

Hypofluorous acid and acetonitrile: the taming of a reagent*

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Abstract

The strong oxidant produced by the reaction of elemental fluorine with acetonitrile containing ca. 10% water has been shown to be hypofluorous acid, HOF, which is stabilized by complexing to the solvent. The reaction represents a new and convenient method of preparing and handling HOF, a unique oxygenating reagent. The presence of acetonitrile results in subtle but significant changes in the chemical behavior of the HOF. Vibrational and NMR spectroscopic studies of the solutions resulting from this reaction, as well as of solutions prepared by dissolving neat HOF in dry acetonitrile, have shown that the complex is a 1:1 hydrogen-bridged entity, in which the HOF proton is most likely bonded to the nitrogen atom of the nitrile. The ^{19}F NMR data indicate that the complexation reaction has an equilibrium constant of ca. 3 at room temperature, and that the enthalpy of formation of the complex is $-14.3 \pm 0.5 \text{ kJ mol}^{-1}$. The success of this method of synthesizing hypofluorous acid is a consequence of the very slow reaction between HOF and low concentrations of water in acetonitrile. This reaction accelerates drastically as the water content increases. As the solution composition approaches 100% water, the rate constant appears to approach a limit of about 0.7 s^{-1} at 25°C , which may be the actual rate of reaction of HOF with the water.

Introduction

Although dubious claims for the synthesis of hypofluorous acid, HOF, were made in the 1930s [2], the first generally credited observation of the

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compound came in 1967, when it was prepared by photolysis of a mixture of F_2 and water condensed in a matrix of solid nitrogen or argon [3]. Macroscopic quantities of HOF were subsequently synthesized by reaction of F_2 with water in a flow system [4]. Hypofluorous acid has been shown to act as a remarkably potent oxygenating and hydroxylating agent toward both inorganic [5] and organic substrates [6]. It has been demonstrated that in many cases the reaction involves actual transfer of an oxygen atom, making HOF a potentially useful reagent for introducing isotopically labeled oxygen into suitable compounds [7]. In fact, the use of HOF has provided the only practical method for making unsymmetrically labeled hydrogen peroxide, $H^{16}O^{18}OH$, and molecular oxygen, $^{16}O^{18}O$ [7]. Recent studies have shown hypofluorous acid to be an important intermediate in the reaction of fluorine with water to give H_2O_2 and O_2 [8] and to play a key role in the concomitant formation of oxygen difluoride [9].

Despite its interesting and unusual properties, studies of the chemistry of hypofluorous acid have been inhibited by the complex apparatus required for its synthesis, as well as by the fact that the compound, once made, is rather unstable, in fact sometimes explosively so [10]. The first inkling that this situation might change came in 1986, when Rozen and Brand observed that fluorine interacted with a 5–10% solution of water in acetonitrile to produce a powerfully oxidizing species that rapidly converted olefins to epoxides* [11]. Rozen and his coworkers have subsequently extended this work to a variety of olefinic systems, as well as to the hydroxylation of tertiary paraffinic C–H bonds and to the oxidation of aromatic amines [12]. This group also found that if the water introduced into the acetonitrile were enriched in ^{18}O or ^{17}O , the epoxides resulting from the oxidation would be labeled with the respective oxygen isotope [12].

Rozen noted that the passage of fluorine through neat acetonitrile produced no oxidizing species, while passage of fluorine through water yielded only H_2O_2 and O_2 . Both water and acetonitrile therefore appeared to be necessary to produce the powerfully oxidizing solution. Furthermore, the oxidizing species appeared to be much too vigorous to be explained away as a peroxy acid, and Rozen suggested that the oxidant could be hypofluorous acid that had interacted in some way with acetonitrile. At first glance, this might seem an improbable suggestion, since HOF is known to react rapidly with water to form H_2O_2 [10]. If it were true, however, it would constitute a novel and convenient means of synthesizing and handling this reagent. In the present paper, we have undertaken to identify and characterize the oxidant that is formed when fluorine reacts with wet acetonitrile and to relate it to the product that results from the interaction of neat HOF with neat CH_3CN .

*The epoxidation reaction was much too rapid to be attributed to the hydrogen peroxide known to be formed in the reaction of fluorine with water. We have observed that a solution of H_2O_2 and HF in acetonitrile does not react significantly with *trans*-stilbene over 2 h at 0 °C.

Experimental

Preparation of hypofluorous acid and its solutions

Neat HOF was prepared in 2–3 mmol quantities by the reaction of elemental fluorine with ice in a recirculating flow system [9]. Dilute solutions in CH₃CN were prepared by transferring the HOF in a nitrogen stream that was bubbled through acetonitrile just above its melting point. Solutions in CH₂Cl₂ or CD₂Cl₂ were prepared similarly, except that the solvent was cooled to –79 °C. A few solutions were prepared at –79 °C in CFCl₃ containing a quantity of CH₃CN approximately equal in moles to the amount of HOF transferred. **CAUTION: Neat liquid HOF can be unpredictably explosive, particularly at temperatures above –40 °C.**

Mixtures containing HOF and CH₃CN in mole ratios between 0.2 and 1 were prepared by cocondensing the two components in a ca. 3/8 in. i.d. Kel-F or Teflon U-tube, warming to about –40 °C, and allowing the components to mix. These mixtures could not be readily analyzed, and their compositions were estimated from the known amounts of CH₃CN introduced and the estimated quantity of HOF produced.

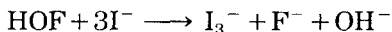
Preparation of solutions from reaction of F₂ with wet acetonitrile

Five cm³ of a 10 wt.% solution of water in acetonitrile were cooled to ca. –15 °C in a Teflon test tube, and fluorine (20 vol.% in argon) was introduced at a rate of ca. 100 cm³ min⁻¹. After 45–50 min, the solution had reached a limiting oxidant concentration of approximately 1.4 mequiv cm⁻³ and a total acidity of approximately 4 M. For most uses the greater part of the excess HF was removed (along with a portion of the remaining water) by agitation with 6–16 mesh silica gel. The stock solution was stored frozen at –79 °C; during use it was generally held in an acetonitrile slush bath at ca. –45 °C. A few experiments were carried out in which a 5 vol.% solution of water in propionitrile was fluorinated.

Analytical procedures

Neat hypofluorous acid was assayed by transfer in a nitrogen stream into an acidified iodide solution, followed by prompt titration of the evolved I₃⁻ with thiosulfate. Solutions of HOF in acetonitrile were assayed similarly after delivering aliquots into an acidic iodide solution. Hydrogen peroxide in solution was determined in like fashion, except that ammonium molybdate was added to catalyze the reaction with iodide. Freshly prepared oxidant solutions contained little or no hydrogen peroxide, but greater or lesser amounts of H₂O₂ developed in the water-containing solutions as the prompt oxidizing power decayed. Total acidity was determined by delivering samples into water, followed by titration with standard base to a phenolphthalein end-point. The HF impurity present in neat HOF preparations was determined by reaction with iodide, followed by potentiometric titration with acid. The

amount of HF present was calculated from the reduction in the acid titer relative to that which would be expected after the reaction:



Spectrometric measurements, codistillation and low-temperature matrix preparation

Mass spectra were measured at the Argonne National Laboratories with a Finnigan 400 quadrupole mass spectrometer and at Bochum with a Balzers quadrupole instrument. Separation of components prior to mass spectrometry was carried out by codistillation through a packed stainless-steel column, following procedures described elsewhere [13]. Gas chromatography/mass spectrometry was carried out with a Perkin-Elmer 900 chromatograph coupled to a Finnigan Ion Trap mass spectrometer. A 30-m wide-bore (0.53 mm i.d.) fused silica capillary column was used, with a 1.5 μm -thick bonded stationary phase of 1% vinyl: 5% phenyl: 94% dimethyl polysiloxane (Supelco). Helium flow was ca. 4 $\text{cm}^3 \text{min}^{-1}$.

Infrared spectra were measured at 2 cm^{-1} resolution with a Bruker IFS 85 Fourier-transform spectrometer. Liquid samples were held between barium fluoride discs at temperatures between ambient temperature and 0 °C. Raman spectra were measured with a Spex 1403 double-monochromator system operating in a photon-counting mode. Excitation was with the 5145-Å line of a Spectra-Physics 5 W argon-ion laser. Polarization measurements were made using Method No. IV of those described in ref. 14. Raman spectra of dilute solutions of HOF in CH_3CN were measured in a sapphire tube at ambient temperature, as were spectra of solutions of HF in CH_3CN . Raman spectra of liquid and solid mixtures of HOF/ CH_3CN in approximately 1:1 mole ratio were measured at low temperature. Samples were contained in glass tubes suspended in a re-entrant Dewar flask [15]. For liquids, the Dewar was cooled with Dry Ice, and the sample temperature was about -50 °C; for solids, the Dewar was cooled with liquid nitrogen or oxygen, and the sample temperature was about -150 °C. Survey Raman spectra were run at resolutions of 2 or 4 cm^{-1} , while a resolution of 1 cm^{-1} was used for precise assignment of the frequencies.

Matrices for infrared spectrometric measurements were prepared by passing an argon/helium mixture over a solid ca. 1:1 mol:mol mixture of HOF and CH_3CN at temperatures of -79 °C and -100 °C, and impinging the gas stream on a CsI plate cooled with liquid helium and mounted in a vacuum shroud that was fitted with CsI windows.

Proton and fluorine NMR spectra were measured with either a Bruker AM 300 or a Nicolet NTC-200 spectrometer. Proton spectra were referenced to an external $\text{Si}(\text{CH}_3)_4$ solution in a solvent closely similar to that used for the sample. Fluorine spectra were referenced to internal CFCl_3 . For quantitative studies at reduced temperatures, the probe temperature was regulated by a heater running against a stream of cooled nitrogen gas. Upfield shifts are indicated as negative.

Kinetic studies

The kinetics of reaction of HOF with acetonitrile–water mixtures were measured by two different methods. For reactions with half-times greater than about 1 min, the reaction was followed by removing samples from the reaction mixture at various time intervals, delivering them into an acidified KI solution and measuring the I_3^- absorbance at 350 nm. Absorbance readings were extrapolated back to the time of mixing with the iodide to correct for reaction of any hydrogen peroxide present. More rapid reactions were carried out using a manually driven stopped-flow mixing system (Hi-Tech Model SFA 11) attached to a Perkin-Elmer 330 UV–visible spectrophotometer. The formation of H_2O_2 at 230 nm was monitored. Mixing syringes of 0.1 and 2.5 cm^3 volume were used, the HOF/ CH_3CN solution being loaded into the smaller syringe, so that a maximum dilution of 25:1 with water could be obtained. The stock HOF solution for kinetic studies was treated with silica gel to remove excess HF. It was diluted with water and CH_3CN to such an extent that the uncertain amount of water remaining in the stock was small compared to the known amount of water added. The data were fitted by a three-parameter least-squares analysis to a first-order rate equation.

Reactions with organic substrates

The reaction of HOF solutions in acetonitrile with *trans*-stilbene was carried out as follows: to ca. 0.7 cm^3 1.4 M HOF in CH_3CN (made from neat HOF) was added 50 mm^3 of aqueous 45% HF, to simulate the solution that resulted from fluorination of wet CH_3CN . This solution was added at $-15\text{ }^\circ C$ to 5 cm^3 ethanol-free chloroform containing 200 mg (1.1 mmol) *trans*-stilbene. After 1.5 min, the reaction was quenched by the addition of 20 cm^3 aqueous 0.1 M $Na_2S_2O_3$. The phases were separated, and the aqueous phase extracted with 10 cm^3 chloroform. The combined chloroform phases were washed with $5 \times 4\text{ }cm^3$ water and dried with $MgSO_4$. The products were identified without separation by proton NMR spectrometry, based on comparison with authentic reference samples.

The reaction of HOF with cyclohexene was carried out by dissolving ca. 1 mmol cyclohexene in 1 cm^3 CH_2Cl_2 or CH_3CN and adding it to a stoichiometric amount of HOF in 2.5–10 cm^3 of solvent (CH_2Cl_2 , CH_3CN or CH_3CH_2CN) at ca. $-20\text{ }^\circ C$. Iodometric assay after 1–2 min indicated complete consumption of the oxidant. The reaction mixture was quenched by addition to aqueous $NaHCO_3$, followed by extraction with CH_2Cl_2 and drying with $MgSO_4$. In some cases, instead of quenching the entire reaction mixture, small aliquots were taken as a function of time, diluted six-fold with CH_2Cl_2 , shaken with solid $NaHCO_3$ and filtered. The products were determined by gas chromatography/mass spectrometry. The epoxide product gave a retention time and mass spectrum similar to those of an authentic sample of cyclohexene oxide. The fluorohydrin product was identified on the basis of its retention time and the molecular ion peak ($m/e = 118$) in its mass spectrum.

Chemicals

Fluorine was obtained from commercial sources either as the neat (97%) gas or as a 20 vol.% mixture in argon. Acetonitrile and methylene chloride were HPLC grade; other chemicals were commercial products of 98% or higher purity. Ordinary deionized water was used for the synthetic experiments, but for kinetic studies this water was redistilled before use first from alkaline permanganate and then from acid dichromate.

Results

General observations

Solutions made by reacting fluorine with wet acetonitrile showed at or near ambient temperature a characteristic ^{19}F NMR resonance at about -9 ppm, far downfield from the HF resonance at ca. -181 ppm. The vibrational spectra of these solutions exhibited a well-defined band in the O–F stretching region (880 cm^{-1} in the Raman spectrum, 884 cm^{-1} in the infrared spectrum). Both the low-field ^{19}F resonance and the O–F spectral band decayed with time as the oxidizing power of the solution decreased. Solutions made by dissolving authentic HOF in acetonitrile showed a similar low-field ^{19}F resonance (between -7 and -9 ppm) and a similar band in the vibrational spectrum (881 cm^{-1}). A solution made by fluorinating wet propionitrile showed a ^{19}F NMR resonance at -7.7 ppm. These values may be compared with the ^{19}F resonance of liquid HOF, which has been measured between $-80\text{ }^\circ\text{C}$ and $-100\text{ }^\circ\text{C}$ at $+21$ ppm [16], and with the O–F stretching band of HOF, which has been found to be 885 cm^{-1} in the solid [17] and 889 cm^{-1} in the vapor phase [18].

In addition to the organic reactions reported by Rozen and Brand [11], solutions made by passing fluorine through wet acetonitrile have been found to oxidize bromide to Br_2 and ClO_2^- to ClO_2 in weakly acidic solution and to oxidize VO^{2+} to VO_2^+ and Co^{2+} to Co^{3+} in 1 M perchloric acid. (In contrast, peroxyacetic acid will oxidize bromide and vanadyl under these conditions, but not chlorite nor Co^{II} .) Solutions made by dissolving authentic HOF in acetonitrile were able to bring about these same oxidations. In addition, these latter solutions efficiently converted *trans*-stilbene to the epoxide under the conditions used by Rozen and Brand [11] to effect epoxidation with the product of fluorination of wet acetonitrile.

The oxidant prepared by fluorinating wet acetonitrile appears to be significantly less volatile than the solvent. It was possible to concentrate the solutions at least two-fold in a rotary evaporator or by passing dry nitrogen through them.

A solution was prepared by passing HOF into cold CFCl_3 containing an amount of CH_3CN comparable to the amount of HOF added. After the bulk of the CFCl_3 had been pumped off, mass-spectrometric examination of the vapor coming off the residual solution showed the presence of HOF (identified by its characteristic molecular ion at $m/e = 36$ [4]), along with the characteristic fragmentation pattern of acetonitrile.

Mixtures of HOF and CH₃CN in mole ratios varying between 0.2 and 1 were subjected to separation by codistillation. Mass-spectrometric monitoring indicated that the two components could be recovered intact.

The vapor evolved from a solid ca. 1:1 mol:mol mixture of HOF and CH₃CN at temperatures of $-100\text{ }^{\circ}\text{C}$ and $-79\text{ }^{\circ}\text{C}$ was deposited in a solid argon matrix and examined by infrared spectrometry. The observed bands could be assigned almost entirely to HOF and its aggregates [19]. Only traces of bands attributable to acetonitrile could be observed.

NMR spectroscopic studies

The proton and ¹⁹F NMR spectra of HOF solutions were found to be strongly dependent on the nature of the solvent. At ambient temperature, a ca. 0.1 M solution of HOF in 1:5 v/v CD₂Cl₂/CCl₄ displayed a proton NMR resonance at 12.8 ppm (doublet, $J=83\text{ Hz}$), which shifted to 14.0 ppm on addition of 0.8 vol.% CD₃CN ($J=78\text{ Hz}$), to 14.5 ppm on addition of 2.5 vol.% CD₃CN (poorly resolved, $J=ca. 72\text{ Hz}$), and to 14.9 ppm on addition of 9 vol.% CD₃CN ($J=74\text{ Hz}$). In neat CD₃CN, the doublet was shifted to 15.5 ppm ($J=73\text{ Hz}$). A sharp proton resonance was not obtained from the product of fluorination of wet CH₃CN, probably because of exchange effects. (The proton resonance of neat HOF has been reported to occur at 16.2 ppm in the liquid at $-80\text{ }^{\circ}\text{C}$ and at 12.3 ppm in the vapor at ambient temperature [16].)

The effect of solvent on the ¹⁹F resonance is even more striking; the data are given in Table 1. In dilute solutions, this resonance also appears as a doublet ($J=72\text{ Hz}$ in CH₃CN, increasing to 80 Hz in CH₂Cl₂). Shifts were the same whether the mixed solution was generated by adding appropriate quantities of a non-polar solvent to a solution of HOF in CH₃CN or by adding appropriate quantities of CH₃CN to a solution of HOF in a non-polar solvent. If we take the chemical shift in a non-polar solvent to be associated with

TABLE 1

Effect of CH₃CN on the ¹⁹F chemical shift of HOF at 25 °C^a

[CH ₃ CN] (mol%)	Cosolvent	¹⁹ F chemical shift (ppm relative to CFCl ₃)
0	CCl ₄ /CD ₂ Cl ₂ ^b	27.5
0	CH ₂ Cl ₂ ^c	21
1.8	CCl ₄	7
4.2	CH ₂ Cl ₂	4.5
6.4	CCl ₄	2
18	CCl ₄	-2
100		-8.5

^a[HOF]=0.005–0.05 M, but always substantially less than the acetonitrile.

^b5:1 v/v.

^c23 vol.% CD₂Cl₂.

uncomplexed HOF and represent it as δ_{HOF} , while taking the chemical shift in pure acetonitrile to be associated with some sort of complex and representing it as δ_{complex} , we may represent any intermediate shift, $\delta(M)$ by the relation

$$\delta(M) = M(\delta_{\text{complex}}) + (1 - M)\delta_{\text{HOF}} \quad (1)$$

where M is the mole fraction of the stoichiometric HOF present as complex. This relation can then be used to estimate the extent of complexation associated with a particular chemical shift, and it allows us to construct a 'Job's plot'. Job [20] noted that for an equilibrium in which two species interact in some stoichiometric ratio to form a third, if solutions of the two reacting species at the same concentration are mixed in varying volume ratios, the concentration of the product species will reach a maximum when the volume ratio is equal to the stoichiometric ratio. The data for the Job's plot are given in Table 2, and the plot itself is shown in Fig. 1. The result clearly points to formation of a 1:1 complex and allows us to write a simple

TABLE 2

'Job's plot' data for complexation between HOF and CH_3CN^a

Volume ratio of reactants	^{19}F shift (ppm)	[Complex] ^b (mol dm ⁻³)
4.1	15.0	0.042
2.0	8.9	0.071
1.0	-1.6	0.100
0.82	-0.60	0.086
0.50	-3.6	0.072
0.165	-5.0	0.032

^aIn methylene chloride at 195 K. Each of the two solutions mixed was approximately 0.26 M in the respective component.

^bCalculated from eqn. (1) with $\delta_{\text{HOF}} = 21$ and $\delta_{\text{complex}} = -8.5$.

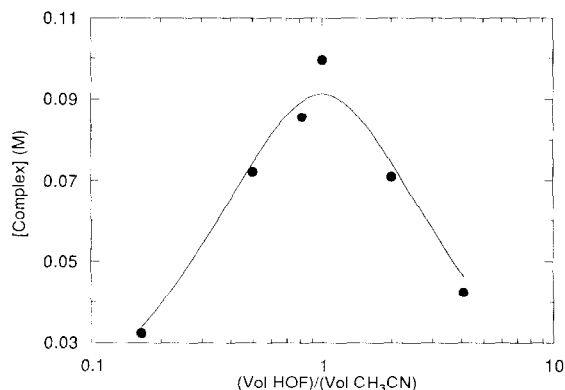


Fig. 1. Job's plot based on the data listed in Table 2. The solid curve is fitted via eqn. (2) with $K = 61 \text{ M}^{-1}$.

TABLE 3

Temperature dependence of complexation between HOF and CH₃CN in methylene chloride^a

T (K)	¹⁹ F shift (ppm)	K_{obs} (mol dm ⁻³) ^b	K_{calc} (mol dm ⁻³) ^c
190	0.0	68	75
205	1.9	38	39
215	3.0	29	26
225	4.5	20	18.5
235	6.1	14.1	13.3
245	7.9	9.7	9.9
255	9.0	7.8	7.5
265	10.5	5.7	5.8
275	11.6	4.6	4.6
285	12.8	3.6	3.7
295	13.8	2.9	3.0

^a[CH₃CN]=0.153 M; [HOF]=0.17 M.^bEquilibrium constant for reaction 2, calculated from eqn. (1) with $\delta_{\text{HOF}}=21$ and $\delta_{\text{complex}}=-8.5$.^cFitted by least-squares analysis to the equation $\ln K_{\text{calc}} = -4.70 + 1714/T$.

complexation equilibrium



The ¹⁹F chemical shift of HOF is not particularly dependent on temperature in neat CH₂Cl₂ nor in neat CH₃CN, but it shows a substantial temperature dependence in solvent mixtures. The change is in the direction of increasing complexation with decreasing temperature, consistent with an exoergic complexation reaction. Making use of eqn. (1), we may calculate the equilibrium constant for reaction 2 as a function of temperature. The data, which are shown in Table 3, allow the enthalpy of complexation ΔH to be estimated as -14.3 ± 0.5 kJ mol⁻¹.

Because of uncertainties regarding the validity of our assumptions, and in particular the uncertainty regarding the limiting ¹⁹F chemical shift values δ_{HOF} and δ_{complex} , the analyses detailed in Tables 2 and 3 probably have only semi-quantitative validity.

Infrared and Raman spectra

Table 4 lists the fundamental infrared absorption frequencies of HOF in mixtures with acetonitrile and compares them with the frequencies reported for various other forms of HOF. The infrared and Raman spectral features of the acetonitrile are also perturbed in these mixtures. The C—C stretching and C—C≡N bending vibrations are shifted to higher frequency by about 1%. The C≡N stretching frequency does not actually shift, but instead decreases in intensity while a new band grows along side it at about 1% higher frequency. The changes in the two stretching frequencies are quite similar to those brought about by the presence of HF. In fact, as little as 1 M HF in acetonitrile has a significant effect on these bands. Since HF is

TABLE 4

Infrared bands of the various forms of HOF

	Frequency (cm^{-1})			Ref.
	O—H stretch	H—O—F bend	O—F stretch	
HOF (gas)	3578	1355	889	18
HOF (Ar matrix)	3572	1350	888	19
(HOF) ₂ (Ar matrix)	3553	1396	(888) ^a	19
(HOF) _n (Ar matrix)	3481	1396(?) ^b	(888) ^a	19
HOF·H ₂ O (Ar matrix)	3342	1430	(888) ^a	19
HOF·HF (N ₂ matrix)	3483	1393	884	3
HOF (solid)	3328	1397	885	17
HOF·CH ₃ CN	3230	1437 ^c	881	^d

^aNot distinguishable from the monomer band.^bThe authors of ref. 19 assigned a band at 1342 cm^{-1} to this vibration, but it seems more reasonable to assume that it is actually indistinguishable from the corresponding band of the dimer.^cMeasured in CD₃CN to avoid interferences from the bands of CH₃CN.^dThis work.

TABLE 5

Reaction of HOF with water in acetonitrile at 25 °C

H ₂ O (mol%)	k (s^{-1})
13.5	9.1×10^{-5}
24	7.7×10^{-4}
41	0.0046
42	0.0049
59	0.0172
73	0.065
74	0.055
88	0.25
94	0.52
97	0.64
99	0.67

always present as an impurity in bulk HOF preparations, the possibility that the effects observed are caused by the HF impurity rather than by the HOF cannot be excluded. However, HF does not appear to have an effect on the C—C≡N bending frequency. The infrared and Raman spectra of mixtures of HOF and DOF with acetonitrile also show a few new and unidentified bands. The infrared spectra of the HOF mixtures show a strong and broad band at about 2860 cm^{-1} , while the DOF mixtures show a similar band at about 2113 cm^{-1} . The Raman spectra of both HOF and DOF mixtures show a depolarized band of moderate intensity at about 64 cm^{-1} .

TABLE 6
Reaction of HOF with cyclohexene

Solvent mixture	Volume ratio	Source of HOF	[C ₆ H ₁₀]/[HOF]	Product
CH ₃ CN	—	a	1.1	Principally epoxide, no fluorohydrin.
CH ₃ CN/CH ₂ Cl ₂	5:1	a	1.1	Principally epoxide, no fluorohydrin.
C ₂ H ₅ CN/CH ₂ Cl ₂	5:1	b	1.1	Principally epoxide, no fluorohydrin.
CH ₃ CN/CH ₂ Cl ₂	1:6	c	1.6	Principally epoxide, no fluorohydrin. Stable with time.
CH ₂ Cl ₂	—	c	0.9	After 5 min mostly epoxide, some fluorohydrin. After 4 h no epoxide, mostly fluorohydrin, other unidentified products.
CH ₂ Cl ₂	—	c	1.2	Quenched with bicarbonate after 2 min; principally epoxide, some fluorohydrin. Stable with time.
CH ₂ Cl ₂ + excess NaF (s)	—	c	1.6	Principally epoxide, some fluorohydrin. Stable with time.

^aFrom the fluorination of wet acetonitrile.

^bFrom the fluorination of wet propionitrile.

^cFrom the dissolution of neat HOF in CH₂Cl₂.

Kinetic studies

The decay of the oxidant formed from fluorination of wet acetonitrile was measured as a function of water content. The resulting pseudo-first-order rate constants appear in Table 5. The slower reactions appeared to be sensitive to the purity of the acetonitrile used, with lower rate constants resulting from the use of purer material. Hence the rate constants for these slower reactions may actually be upper limits.

Reactions of HOF with cyclohexene

In Table 6 are summarized the results of experiments in which cyclohexene was oxidized in various solvent mixtures and under various reaction conditions by neat HOF and by the oxidizing solutions obtained from the fluorination of wet acetonitrile and propionitrile.

Quantitative product yields were not determined, but visual inspection of the GC peak heights suggests that the principal products were present in quantities comparable to the amounts of substrate consumed.

Discussion

The results reported indicate clearly that the oxidant formed by passing fluorine through wet acetonitrile is the same as that formed by dissolving authentic HOF in the dry solvent. It may immediately be concluded, therefore, that the oxidant is either HOF itself or a product of the reaction between

HOF and CH_3CN . We have observed that even dilute solutions of the oxidant in CH_3CN show the characteristic O–F stretching vibration of HOF, while relatively concentrated HOF/ CH_3CN or HOF/ CD_3CN mixtures show the corresponding O–H stretching and H–O–F bending vibrations in addition. The vapor over these more concentrated mixtures gives rise to mass spectral peaks that can be assigned to HOF and CH_3CN , while the mixtures themselves can actually be separated into their two original components by codistillation. From all this we may reasonably conclude that the oxidant is, in fact, some form of HOF, and that any interaction with the acetonitrile must be reversible in nature.

The decrease in volatility of HOF dissolved in CH_3CN (the neat compound is estimated to boil somewhat below room temperature [10]), along with the enhanced stability noted by Rozen *et al.* and quantified in our kinetic studies, suggests strongly that some interaction with the solvent is taking place. Analysis of the variation of the ^{19}F shift with solvent composition and temperature, though perhaps only semi-quantitative in nature, indicates a reversible interaction of HOF with CH_3CN to form a 1:1 complex, with an equilibrium constant of ca. 3 at 25 °C and an enthalpy change of -14.3 ± 0.5 kJ mol $^{-1}$.

The most obvious form for such a complex to take is that of a hydrogen-bridged species in which the HOF proton is bonded to the nitrogen atom of the nitrile. There exists a substantial literature concerning the effect of such hydrogen bonding on an acidic molecule [21]. The proton NMR resonance almost invariably shifts downfield, reflecting a reduced shielding around the proton. This is usually explained by the partial removal of the proton from the electron cloud of the atom to which it is normally bonded. In the vibrational spectrum of a hydrogen-bonded compound, the stretching vibration involving the acidic proton decreases in frequency and broadens, while the bending vibration increases in frequency.

The proton NMR resonance of HOF dissolved in methylene chloride, which has a value similar to that of gaseous HOF, shifts significantly downfield as acetonitrile is added, as would be expected for the formation of a hydrogen-bonded complex. The resonance in liquid HOF is still further downfield, which probably reflects hydrogen-bonded association in the liquid. The ^{19}F resonance, on the other hand, is about the same in a methylene chloride solution as it is in the neat liquid, and it shifts upfield as acetonitrile is added. (The ^{19}F resonance in CCl_4 , however, is significantly further downfield than it is in CH_2Cl_2 .) It is worth remarking that we have made here the first measurement of proton–fluorine coupling through an oxygen atom. The coupling appears to decrease from 80–82 Hz in an inert solvent to about 72 Hz in acetonitrile.

Hypofluorous acid complexed with acetonitrile has the lowest O–H stretching frequency and the highest F–O–H bending frequency reported for any form of HOF. This is true even though solid HOF is known to be hydrogen-bonded [22], while hydrogen bonding must almost certainly be predominant in the matrix-isolated dimer and polymer and in the matrix-

isolated complexes with HF and H₂O. The O–F stretching frequency of HOF is also at its lowest in the acetonitrile complex, but the effect is very small. This is predictable if we consider that the O–F bond is expected to be practically orthogonal to the hydrogen bond [22, 23].

The effect of hydrogen bonding on the molecular vibrations of the acceptor molecule is generally smaller and less clear cut than the effect on the donor. Nitrogen bases are known to show an increase in vibration frequency with hydrogen bonding [24]. While this is not inconsistent with our observations, we cannot reliably separate out the effect of the HOF from that of the unavoidable HF impurity. This is especially true in as much as HF is almost certainly a stronger acid than HOF and may therefore have a disproportionately greater effect on the acetonitrile vibration frequencies.

Several unidentified bands appear in the vibrational spectra of the HOF/CH₃CN and DOF/CH₃CN complexes. While some of these may result from impurities, it is tempting at least to assign the 64 cm⁻¹ Raman band to a vibration involving the N---H hydrogen bond. The absence of deuterium isotope effect has been observed for such vibrations in other systems [21].

Our kinetic studies show that the rate of reaction of HOF with water in acetonitrile decreases dramatically as the water concentration drops. At a water concentration of 15 mol%, the HOF has a half-life of about 3 h, which is significantly longer than its half-life at moderate concentrations in the gas phase [10]. It is this behavior that makes possible the synthesis of HOF by fluorination of wet acetonitrile. Otherwise the HOF would not persist long enough to be isolated! We are unable to account quantitatively for the kinetic data in Table 5. Variations in the activities of the water and acetonitrile must be taken into consideration, along with the complexation equilibrium itself. An unexpected observation is the leveling off of the rate around 0.7 s⁻¹ at 25 °C as the acetonitrile concentration approaches zero. We may reasonably conclude that this is actually the rate of the reaction of HOF with water. If this conclusion is correct, the reaction with water is considerably slower than we might have expected; we may compare it to a constant of ca. 3 × 10⁵ s⁻¹ at 25 °C for the reaction of molecular fluorine with water [8]. A detailed kinetic study of the reaction between HOF and water is presently under way.

Several differences in chemical behavior between neat HOF and HOF in acetonitrile warrant comment. Neat HOF has been reported to oxidize aqueous Ag^I [10], but when HOF in acetonitrile was added to an acidic AgNO₃ solution, no oxidation was observed. This discrepancy appears to result from interference by the acetonitrile. We have observed that the addition of modest amounts of acetonitrile brings about the rapid discharge of the color of aqueous Ag^{II} and also prevents the oxidation of aqueous Ag^I by cesium fluoroxysulfate, CsSO₄F, which normally accomplishes this oxidation almost instantly.

The reaction of neat HOF with most olefins has been reported to yield fluorohydrins [6], whereas Rozen *et al.* report the formation of epoxides [11, 12]. We must note, however, that prior work with neat HOF has always

been carried out in relatively non-polar solvents, such as CH_2Cl_2 , and never in the presence of acetonitrile. Our studies of the reactions of HOF with cyclohexene in various solvent mixtures (Table 6) show that an epoxide is formed initially in all cases, regardless of how the HOF may have been made and whether or not acetonitrile is present. In the absence of acetonitrile, however, this initially-formed epoxide is rapidly converted to the fluorohydrin. Carrying out the reaction in the presence of NaF stabilizes the epoxide product, as does very prompt quenching of the reaction mixture with aqueous bicarbonate. The presence of as little as 14 vol.% acetonitrile also stabilizes the epoxide. We may conclude from these observations that the fluorohydrin is a secondary product formed by the addition of HF in the reaction mixture to the initially-produced epoxide. This addition can be prevented by rapid quenching with bicarbonate, which neutralizes the HF, or by absorbing the HF on NaF. Acetonitrile also prevents the addition of HF and stabilizes the epoxide, presumably by tying up the HF as a hydrogen-bonded complex [25].

The few experiments that we have carried out with the fluorination of wet propionitrile yield a product that exhibits a ^{19}F NMR shift and chemical behavior very similar to what we observe in the acetonitrile system, and we may reasonably surmise that analogous complexation is taking place.

Conclusion

Our results would appear to indicate fairly conclusively that HOF interacts with acetonitrile to form a 1:1 hydrogen-bonded complex. Further elucidation of the structure of this complex in the solid phase by X-ray and/or neutron diffraction would seem very much worthwhile.

The easily prepared complex should have enormous practical significance for the application of HOF as an oxidizing reagent. Instead of a reagent that is difficult to prepare and dangerous to handle, we have in the acetonitrile solutions of HOF a 'tamed' reagent that can be readily synthesized and worked with in almost any laboratory, but that nonetheless is a uniquely powerful oxygenating agent. Rozen and his group have already begun the exploitation of this unusual material, and we would expect to see its use and investigation increase steadily in the future.

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