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Raman Spectra of $KClO_4$ and $KBrO_4$ in Anhydrous HF and the Acid Strengths of Perchloric and Perbromic Acids[1]

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Perchlorate and perbromate ions are partially protonated in anhydrous HF, and the Raman spectra of such solutions show peaks attributable both to the anions and to their undissociated conjugate acids. Quantitative analysis of the spectra as a function of concentration permits evaluation of the equilibrium constants for protonation. Perbromic acid is found to have 6 times the acid strength of perchloric acid. From comparison with data on other acids in aqueous solution and in CF_3CO_2H, the acid dissociation constant of $HBrO_4$ in aqueous solution is estimated to be $10^{8.5}$. If the relative acidities of $HBrO_4$ and $HClO_4$ in HF remain the same for the neat acids, $HBrO_4$ will have a Hammett acidity function, H_0, of about −13.8. Relative Raman scattering coefficients for the strongest bands of the two anions and their conjugate acids are also reported.

Introduction

The acid strengths of very strong protic acids such as H_2SO_4, $HClO_4$, and HSO_3F have usually been determined by studies of the highly concentrated or anhydrous acids. In the case of the recently prepared $HBrO_4$, however, the acid is not sufficiently stable at high concentration for such studies to be practical, and alternative methods must be sought.

Anhydrous HF is a very acidic solvent ($H_0 \approx -11$),[2] and it may be expected to protonate partially the anions of even rather strong protic acids:

$$2HF + A^- \rightleftharpoons HA + HF_2^- \qquad (1)$$

If equilibrium 1 lies sufficiently far to the right, Raman spectra of the solution should show vibrational bands of the undissociated acid HA. If the concentration of HA represents a significant fraction of the initial concentration of A^-, it should be possible to estimate the equilibrium constant of reaction 1 and thus obtain a measure of the acid strength of HA.

In the present paper, we report the application of this approach to a study of the Raman spectra of perchlorate and perbromate salts dissolved in anhydrous HF.

Experimental Section

Reagents. Anhydrous hydrogen fluoride (Matheson, 99.9%) was purified by the following method:[3] A Monel vessel containing the liquid HF was pressurized to 2000 torr with F_2 (Linde, 98%) and allowed to stand for 2 days at room temperature to oxidize organic matter and water. The fluorine was then pumped off at −195 °C, and the HF was twice distilled from trap to trap on a Monel vacuum line. Center fractions were collected. This treatment yielded a product that was free of fluorescing impurities and had a specific conductivity of approximately $10^{-4}\ \Omega^{-1}\ cm^{-1}$. This conductivity sets an upper limit of about 10^{-3} M to the concentration of H_2O in HF.

Potassium perbromate was prepared by the method of Appelman[4] and dried in air at 110 °C. Reagent grade potassium perchlorate was dried similarly. Antimony pentafluoride (Ozark-Mahoning, distilled) was redistilled under vacuum prior to use.

Spectral Cell. The spectral cell consisted of a drilled-out cylinder of synthetic sapphire of 3.94 in. length, $^3/_8$ in. o.d., and $^1/_4$ in. i.d. The axis of the cell was made to coincide with the optical axis of the boule from which it was cut by the manufacturer (Inasco, Inc., Quakertown, PA). This facilitated polarization measurements, since no polarization bias was introduced into the scattered light. The cell had a flat bottom at one end, and its open end was attached to a Teflon PFA valve that was equipped with $^3/_8$ in. tube fittings (Fluoroware, Inc., Chaska, MN). No significant corrosion or loss of transparency of the sapphire was observed after numerous fillings of the cell with hydrogen fluoride solutions and with other corrosive liquids, such as bromine trifluoride and bromine pentafluoride.

Table I. Vibrational Frequencies in the Raman Spectra of Perchlorate Ion and Perchloric Acid (cm^{-1})

ClO_4^-			$HClO_4$[a]		
in HF	in H_2O[c]	assignt	in HF	anhydrous acid[d]	probable assignt
935 p	935	ν_1	1045 p	1032	Cl-O str
458 dp	462	ν_2	415 dp	425	O-Cl-OH bend
N.O.[b]	1102	ν_3	1214	1182	Cl-O-H bend
620 dp	628	ν_4	N.O.[b]	1312	Cl-O str
			765 p	738	Cl-OH str
			578 dp	572	O-Cl-O bend

[a] Incomplete set of frequencies. [b] Not observed. [c] Reference 8. [d] Reference 10.

Solutions. Each solution was made up by adding a weighed amount of salt to the cell, evacuating and reweighing the cell and its contents, condensing in hydrogen fluoride on the metal vacuum line, stirring the mixture at room temperature, and again weighing the cell and its contents. Molar concentrations were calculated from the weights and densities of the components, with the volumes assumed to be additive. The following densities were used ($g\ cm^{-3}$): $KClO_4$, 2.5298;[5] $KBrO_4$, 3.08;[6] HF, 0.9546.[7]

The perchlorate solutions were stable at all concentrations, but perbromate solutions ≥1 M sometimes decomposed abruptly, turning brown and liberating gas. On three occasions, the increase in pressure blew the cell free of its valve. Because of this instability, concentrated solutions of $KBrO_4$ in HF should be handled with great care (e.g., behind a protective barrier).

Spectral Measurements. Raman spectra were obtained with a Spex Model 1403 spectrometer operated in the photon-counting mode and controlled by a SCAMP computer (Norland Corp.). The 514.5-nm line of a Spectra-Physics Model 165 argon ion laser was used for excitation. Extraneous plasma lines were eliminated with a Spex Lasermate grating monochromator. Laser power at the sample ranged from 50 to 500 mW, and the entrance and exit slits were set for a spectral bandwidth of 2.5 cm^{-1}.

The vertical laser beam entered the spectral cell through its flat bottom, and the scattered light was observed at an angle of 90° to the beam. Polarization measurements were made by rotating a polarization analyzer, mounted in the path of the scattered light, through an angle of 90°. A polarization scrambler was present in front of the entrance slit of the spectrometer. All spectra were obtained

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(1) Work performed under the auspices of the Office of Energy Research, Division of Chemical Sciences, U.S. Department of Energy, under Contract W-31-109-Eng-38.

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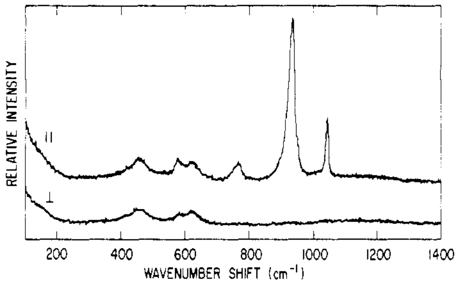

Figure 1. Raman spectra of a 1.12 M solution of $KClO_4$ in HF, recorded with parallel and perpendicular polarization.

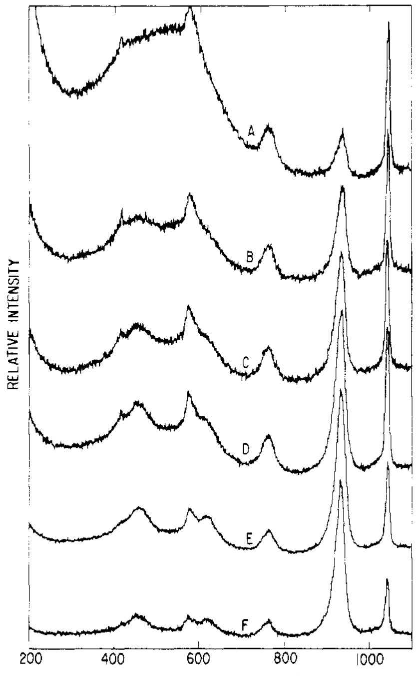

Figure 2. Raman spectra of $KClO_4$ solutions in HF, showing the effects of increasing concentration (M): (A) 0.080; (B) 0.248; (C) 0.367; (D) 0.509; (E) 0.872; (F) approximately 1.2 (saturated solution).

at room temperature (23 ± 2 °C).

Results

Raman Spectra. The spectra of $KClO_4$–HF solutions (Figures 1 and 2) indicate partial protonation of perchlorate ion by hydrogen fluoride:

$$ClO_4^- + 2HF \rightleftharpoons HClO_4 + HF_2^- \qquad (2)$$

We observe a very strong band produced by vibration ν_1 of the tetrahedral ClO_4^- ion at 935 cm^{-1}, and on either side of this band we see prominent bands of $HClO_4$ at 765 and 1045 cm^{-1}. Overlapping bands of both $HClO_4$ and ClO_4^- are also present in the low-frequency region. The assignments of these bands, corresponding to those of other investigators,[8-10] are shown in Table I. The region from 700 to 1100 cm^{-1} was most useful for observing changes in the concentrations of solute species, since the solvent has no prominent bands in this region. Below 700 cm^{-1}, a broad band of hydrogen fluoride partially obscures solute bands in the dilute solutions. As the solutions become progressively more dilute, bands of $HClO_4$ increase in intensity relative to those of ClO_4^-, reflecting the changes in the concentrations of these species produced by equilibrium 2.

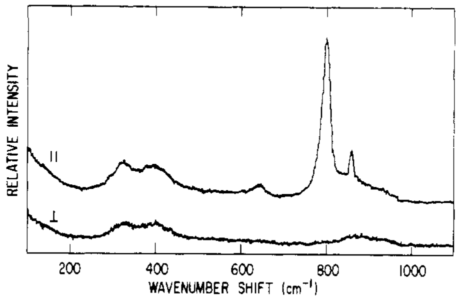

Figure 3. Raman spectra of a 0.928 M solution of $KBrO_4$ in HF, recorded with parallel and perpendicular polarization.

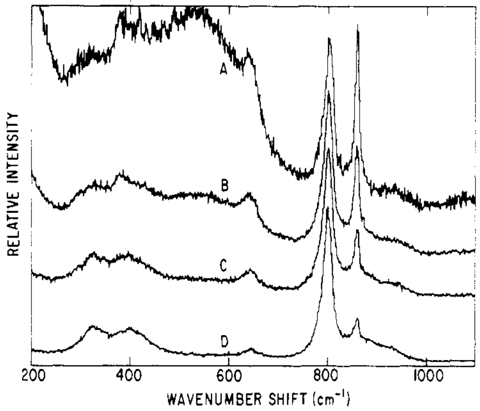

Figure 4. Raman spectra of $KBrO_4$ solutions in HF, showing the effects of increasing concentration (M): (A) 0.055; (B) 0.154; (C) 0.415; (D) 1.315.

Table II. Vibrational Frequencies in the Raman Spectra of Perbromate Ion and Perbromic Acid (cm^{-1})

BrO_4^-			$HBrO_4$[a]	
in HF	in H_2O[b]	assignt	in HF	probable assignt
802 p	798	ν_1	860 p	Br–O str
327 dp	331	ν_2	380 dp	O–Br–OH bend
880 dp	883	ν_3	642 p	Br–OH str
398 dp	410	ν_4	935 dp	Br–O str

[a] Incomplete set of frequencies. [b] Reference 11.

Similar features are apparent in the spectra of $KBrO_4$–HF solutions (Figures 3 and 4), indicating the production of undissociated perbromic acid:

$$BrO_4^- + 2HF \rightleftharpoons HBrO_4 + HF_2^- \qquad (3)$$

We observe a very strong band of BrO_4^- at 802 cm^{-1} (ν_1) and strong bands of $HBrO_4$ at 642 and 860 cm^{-1}. Our assignments of these bands and of others originating in $HBrO_4$ and BrO_4^- are shown in Table II. The vibration frequencies of perbromic acid are of particular interest, since no molecular spectra of this species have been reported heretofore; the acid dissociates completely in dilute aqueous solutions and is unstable in the anhydrous state.[11]

The acid fluorides ClO_3F and BrO_3F are known to form when strong Lewis acids are added to perchlorate and perbromate solutions in HF.[12,13] To ascertain possible interference from these species in our experiments, we added small quantities of SbF_5 to some of our solutions. In the perchlorate solutions this caused appearance of the very intense 1061-cm^{-1} ClO_3F band, while in the perbromate solutions the analogous 873-cm^{-1} band of BrO_3F appeared.[14] These bands are not

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Table III. Ratios of Areas of Designated Raman Bands in the $KClO_4$-HF System as a Function of Concentration

$[KClO_4]_0$, mol/L	$[HF]_0$, mol/L	$[HClO_4]$,[a] mol/L	$A_{ClO_4^-}^{935}/A_{HF}^{3350}$		$A_{HClO_4}^{1045}/A_{ClO_4^-}^{935}$	
			measd	calcd[a]	measd	calcd[a]
0.0796	47.51	0.059	0.00456	0.0043	1.234	1.22
0.167	47.28	0.103	0.01268	0.0133	0.712	0.697
0.248	47.06	0.136	0.0254	0.0233	0.517	0.524
0.367	46.76	0.176	0.0402	0.0401	0.393	0.399
0.509	46.38	0.216	0.0629	0.0623	0.308	0.319
0.624	46.08	0.244	0.0849	0.0814	0.265	0.278
0.748	45.76	0.271	0.105	0.103	0.225	0.246
0.872	45.44	0.295	0.127	0.126	0.202	0.221
0.986	45.14	0.316	0.148	0.147	0.182	0.204
1.116	44.80	0.337	0.168	0.173	0.172	0.187

[a] Calculated for $K_2 = 7.5 \times 10^{-5}$ M^{-1}.

Table IV. Ratios of Areas of Designated Raman Bands in the $KBrO_4$-HF System as a Function of Concentration

$[KBrO_4]_0$, mol/L	$[HF]_0$, mol/L	$[HBrO_4]$,[a] mol/L	$A_{BrO_4^-}^{802}/A_{HF}^{3350}$		$A_{HBrO_4}^{860}/A_{BrO_4^-}^{802}$	
			measd	calcd[a]	measd	calcd[a]
0.0545	47.56	0.027	0.00893	0.0085	0.506	0.505
0.0849	47.48	0.036	0.0152	0.0148	0.403	0.384
0.154	47.27	0.052	0.0319	0.0311	0.265	0.268
0.246	47.01	0.069	0.0543	0.0544	0.199	0.205
0.361	46.70	0.085	0.0857	0.0854	0.152	0.162
0.415	46.53	0.091	0.103	0.101	0.133	0.148
0.679	45.78	0.118	0.181	0.177	0.101	0.110
0.928	45.08	0.138	0.250	0.253	0.0874	0.092
1.315[b]	43.98	0.162	0.360	0.380	0.0646	0.074
1.713[b]	42.87	0.182	0.517	0.518	0.0459	0.063
2.111[b]	41.72	0.198	0.640	0.667	0.0381	0.055
2.583[b]	40.39	0.213	0.836	0.854	0.0293	0.047

[a] Calculated for $K_3 = 1.2 \times 10^{-5}$ M^{-1}. [b] Not used in least-squares fit.

visible in the spectra of Figures 1–4, and we therefore conclude that significant quantities of ClO_3F and BrO_3F are not formed in our solutions in the absence of SbF_5.

Equilibrium Constants. The equilibrium constants for reactions 2 and 3 were obtained from measured ratios of certain peak areas. The area, A_i^f, of a Raman peak at frequency f produced by species i is given by

$$A_i^f = C_i S_i^f I \tag{4}$$

where C_i is the concentration of the species, S_i^f is its Raman scattering coefficient at frequency f, and I is the intensity of the exciting light. When the area of a peak produced by species i is compared with that of a peak produced by species j under identical conditions, the exciting light intensity drops out of the ratio and only the areas, concentrations, and scattering coefficients remain:

$$\frac{A_i^f}{A_j^f} = \frac{C_i S_i^f}{C_j S_j^f} \tag{5}$$

We have used the strong peak of the HF solvent at 3350 cm^{-1} as an internal standard in our measurements. Table III shows measured ratios of $A_{ClO_4^-}^{935}/A_{HF}^{3350}$ and $A_{HClO_4}^{1045}/A_{ClO_4^-}^{935}$ as functions of the potassium perchlorate concentration. Table IV shows measured ratios of $A_{BrO_4^-}^{802}/A_{HF}^{3350}$ and $A_{HBrO_4}^{860}/A_{BrO_4^-}^{802}$ as functions of the potassium perbromate concentration.

The equilibrium constant for reaction 2 is given by

$$K_2 = \frac{[HClO_4][HF_2^-]}{[ClO_4^-][HF]^2} = \frac{X^2}{([KClO_4]_0 - X)([HF]_0 - 2X)^2} \tag{6}$$

where $[KClO_4]_0$ is the initial concentration of potassium perchlorate, $[HF]_0$ is the initial concentration of hydrogen fluoride, and X is the concentration of perchloric acid and HF_2^- at equilibrium. (Equation 6 will be valid so long as the quantity of HF_2^- formed in reaction 2 is large compared with that formed by reaction of basic impurities such as water.)

From eq 5 we may now derive

$$\frac{A_{ClO_4^-}^{935}}{A_{HF}^{3350}} = \frac{S_{ClO_4^-}^{935}}{S_{HF}^{3350}}\left(\frac{[KClO_4]_0 - X}{[HF]_0 - 2X}\right) \tag{7}$$

and

$$\frac{A_{HClO_4}^{1045}}{A_{ClO_4^-}^{935}} = \frac{S_{HClO_4}^{1045}}{S_{ClO_4^-}^{935}}\left(\frac{X}{[KClO_4]_0 - X}\right) \tag{8}$$

The right-hand sides of these equations are weak functions of K_2. To determine K_2, we took an estimated value, calculated X for each experiment in Table I, and fitted eq 7 and 8 by a linear least-squares analysis. We repeated the process with other estimated values of the constant. The best value of K_2 was taken to be that which yielded the smallest value for the sum of the squares of the residuals $Q = \sum_i (Y_i - Y_i^{calcd})^2$.[15] The best values obtained from eq 7 and 8 were averaged to give a final K_2 of (7.5 ± 1.5) × 10^{-5} M^{-1}. Area ratios calculated with this constant are given in Table III, as are the calculated concentrations of $HClO_4$.

The equilibrium constant for reaction 3 was determined by a strictly analogous procedure using the ratios $A_{BrO_4^-}^{802}/A_{HF}^{3350}$ and $A_{HBrO_4}^{860}/A_{BrO_4^-}^{802}$. The data at perbromate concentrations above 1 M were not used in the calculation, however, since it appeared that other effects were coming into play at these high concentrations. Our final value of K_3 was (1.2 ± 0.4)

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(15) This rather cumbersome procedure has been used because the weak dependence of eq 8 and 9 on K_2 leads to poor convergence if an attempt is made to fit K_2 directly by a nonlinear least-squares treatment.

$\times 10^{-5}$ M^{-1}. Area ratios calculated with this constant are given in Table IV, as are the calculated concentrations of $HBrO_4$.

The fact that eq 6 and its analogue for the perbromate system provide reasonable representations of our data implies that the concentration of water or other basic impurity is low compared to the concentration of undissociated acid; i.e., reactions 2 and 3 are the preponderant sources of HF_2^-. This, in turn, supports the upper limit that we have estimated for the water content in our HF (see Experimental Section).

In the foregoing treatment we have taken no account of variations in the activity coefficients of the species involved in reactions 2 and 3. Although we could not expect equilibria of this type to be inordinately sensitive to ionic strength, some variation of K_2 and K_3 with salt concentration must almost certainly take place. However, the activity data that would be needed for a more sophisticated analysis do not appear to be available, and we shall simply absorb the effects of varying activity coefficients into the overall uncertainty of our results.

Once K_2 has been determined, the fits of the data to eq 7 and 8 give the ratios of scattering coefficients $S_{ClO_4^-}{}^{935}/S_{HF}{}^{3350} = 9.8$ and $S_{HClO_4}{}^{1045}/S_{ClO_4^-}{}^{935} = 0.43$. From K_3 and the analogous equations for the perbromate system, we obtain $S_{BrO_4^-}{}^{802}/S_{HF}{}^{3350} = 14.4$ and $S_{HBrO_4}{}^{860}/S_{BrO_4^-}{}^{802} = 0.53$.

Discussion

The equilibrium constants for reactions 2 and 3 indicate the extent to which ClO_4^- and BrO_4^- are protonated in anhydrous HF and hence reflect the relative acidities of $HClO_4$ and $HBrO_4$. It appears that the acid strength of $HBrO_4$ is 6 times that of $HClO_4$. We know of no theoretical argument that could unambiguously predict this conclusion, even to within 1 order of magnitude. The closest analogy would be with the oxyacids of periodic group 6, where H_2SeO_4 is reported to be *weaker* than H_2SO_4 by about a factor of 10.[16] If we consider group 5, the much weaker H_3PO_4 and H_3AsO_4 have nearly the same acid dissociation constants in aqueous solution.[17,18]

It is perhaps of interest to note that cryoscopic measurements have shown the perchlorate ion to be even more extensively protonated in sulfuric acid than we have found it to be in hydrogen fluoride.[19] The Hammett acidity function, H_0, for H_2SO_4 is about -12,[20] which makes it a substantially more acidic solvent than HF.[2]

From a comparison of their acid strengths when they are dissolved in trifluoroacetic acid, Bessière has estimated the aqueous dissociation constants of a number of strong acids.[21,22] He gives pK_{H_2O} values of -3.7, -6.0, and -7.7 for hydrochloric, sulfuric, and perchloric acids, respectively, where

$$pK_{H_2O} = -\log \frac{[H^+][A^-]}{[HA]}$$

From our results, we may estimate pK_{H_2O} for perbromic acid to be about -8.5 on Bessière's scale.

Although the strength of an acid present as a dilute solute cannot be directly related to that of the neat acid, the close structural similarity between the perchlorate and perbromate ions[6] leads us to suggest that the *relative* acid strengths of neat $HClO_4$ and $HBrO_4$ will probably parallel the relative acid strengths of the dilute acids in anhydous HF. The Hammett H_0 function of 80% $HClO_4$ has been determined to be -10.7_5,[23] and a value of -13.0 has been suggested for the anhydrous acid.[24] We therefore suggest that H_0 for anhydrous $HBrO_4$ should be around -13.8. This makes perbromic acid a very respectable superacid.

Acknowledgment. We wish to thank Professor Henry Selig of the Hebrew University, Jerusalem, for carrying out some preliminary measurements that suggested this project.

Registry No. HF, 7664-39-3; $KBrO_4$, 22207-96-1; $KClO_4$, 7778-74-7; $HBrO_4$, 19445-25-1; $HClO_4$, 7601-90-3.

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