_2F_3^-$, $H_3F_4^-$ and $H_4F_5^-$ are formed with increase in HF molarity. The change in conductance and marked decrease in concentration of free F^- are adequately described by a mathematical model based on each of the equilibrium constants for the formation of $H_2F_3^-$ to $H_4F_5^-$ being about one-quarter of that for the linear ion HF_2^-. HF_2^-, $H_2F_3^-$ and $H_4F_5^-$ have been characterized crystallographically and there is infra red spectroscopic evidence for $H_3F_4^-$. [9]

The F^- ion could be regarded as being coordinatively saturated with four HF molecules. Therefore, it seems likely that as the HF concentration is increased HF-solvated monomeric anions will be replaced by polymeric anions, possibly having chain and cyclic structures as are known to occur in the solid and gas phases. At any composition up to 100 mole % HF, all protons will be associated directly with water molecules. In relatively dilute HF solution the proton is likely to be aquated by several molecules i.e. be present as $H^+(OH_2)_n$, as in aqueous solutions of strong mineral acids.

DILUTE SOLUTIONS OF H_2O IN HF

In extremely dilute solutions of H_2O in the strongly acidic solvent HF, the Bronsted base H_2O will be protonated to the entity H_3O^+, itself solvated by HF molecules. The resulting solution will be basic relative to neutral HF because of enhancement of the concentration of the Lewis base F^- through displacement, as a result of the protonation, of the position of equilibrium for self-ionization of HF.

However many such solutions are not as basic as might be expected. The Hammett function for 0.5 mole % of H_2O in HF is -10.11 [1] whereas that of a KF solution of equal strength is -9.5 [1]. If each H_2O molecule was protonated, the concentration of the base F^- would be expected to be identical with that from KF. With dilution of both solutes, H_2O and KF, the basicities of the two solutions approach each other, e.g. at 0.1 and 0.02 mole %, the H_0 values are -10.57 and -10.87 for H_2O and -10.30 and -10.79 for KF. [1]

Also, accurately measured values of conductances in HF of H_2O and KF at $0°C$ [10] are very similar up to concentrations of about 0.05 molal. Then they diverge steadily until, at 0.5 molal, the conductance of the solution of H_2O is almost exactly two-thirds of that of KF.

Both conductance and acidity measurements suggest that for water in very dilute solution (0.02–0.05 molal) the solvated ionic entities are H_3O^+ and F^-. Solvated H_3O^+ would be expected to have an ionic mobility similar to solvated K^+. Marked reduction in basicity (i.e. in concentration of free F^- ion) and conductance relative to equimolar solutions of KF occurs as the water concentration is increased.

Two possible explanations of these observations depend on the strong hydrogen bonding expected in the H_2O-HF systems. Either there could be concentration-dependent equilibrium amounts of species like $H_5O_2^+$, leading to a reduction in the number of F^- ions (and cations) or there could be very strong hydrogen bonding between the three hydrogen atoms of the pyramidal entity H_3O^+ and a fluoride ion. The latter effect would affect the acid-base interactions of fluoride ions, protons and indicators in Hammett function determinations. It would lower the mobility of ions in conductance measurements, particularly that of F^- which is abnormally high in

ACIDITY OF PURE HF

It is now apparent that all determinations prior to 1976 of values of H_0 for HF were too 'low', i.e. not sufficiently negative; and the reasons for the incorrect values are clear. Spectrophotometric measurements were made on the driest possible HF using indicators with supposedly known basicity constants. In two separate studies H_0 values of -10.2 [4] and -9.7 [5] were reported for HF of best possible purity. It was assumed [4] that the only impurity likely to reduce the acidity of pure HF would be water. There is now good experimental evidence that HF, even if totally water-free, would be basic under the conditions in which it is usually purified, stored and studied - namely in equipment made from Kel F or similar polymers.

In recording spectra of transition metal cations in anhydrous HF, Barraclough, Cockman and O'Donnell [11] frequently encountered an impurity band at 280 nm. Subsequently slow reduction of Np(VI) to Np(V) in strongly acidic HF was ascribed to this impurity [12]. It has been shown in many experiments that the 280 nm band increases in intensity with increase in HF acidity. It is much more intense in SbF_5–HF solutions than in BF_3–HF. Its intensity increases with prolonged standing in Kel F equipment, particularly if the Kel F is new. The 280 nm band can be quenched by treating solutions with small amounts of F_2 [13]. The likely explanation is that low molecular weight, partially unsaturated halocarbon is leached from the Kel F and protonated. Therefore HF stored in Kel F is always likely to be basic because of the fluoride resulting from protonation.

In determining H_0 for HF Gillespie circumvented this and the trace moisture problem by using the same experimental approach he had adopted with H_2SO_4 and HSO_3F. He and Liang [1] used a range of indicators for the spectrophotometric determination of H_0 for HF made basic with known concentrations of KF and made acidic with known additions of SbF_5. As for H_2SO_4 and HSO_3F, the point of inflexion in the plot of H_0 values vs. concentration of added base or acid was taken as H_0 for pure HF, giving a value of −15.05 [1]. This value may be compared directly, because of the methodology used, with H_0 values of −11.93 for H_2SO_4 [14], −15.07 for HSO_3F [15] and −14.00 for CF_3SO_3H [16]. HF and HSO_3F with almost identical H_0 values are the most acidic single liquids for which acidity measurements have been made.

However, in the context of the wide use of anhydrous HF in organic and inorganic synthesis, there is a far more significant implication underlying the Gillespie and Liang observations. Their plot of H_0 from strongly basic to strongly acidic HF is virtually vertical over about 8 units of H_0 at 100% HF, values of H_0 being −10.58 for 0.05 mole % KF and −19.53 for the same concentration of SbF_5. This range is in good agreement with work from Trémillon's group where the chloranil electrode was used to measure values in HF of R(H), where the R(H) scale is an acidity scale referred to R(H) = 0 for aqueous solutions with pH = 0 [17]. They report R(H) values of 14.2 for 1 M NaF and 27.9 for 1 M SbF_5.

Both investigations indicate a change of acidity(or basicity) of some 12 or 13 powers of 10 between 1 M base and 1 M acid. Trémillon's group report an autoprotolysis constant for HF at 0°C of $10^{-13.7}$ [17]. On the basis of conductance measurements, which are likely to be subject to effects of impurities as shown above, pK_{ap} has usually been taken to be in

the region of 11 or 12. The near-vertical sections of the H_0 plots for basic and acidic H_2SO_4 and HSO_3F are very much shorter than for HF. This reflects buffering resulting from much greater self-ionization for those two acids. The implications of these differences in synthetic chemistry will be demonstrated below.

LEWIS ACIDITY IN HF

While SbF_5 has been recognized for a long time as the strongest Lewis acid in the HF system, Gillespie and Liang have shown SbF_5-HF solutions to be more acidic than previously believed [1]. The most concentrated solution (0.6 mole %) studied by them, because of limits on basicities of available indicators, has $H_0 = -21.13$. This solution is much more acidic than HSO_3F-SbF_5-SO_3 mixtures, often dubbed 'magic acids'. There is good experimental evidence, e.g. in the stabilization of HF solutions of Ti(II) discussed below, that more concentrated SbF_5-HF solutions are considerably more acidic.

Gillespie and Liang established an order of Lewis acid strengths $SbF_5>AsF_5>TaF_5>NbF_5$. The appropriate H_0 values, all at 0.5 mole % of solute for purposes of comparison, are -20.87, -19.49, -18.92 and -17.25, this last value being obtained by extrapolation from 0.4 mole %. R(H) values show the same order of acid strengths and similar magnitudes of differences in respective values [17]. In synthetic work BF_3 is widely used as a non-oxidizing, weak Lewis acid. Unfortunately Gillespie and Liang studied pentafluorides only. Devynck *et al* show BF_3 to be marginally stronger than NbF_5. Both studies show PF_5 to have little or no significant Lewis acidity in HF. The order of Lewis acidity $TaF_5>BF_3>NbF_5>PF_5$ was also reported by Gut and Gautschi using hydrogen electrode potentiometry [18].

EXPLOITATION OF THE ACIDITY OF HF IN SYNTHESIS

Inorganic chemists seem to have been less enterprising than their organic colleagues in exploiting the acidity of HF in synthetic and other experimental work. Members of the Melbourne group used enhanced acidity of HF to dissolve binary fluorides and recorded UV-visible spectra of cations in HF [11,12] and they have recovered crystalline solids from acidic HF solutions for structural investigation [13]. They have dissolved d- and f-transition metals in acidic HF to produce stable HF solutions of cations in unusually low oxidation states, e.g. U^{3+}[12], Cr^{2+}, V^{2+} and Ti^{2+}. [19]
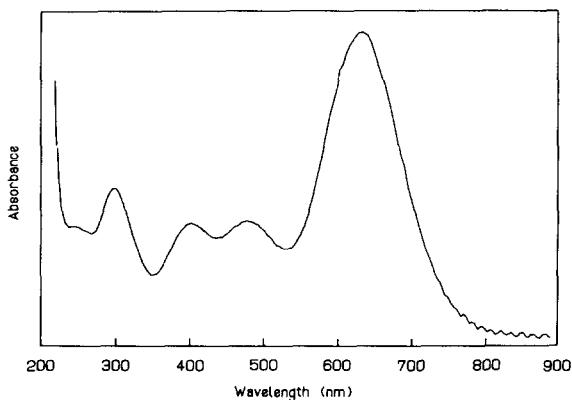
Figure. Spectrum of I_2^+ in HF-GeF$_4$

TABLE 1

Spectra of polyiodine cations in superacidic media (peak positions, nm)

In Fluorsulphuric Acid [20]	In Hydrogen Fluoride [13]
I_2^+: 640 490 410	For $I_2+F_2+GeF_4$: 630 479 400 297
I_3^+: 470 305	For I_2+F_2: 468 318 280
I_5^+: 450 345 270 240	

TABLE 2

Acidity[*] of media for oxidative generation of iodine cations

	H_2SO_4	HSO_3F	HF
I_3^+	H_2SO_4 + 0.05M HSO_4^- $H_0 \simeq -11.9$	$-$[**]	HF + 0.05M F^- $H_0 \simeq -10.3$ (Some ev. for I_5^+)
I_2^+	H_2SO_4 + 65% SO_3 $H_0 \simeq -14.8$	HSO_3F + 0.05 M SO_3F^- $H_0 \simeq -13.8$[†]	HF + GeF_4 $H_0 \simeq -15$

[*]Approximate H_0 values are taken from Refs. 1,14,15 and selected on the assumption that the concentration of base, i.e. HSO_4^-, SO_3F^- or F^-, from the appropriate redox reaction is approximately 0.05M.

[**]Generation of I_2^+, I_3^+ in HSO_3F depends on control of $I_2:S_2O_6F_2$ stoichiometry rather than on acidity of the medium. [20]

[†]I_2^+ slowly disproportionates under these conditions, but the disproportionation can be prevented by increasing the acidity of HSO_3F with SbF_5. [20]

Stability of Ti^{2+} solutions is particularly dependent on acidity of the
medium, being limited to HF solutions between 2 M and 3 M in SbF_5.

Comparison of the preparation of iodine cations by oxidation of the
element in HF and other superacidic media provides an elegant example of
the greater need for conscious control of acidity and basicity in HF than
in related solvents.

For many years solutions of different colours had been observed when
elemental iodine was added to anhydrous sulphuric acid and to oleum. The
deep blue solutions in 65% oleum were considered for some time to contain
I^+. Gillespie and co-workers used the powerful oxidant $S_2O_6F_2$, in specific
stoichiometric ratios relative to I_2 in the solvent HSO_3F, to oxidize I_2
to I_5^+, I_3^+ and I_2^+. On reduction, $S_2O_6F_2$ gives the highly mobile ion
SO_3F^-, the base of the solvent system. Initially Gillespie identified the
different iodine cations by using cryoscopic and conductance measurement
to monitor the total number of particles and the number of SO_3F^- anions
generated in solution in the redox reaction. His spectrum of I_2^+ in HSO_3F
was virtually identical with that of the blue oleum solutions. He and
Passmore have provided details of this and related work in a review. [20]

As an oxidant in HF, F_2 is the counterpart of $S_2O_6F_2$ in HSO_3F, being
reduced to F^-, the base of the system. In Melbourne work [13], controlled
oxidation by F_2 of I_2 suspended in "neutral" HF produced a solution, the
spectrum of which indicated the presence of I_3^+ with some I_5^+. As stated
above F^-, resulting either from reduction of F_2 or from protonation of
impurities in the HF, would reduce H_0 from −15 (for the pure liquid) to
about −10 to −11. GeF_4 is a Lewis acid of about zero strength in HF [13];
but it can accept F^- ions in HF and so prevent the solution from becoming
strongly basic. The spectrum in the Figure is that of a solution of HF
saturated with GeF_4 and in which I_2 had been oxidized by a controlled
amount of F_2. It indicates the formation of I_2^+ in nearly neutral HF as
the data in Table 1 show.

The reported conditions for the formation of some iodine cations are
summarized in Table 2. Even for superacidic media, it appears that at H_0
values less negative than −14 or −15, I_2^+ will accept a base to initiate
disproportionation reactions to form I_3^+ or I_5^+ and covalent species such
as $I(HSO_4)_n$, $I(SO_3F)_n$, or IF_n. A pivotal point seems to be provided by
the fact that I_2^+ shows some tendency to disproportionate in HSO_3F unless
the medium is made more acidic with SbF_5. However it must be recognized
that a particular species might be stabilized within certain acidity limits
by offsetting increased oxidant concentration against increased basicity

of the medium. These observations suggest that if I_2 or other non-metals were to be oxidized by F_2 in highly acidic HF, species of higher formal oxidation state than those already reported might be prepared.

ACKNOWLEDGEMENTS

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