Thermodynamics of Formation of Aqueous Monofluoro-, Difluoro-, and Amidofluorophosphoric Acids

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Aqueous equilibrium constants for reactions involving fluoro-, hydroxy-, and amido-substituted phosphoric acids with HF have been determined at several temperatures. From these values, the formation thermodynamics have been calculated for monofluorophosphoric acid, difluorophosphoric acid, and amidofluorophosphoric acid. The stability of the OH-substituted compounds is distinctly greater than both the F- and the NH_2-substituted compounds.

The present determination of the thermochemical properties for aqueous fluorophosphates was undertaken to provide additional experimental values for the thermodynamics of formation of small phosphorus compounds. It is a part of a larger effort (*1–3*) directed toward increasing our understanding of substituent effects involving main group elements.

The first part of the work consists of determining the $\Delta G°$, $\Delta H°$, and $\Delta S°$ of reaction 1 by using the ^{31}P NMR to measure

$$H_2PO_3F(aq) + H_2O(l) \rightleftarrows HF(aq) + H_3PO_4(aq) \quad (1)$$

the equilibrium concentrations of monofluorophosphate and phosphate in relatively dilute aqueous solutions. These results are used along with literature values on the thermodynamics of formation of phosphoric acid, water, and hydrofluoric acid to calculate the thermochemical properties of the various aqueous monofluorophosphate species.

The water–hydrofluoric acid–phosphoric acid system has been studied previously by five groups (*4–9*). Although quantitative equilibrium data are given in all of these studies, only one (*9*) was conducted in the high water concentration region and could therefore be used to compute the free energy of formation for the aqueous fluorophosphate ion and aqueous monofluorophosphoric acid. The resulting free energy of hydrolysis of monofluorophosphoric acid obtained from this work disagrees with the values of the free energies obtained from the other researchers (*5–8*) when extrapolated from moderate water concentrations to dilute aqueous solutions. More importantly, for reaction 2 a positive free energy change

$$HPO_3F^-(aq) + H_2O(l) \rightleftarrows HF(aq) + H_2PO_4^-(aq) \quad (2)$$

is calculated using the thermochemical data from ref 9. This appears to be inconsistent with the chemical fact that monofluorophosphate is thermochemically unstable with respect to hydrolysis at all pH values (*3*).

In the second part of this study, the fluoride switching reactions among phosphoric acid, monofluorophosphoric acid, and difluorophosphoric acid have been studied in HF–H_2O–H_2SO_4 mixtures. This method yields approximate values for the thermodynamics of hydrolysis and formation of difluorophosphoric acid. No thermochemical data are available for this species or its anion.

In a kinetic study of the basic reactions of substituted fluorophosphoric acids, we have discovered that ammonia reacts reversibly with difluorophosphate to form the monoamidofluorophosphate ion. The equilibrium constant for this reaction has been determined at 25 °C. No previous thermochemical data are available on the formation of P–N bonds in simple inorganic compounds.

Experimental Section

The chemicals and instrumentation used in this work are the same as those used in two previous studies of the fluorophosphate system (*2, 3*).

The dilute aqueous solutions used in this work were prepared by weight, with concentrations expressed in molalities and the standard state for the solute taken as the hypothetical 1 *m* solution.

Phosphorus magnetic resonance spectra were obtained using a Varian XL-200 spectrometer. All spectra involving HF solutions were recorded for samples in 10-mm NMR tubes with Teflon sleeves and caps. Temperature during the acquisition of NMR data were controlled to within ±0.3 °C and calibrated with a mercury in glass thermometer. Because of the long time involved, equilibration of some of the experiments was done externally to the NMR in a temperature bath controlled to ±1 °C. The samples were then transferred to the NMR for a 5-min equilibration prior to data acquisition.

Prior experiments (*3*) indicated a detection limit of minor P species in our instrument to be about 0.0006 mole fraction. The equilibrium mole fractions of fluorophosphate in the determinations of K_1 reported here ranged from 0.05 to 0.005.

Procedure and Equilibrium Constant Calculations

Hydrolysis of Monofluorophosphoric Acid. The equilibrium constant for the hydrolysis of monofluorophosphoric acid was studied by allowing mixtures of phosphoric acid, monofluorophosphoric acid, and hydrofluoric acid to equilibrate. These solutions were approximately 0.3 mol kg^{-1} in phosphorus and from 2 to 8 mol kg^{-1} in HF. The solutions were allowed to equilibrate for at least 5 half-lives on the basis of the pH and the rate constants given in the literature (*10*), and equilibrium was approached from both reaction directions.

The thermochemical equilibrium expression for the hydrolysis reaction, eq 1, is given by eq 3, where the HF

$$K_1 = m_{HF}m_{H_3PO_4}/m_{H_2PO_3F}X_{H_2O} \quad (3)$$

concentration is calculated from the stoichiometric concentration by eq 4. K_D is the formation constant for the bifluoride ion (*11*), $K_{a,HF}$ is the acid dissociation constant of HF (*11*), and H is equal to $\gamma^2 m_H$ as defined in previous work (*2, 3*) and

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$$m_{HF} = m^\circ_{HF}\{1 + K_{a,HF}/[H(1 + K_D m_{HF})]\}^{-1} \quad (4)$$

is calculated from the PH coupling constant of a small amount of phosphorus acid added for this purpose. The ratio of phosphoric acid to monofluorophosphoric acid was determined from the integration of their respective NMR peaks with corrections for the fraction ionization, as in eq 5.

$$m_{H_3PO_4}/m_{H_2PO_3F} = (I_{POH}/I_{PF})(1 + K_{a,H_2PO_3F}/H)/(1 + K_{a,H_3PO_4}/H) \quad (5)$$

The equilibrium constants determined by this method are reported in Table 1. A major source of uncertainty was the determination of the fraction of monofluorophosphoric acid present when each of its doublet peaks accounted for only about 0.5% of the total phosphorus present.

In previous work (4–8), determinations have been done at high phosphoric acid and hydrofluoric acid concentrations and the equilibrium constant has been calculated using the molar concentrations of all species, including water, in the equilibrium expression. Even when corrected to the same standard states used here, the values determined at these concentrations are much smaller than the values of K_1 obtained here. Plakhotnic et al. (6) have extrapolated their equilibrium determinations from their lowest HF concentrations, $\sim$20 mol kg^{-1} HF, to pure water. This extrapolation contains large uncertainties, but the resulting $K \approx 6.7$ for reaction 1, with 1 M water as a standard state, can be converted to a thermodynamic value (based on liquid water as the standard state) of $K_1 \approx 370$ in fair agreement with the $K_1 = 645$ obtained in this work.

Dutt and Gupta (9) have reported $K_6 = 1.49 \times 10^6$ for reaction 6. Values of pK_{a1} = 0.54 and pK_{a2} = 4.80 (*12, 13*)

$$PO_3F^{-2}(aq) + 2\,H^+(aq) + H_2O(l) \rightleftarrows H_3PO_4(aq) + HF(aq) \quad (6)$$

for H_2PO_3F are used along with this value to give $K_1 = 7$, in poor agreement with the value reported here.

Fluoride-Transfer Reactions. The direct NMR determination of equilibrium constants for hydrolysis in water is restricted to values of K between about 10^{-4} and 10^4. To determine equilibrium constants for hydrolysis reactions of more or less energetic reactions than these or for compounds with more than one hydrolyzable F, a different technique or solvent is needed. The approach used here is to measure the equilibrium constant of the hydrogen fluoride switching reaction, eq 7, in solvents with reduced water activity. The

$$H_2PO_3F(S) + XPO_3H_2(S) \rightleftarrows H_3PO_4(S) + XFPO_2H(S) \quad (7)$$

approximate value for the equilibrium constant for hydrolysis of $XFPO_2H$ in water, eq 8, would then be equal to K_1/K_7.

$$XFPO_2H(aq) + H_2O(l) \rightleftarrows XPO_3H_2(aq) + HF(aq) \quad (8)$$

To test the validity of these assumptions, this method is applied to phosphorus acid, for which directly measured equilibrium constants are available. The results are given in Table 2. For this test compound, the hydrolysis constants obtained from the switching reactions are well within experimental uncertainty of the directly measured values.

The results of the application of this method to difluorophosphoric acid are also shown in Table 2. No previous measurements of the hydrolysis equilibrium constants have been made for this compound.

Table 1. Equilibrium Constants for the Hydrolysis of Monofluorophosphoric Acid

t/°C	n[a]	K_1[b]	K_1(calcd)[c]
5	5	820 ± 110	830
25	12	640 ± 230	540
45	6	290 ± 110	360
65	10	270 ± 60	260
85	5	200 ± 60	190

[a] n = number of experiments. [b] Uncertainties are standard deviations. [c] Smooth values calculated from thermochemical values of $\Delta H_1^\circ = -15.3$ kJ mol^{-1} and $\Delta S_1^\circ = 1$ J K^{-1} mol^{-1}.

Table 2. Hydrofluoric Acid Switching Reactions between Phosphoric and Phosphorous Acid or Monofluorophosphoric Acid: Hydrolysis Equilibrium Constants for Monofluorophosphorous and Difluorophosphoric Acid

	K_7					
t/°C	solvent 1[a]	solvent 2[b]	solvent 3[c]	av	calcd $K_8 = K_1/K_7$	measd K_8[d]
			X = H			
5	0.52	0.57	0.84	0.63	1310	1150
25	0.52	0.72	0.89	0.70	770	710
45	1.17	1.88	0.88	1.24	290	460
65	1.17	1.49	1.07	1.23	211	310
			X = F			
5	0.068	0.11	0.053	0.073	11300	
25	0.085	0.069	0.056	0.069	7800	
45	0.070	0.073	0.054	0.065	5500	
65	0.068	0.091	0.052	0.068	3800	

[a] 40% HF/60% H_2O. [b] 25% H_2SO_4/30% HF/45% H_2O. [c] 50% H_2SO_4/20% HF/30% H_2O. [d] Directly measured values from ref 3.

Table 3. Equilibrium Constant for Formation of Amidofluorophosphate from HF and Difluorophosphate,[a] Equation 9, at 25 °C

pH	$m_{F_2PO_2}$/ (mol kg^{-1})	$m_{H_2NPFO_2}$/ (mol kg^{-1})	m_F/ (mol kg^{-1})	$K_9 \times 10^7$
7.89	0.32	0.35	1.35	4.6
7.14	0.64	0.03	1.03	4.4
8.79	0.01	0.65	1.65	4.3

[a] All solutions contain 1 mol kg^{-1} NH_4F.

Reaction of Ammonia with Difluorophosphate. Aqueous ammonia reacts with difluorophosphate when the pH is greater than 9 to displace one fluoride, as given in eq 9. The

$$NH_3(aq) + F_2PO_2^-(aq) = FPO_2NH_2^-(aq) + H^+(aq) + F^-(aq) \quad (9)$$

amidofluorophosphate that is produced has a P chemical shift of 7.46 ppm and coupling constant J_{PF} = 910.2 Hz. When this solution is acidified, the difluorophosphate reappears, indicating reaction 9 is reversible.

The results of a series of studies of the equilibrium mixtures of aqueous ammonium fluoride and sodium difluorophosphate at pH values between 7 and 9 are given in Table 3. An activity coefficient of 0.61 is estimated for these solutions, and the concentration of ammonia is calculated from the original ammonium fluoride concentration and the pK_a of ammonium ion of 9.24. An average $K_9 = (4.4 \pm 1.8) \times 10^{-7}$ is obtained at 25 °C, the uncertainty being largely due to the uncertainty in the estimated activity coefficient. An independent value of the equilibrium constant can be obtained from the ratio of the measured rate constants in the forward direction, $k_9 = 5 \times 10^{-5}$ M^{-1} s^{-1}, and the reverse direction, $k_{-9} = 1.5 \times 10^2$ M^{-2} s^{-1}. These values lead to a value of $K_9 = 3.3 \times 10^{-7}$ in good agreement with the directly measured value.

Discussion and Thermochemical Calculations

Substituent Effects. There are a great many studies of the energetics of hydrolysis of various phosphorus oxygen compounds (*14*), but few studies of phosphorus with atoms other than oxygen. For reaction 10 one might expect the

$$H_2O(aq) + XPO_2F^-(aq) = HX(aq) + HOPO_2F^-(aq) \quad (10)$$

fluoro and amido substituents to bracket the hydroxy value. That is not the case. We have $K_{10} = 4.5 \times 10^3$, 1, and 6.9×10^6 for X = F, OH, and NH_2, respectively, with the P–O bond appearing to be more stable than either the P–F or P–N bond.

The hydrolysis energetics of only one amidophosphate has been studied previously, namely, creatine phosphate. This compound and another amidophosphate, arginine phosphate, are used for energy storage in muscle tissue. The equilibrium constant for the hydrolysis of creatine phosphate is 4×10^7. This value is only slightly larger than the value for the hydrolysis of amidofluorophosphate, indicating that, in spite of its more complicated structure, the driving force of the reaction is just the breaking of the weak N–P bond and the formation of the stronger O–P bond.

Thermodynamics of Hydrolysis and Formation. The thermochemical values of hydrolysis in aqueous solution are calculated to be $\Delta G_1° = -15.5$ kJ mol^{-1}, $\Delta H_1° = -15.3$ kJ mol^{-1}, and $\Delta S_1° = 1$ J K^{-1} mol^{-1} for monofluorophosphoric acid on the basis of the equilibrium constants in Table 1. The corresponding values of difluorophosphoric acid are $\Delta G_8 = -22.2$ kJ mol^{-1}, $\Delta H_8 = -14.1$ kJ mol^{-1}, and $\Delta S_8 = +27$ J K^{-1} mol^{-1}. The entropy of hydrolysis for H_2PO_3F is close to zero as was the corresponding value for H_2PO_2F. This is the value expected for an isoelectric reaction. The unusually high value of $\Delta S = +27$ J K^{-1} mol^{-1} for the hydrolysis of difluorophosphoric acid may originate in the same manner as does its low entropy of ionization; the neutral acid has an exceptionally low entropy because of a structure that resembles the $H_3O^+PO_2F_2^-$ ion pair (*2*).

The thermodynamics of formation for the phosphorus species involved in this work are calculated on the basis of the above determinations and the NBS reference values for phosphoric acid (*16*) and reported in Table 4. The NBS values for the Gibbs free energy of formation of monofluorophosphoric acid and monofluorophosphate apparently are currently based on the erroneous data of Dutt and Gupta (*9*). No previous values have been reported for difluorophosphoric acid, difluorophosphate, and amidofluorophosphate.

Table 4. Thermodynamics of Formation of Monofluorophosphoric Acid, Difluorophosphoric Acid, Amidofluorophosphoric Acid, and Their Anions at 25 °C

compound	$\Delta G_f°$/ (kJ·mol^{-1})	$\Delta H_f°$/ (kJ·mol^{-1})	$S°$/ (J·K^{-1}·mol^{-1})
H_3PO_4(aq)[a]	−1142.54	−1288.34	158.2
H_2FPO_3(aq)	−1186.7	−1307.3	176
$HFPO_3^-$(aq)	−1183.6	−1324.2	109
FPO_3^{2-}(aq)[b]	−1156.2	−1332.1	−9
HF_2PO_2(aq)	−1224.2	−1327.6	168
$F_2PO_2^-$(aq)	−1222.5	−1335.4	136
$H_2NPO_2F^-$(aq)	−934.0		

[a] Reference 16. [b] Based on ionization thermodynamics of $HFPO_3^-$ in ref 13.

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