Thermodynamics of Ionization of Monofluoro- and Difluorophosphoric Acids

John W. Larson* and Bangli Su†

Department of Chemistry, Marshall University, Huntington, West Virginia 25755-2520

Phosphorus-31 nuclear magnetic resonance has been used in determining the thermodynamics of acid ionization of aqueous monofluoro- and difluorophosphoric acids. Thermodynamic values for acid ionization at 25 °C are $\Delta G° = 3.1$ kJ mol^{-1}, $\Delta H° = -16.9$ kJ mol^{-1}, and $\Delta S° = -67$ J K^{-1} for monofluorophosphoric acid and $\Delta G° = 1.7$ kJ mol^{-1}, $\Delta H° = -7.8$ kJ mol^{-1}, and $\Delta S° = -32$ J K^{-1} mol^{-1} for difluorophosphoric acid.

The present determination of the thermochemical values for the ionization of aqueous fluorophosphates was undertaken as a part of a larger effort (*1-3*) directed toward increasing our understanding of substituent effects involving second-row elements.

The thermodynamic properties for the ionization of monofluorophosphoric acid, eq 1, and difluorophosphoric acid, eq 2, are determined by measuring the P chemical shifts or

$$H_2PO_3F(aq) \rightleftarrows H^+(aq) + HPO_3F^-(aq) \qquad (1)$$

$$HPO_2F_2(a) \rightleftarrows H^+(aq) + PO_2F_2^-(aq) \qquad (2)$$

PF coupling constants as a function of the degree of ionization. Either phosphorous or hypophosphorous acid is used in these measurements as an internal reference acid to determine a combination of the H$^+$ concentration and the mean activity coefficients. The fluorophosphoric acids are moderately strong acids that undergo hydrolysis in acid solutions so that any method used to determine their K_a's must contend with changing concentrations and with fairly high ionic strengths. The NMR method used in this work is independent, to a first approximation, of both the concentrations of the species and their activity coefficients and therefore well suited to these acids.

Values for the first acid ionization constant of monofluorophosphoric acid have been reported as a part of three kinetic studies (*4-6*) of the acid-catalyzed hydrolysis of the acid. These values contain large uncertainties because the ionization constant was assumed to be temperature independent and because the activity coefficients of all of the species were taken as unity. One potentiometric study (*7*) of this constant has been made as a function of temperature, but the values obtained from this study disagree by more than 2 orders of magnitude with those of the kinetic studies.

The only quantitative data relevant to the ionization studies on difluorophosphoric acid is a value of K_a of 0.45 used to fit kinetic data (*5*) on the hydrolysis of this species between 15 and 35 °C.

Experimental Section

A concentrated solution of phosphorous acid (5.28 mmol of H_3PO_3/g of solution) was made from the pure acid (Aldrich). The concentration of this solution, a concentrated solution of hydrofluoric acid and a concentrated hydrochloric acid solution (Fischer Scientific; 19.85 and 10.22 mmol/g, respectively), and concentrated phosphoric acid (J. T. Baker Co.; 9.01 mmol/g) were analyzed by standard acidimetric titration methods. The HF was stored, dispensed, and analyzed using plastic labware. The sodium monofluorophosphate (Ozark-Mahoning) was used without further purification. The NMR spectra of difluorophosphoric acid (Strem) and solutions made from it exhibited very wide lines, presumably from paramagnetic impurities. Potassium difluorophosphate was therefore made by fusing stoichiometric amounts of potassium hexafluorophosphate (Ozark-Mahoning) with sodium metaphosphate (*9*). The latter compound was obtained by heating sodium dihydrogen phosphate (MCB) to 1000 °C in a Pt crucible. The NMR of the resulting salt indicated the compound consisted of 95 mass % of the phosphorus as difluorophosphate and 5 mass % as pyrophosphate. A mixture of mass ratio 3:2 of concentrated fluoro- and difluorophosphoric acid was also prepared by slowly adding concentrated HF to phosphorus oxytrichloride (Fischer Scientific) in a 2:3 ratio by mass.

Table 1. Coupling Constants and Chemical Shifts (Relative to 85 mass % Phosphoric Acid) for Aqueous Phosphorus, Phosphoric, Monofluorophosphoric, and Difluorophosphoric Acid Species

species	δ/ppm	J_{PH}/Hz	J_{PF}/Hz
$H_2PO(OH)$	+14.25	575.9	
H_2PO_2	+7.96	518.4	
$HPO(OH)_2$	+5.88	686	
HPO_2OH^-	+3.28	629.5	
HPO_3^{2-}	+3.76	567.8	
$PO(OH)_3$	+0.69		
$PO_2(OH)_2^-$	+0.81		
$PO_3(OH)^{2-}$	+3.14		
$FPO(OH)_2$	−4.84		916.7
FPO_2OH^-	−3.73		907.8
FPO_3^{2-}	+1.64		867.8
$F_2PO(OH)$	−14.93		962
$F_2PO_2^-$	−14.24		962

The sample solutions used in this work were prepared by mass, with concentrations expressed in terms of 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. Temperatures during the acquisition of NMR data were controlled to within ±0.3 °C and calibrated with a mercury in glass thermometer.

Procedure and Equilibrium Constant Calculations

Acid Ionization Constant of Monofluorophosphoric Acid. In general both the phosphorus chemical shift and coupling constant for a phosphorus acid will be affected by its extent of protonation. The protonation reaction is fast on

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* To whom correspondence should be addressed.

† Permanent address: Chemical Engineering Department, Northwest University, Xi'an, Shaanxi Province, People's Republic of China.

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Table 2. Acid Ionization Constants of Monofluorophosphoric and Difluorophosphoric Acids

	H_2FPO_3				HF_2PO_2			
t/°C	property[a]	pK_a	av	calcd[b]	property[a]	pK_a	av	calcd[b]
5	δ_{PF}, J_{PH}, 18	0.20			δ_{PF2}, J_{PF}, 12	0.15		
	δ_{PF}, J_{PH2}, 12	0.32	0.32_5	0.32_9	δ_{PF2}, δ_{PF}, 17	0.25	0.23	0.20
	J_{PF}, J_{PH}, 12	0.38			δ_{PF2}, J_{PH2}, 12	0.30		
	J_{PF}, J_{PH2}, 12	0.40						
25	δ_{PF}, J_{PH2}, 15	0.55			δ_{PF2}, δ_{PF}, 23	0.30		
	δ_{PF}, J_{PH}, 14	0.52	0.53_8	0.54_1	δ_{PF2}, J_{PF}, 22	0.29	0.29	0.30
	J_{PF}, J_{PH2}, 13	0.54			δ_{PF2}, J_{PH2}, 16	0.29		
	J_{PF}, J_{PH}, 12	0.54						
45	δ_{PF}, J_{PH}, 21	0.75			δ_{PF2}, J_{PH}, 21	0.32		
	J_{PF}, J_{PH}, 18	0.74	0.74_5	0.72_8	δ_{PF2}, J_{PF}, 15	0.30	0.31	0.39
65	Δ_{PF}, J_{PH2}, 16	0.85			δ_{PF2}, δ_{PF}, 29	0.56		
	δ_{PF}, J_{PH}, 16	0.85	0.88_0	0.89_2	δ_{PF2}, J_{PF}, 17	0.48	0.52	0.46
	J_{PF}, J_{PH}, 12	0.94						

[a] Measured property, reference property to determine H, number of points. [b] Calculated on the basis of thermochemical values in Table 3.

the NMR time scale so that the value of both the chemical shift and the coupling constants of an aqueous acid are the weighted average of the values of the protonated form and the value of the deprotonated form. Values of chemical shifts and coupling constants for species involved in this work are reported in Table 1.

A typical run consisted of making a solution of approximately 0.2 mol kg^{-1} reference acid and 0.3 mol kg^{-1} Na_2PO_3F in a 10-mm, Teflon-lined NMR tube. The reference acid used was either H_3PO_3 or H_3PO_2. These acids have PH coupling constants that are indicative of their degree of ionization and therefore provide an instantaneous measure of the activity of the hydrogen ion in solution. This internal reference is critical to the eventual calculation of the pK_a. This solution was equilibrated at the temperature of the measurement for 10 min. The NMR tube was then removed, and concentrated HCl was quickly added dropwise, the tube reinserted into the instrument, and the spectrum recorded after the NMR tube had reached its normal spin rate. The solution was out of the NMR (and away from the equilibration temperature) for between 15 and 30 s during the addition of the HCl. Addition of a drop or two more of HCl was repeated until most of the monofluorophosphate had hydrolyzed. The only experimental quantities that directly entered into the equilibrium calculations were the phosphorus–hydrogen coupling constant, J_{PH}, of the phosphorus reference acid and either the phosphorus–fluorine coupling constant, J_{PF}, or the phosphorus chemical shift of monofluorophosphoric acid.

The equilibrium expression for reaction 1 may be written as eq 3. The value of $m_{HPO_3F}/m_{H_2PO_3F}$ may be related to the

$$K_1 = (m_{HPO_3F}/m_{H_2PO_3F})(m_H\gamma_{HPO_3F}\gamma_H/\gamma_{H_2PO_3F}) \qquad (3)$$

experimental PF coupling constants or the chemical shift. The value of m_H times the activity coefficient term is defined as the function H and is obtained from the coupling constants of the reference acid, HR, by eq 4 (*1*). The validity of eq 4

$$H = K_{a,HR}\,(J_{PH} - J^{\circ}_{PH,R^-})/(J^{\circ}_{PH,HR} - J_{PH}) \qquad (4)$$

depends on the activity coefficients of the H_2PO_3F and HPO_3F^- to be approximately equal to that of HR and R^-, respectively. Because of the similar structures and charges of the reference acid, this assumption, which is exact in the region of the Debye–Huckel limiting law, should be fairly accurate even at the highest ionic strengths of the solutions studied, typically about 2 mol kg^{-1}.

The most straightforward way of analyzing the data is to plot either the PF coupling constant or the P chemical shift of monofluorophosphoric acid as a function of $-\log(H)$ as is shown in Figure 1. The value of $-\log(H)$ at the inflection point of the curve is equal to the pK_a of the acid. Results of these determinations are reported in Table 2, where the pK_a's are based on the best fit of about 15 points to graphs such as in Figure 1. Two different reference acids were used at each temperature, and usually both the PF coupling constant and the P chemical shift were used in the determination. For monofluorophosphoric acid, these two properties were of comparable accuracy in determining the pK_a because although the change in the coupling constant on ionization is less than the change in the chemical shift, it can be measured more accurately. The consistency of the determined pK_a values when different reference acids are used provides experimental support for the method used in estimating the activity coefficients. The constancy of the pK_a's with respect to changing the property used to estimate the acid to conjugate base ratio supports the implied assumption that the only major factor that affects the chemical shift and coupling constants is the degree of protonation and that other effects such as specific hydrogen bonding or ionic strength changes are negligible.

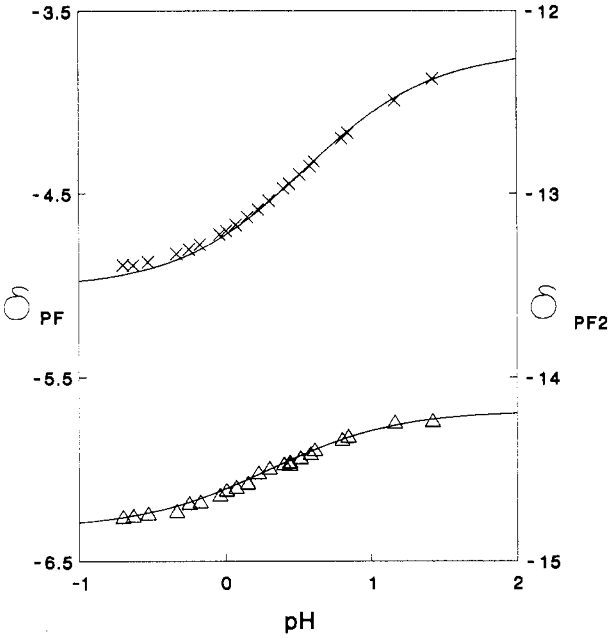

Figure 1. Chemical shift of (×) monofluorophosphoric acid and (Δ) difluorophosphoric acid as a function of pH at 25 °C.

Linear methods of determining equilibrium constants from NMR data (*8*) were also used to calculate the K_a with almost identical results. Such methods are dependent on assumptions as to reference coupling constants or chemical shifts and may contain an intrinsic bias toward certain data points. These disadvantages seemed to outweigh the advantages associated with a linear regression.

The value of the first ionization constant of monofluorophosphoric acid obtained at 25 °C, $K_1 = 0.29$, is in good agreement with the value of 0.28 estimated from the potentiometric titration curve of the acid *(9)*. It is somewhat lower than the value of 0.8 used to obtain the best fit of kinetic data on the hydrolysis of monofluorophosphoric acid in H_2O at 40 and 80 °C. The values obtained here are in poor agreement with the value of $K_1 = 0.038$ obtained from a potentiometric determination *(7)*.

Acid Ionization Constant of Difluorophosphoric Acid. Data on the chemical shift of difluorophosphoric acid in solutions of this acid with monofluorophosphoric acid, phosphorous acid, or hypophosphorous acid were also collected to determine the ionization constant for this acid. For this acid the change in the PF coupling on ionization was too small (~3 Hz) to be useful in determining K_a. Monofluorophosphoric, phosphorous, and hypophosphorous acids were used as internal reference acids to obtain empirical values for the function H. The experimental procedures and analysis were analogous to those used for monofluorophosphoric acid.

The results of the analysis of these data are also reported in Table 2.

Thermodynamics of Ionization. The $\Delta G°$, $\Delta H°$, and $\Delta S°$ of ionization are given for monofluoro- and difluorophosphoric acids in Table 3. These values are calculated from the van't Hoff isochore of pK_a's against $1/T$ along with the corresponding values from some related acids.

The thermodynamics of ionization of monofluorophosphoric acid follows the pattern established by other phosphorus oxy acids *(1, 3)*. Its entropy of ionization is close to -70 J K^{-1} mol^{-1} obtained for other acids in this series, and its smaller pK_a compared to phosphoric acid is almost completely due to its more exothermic enthalpy of ionization. The entropy of ionization of difluorophosphoric acid, in contrast, is about 5 standard deviations less negative than phosphoric acid. It is possible that, because the acid is so strong, the undissociated acid resembles an ion pair of H_3O^+ and $PO_2F_2^-$. An acid in this form would be expected to have a lower enthalpy and a lower entropy of ionization than normal. This would also provide an explanation for the small change in the coupling constant and chemical shift that occurs on ionization of this acid when compared to other related acids.

Table 3. Thermodynamics of Ionization of Monofluorophosphoric Acid. Difluorophosphoric Acid, Phosphoric Acid, Monofluorophosphorus Acid, and Phosphorus Acid at 25 °C

acid	$\Delta G°$/ (kJ mol^{-1})	$\Delta H°$/ (kJ mol^{-1})	$\Delta S°$/ (J K^{-1} mol^{-1})	ref
$H_2[FPO_3]$	3.1 ± 0.1[a]	−16.9 ± 0.5[a]	−67 ± 2[a]	this work
$H[F_2PO_2]$	1.7 ± 0.4[a]	−7.8 ± 2.3[a]	−32 ± 8[a]	this work
$H_3[PO_4]$	12.25	−7.74	−67.1	10
$H[HFPO_2]$	2.2	−26.0	−94	3
$H[HPO_3]$	7.15	−14.86	−73.8	1

[a] Standard deviation.

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