An Acidity Scale for Brönsted Acids Including $H_3PW_{12}O_{40}$

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Abstract: The calorimetric titration of $H_3PW_{12}O_{40}$ (H_3PW) with a series of bases in CH_3CN gives equilibrium constants and enthalpies for the three deprotonation steps. These results show that solutions of H_3PW in any solvent whose basicity is equal to or weaker than CH_3CN will only furnish one strong proton per molecule of acid for stoichiometric or catalytic reactions. In more strongly basic solvents (S), more S_2H^+ species are available, but their strength is less being leveled by the solvent basicity. In drying H_3PW, it is critical to avoid the weaker acids formed by reducing the material or forming the anhydride. Calorimetric titration of a series of samples subjected to different drying procedures establishes the best procedure for preparing the anhydrous acid. For most donors, the enthalpies of reaction for the first protonation step fit the ECW model. The W term provides a measure of the dissociation energy of the conjugate base in acetonitrile. $E_A{}^*$ and $C_A{}^*$ permit calculation of the enthalpies for the reaction in acetonitrile of $(CH_3CN)H^+$ and H_3PW with the >100 bases in the ECW correlation. The $C_A{}^*/E_A{}^*$ ratio of 2.88 indicates significant covalency in the interactions of this acceptor. This fitting of the enthalpies by using solvation minimized, donor parameters for neutral adducts indicates that the choice of enthalpies in acetonitrile as the solvent provides a temperature-independent, solution, Brönsted acidity scale that permits comparisons with neutral acceptors. The enthalpies of reactions of pyridine with a series of Brönsted acids in acetonitrile solvent is offered, leading to the following acidity order: $H_3PW_{12}O_{40} > CF_3SO_3H > p\text{-}CH_3C_6H_4SO_3H \cong H_2SO_4 > CF_3COOH > ClC_6H_4COOH$.

Introduction

The utility of heteropolyacids (HPA) as catalysts for redox and acid-catalyzed reactions has stimulated considerable interest in these compounds. Our interest in acid catalysis led us to investigate the acidity of these materials. The acid $H_3PW_{12}O_{40}$ (abbreviated as H_3PW) was selected for study because it is reported to be among the strongest acids in the series, it is commercially available as a crystalline hydrate, and it has been thoroughly studied and reviewed.[1−19] The Keggin structure, often illustrated in the literature,[20] is composed of a central PO_4 tetrahedron surrounded by 12 MO_6 octahedra (where M is W or Mo) arranged in four groups of three-edge-sharing, M_3O_{13}

octahedra. There are four types of oxygen atoms (internal, edge-sharing, corner-sharing, and terminal) in this structure.

The secondary structure linking these polyanion units depends upon the degree of hydration. For example, $H_3PW_{12}O_{40} \cdot 6H_2O$ consists of two sets of three-dimensional networks in which four polyanions are connected by hydrogen bonding of terminal protons of $(H_2O)_2H^+$ to bridging terminal oxygen atoms (O_t) of the polyanions. Two sets of networks penetrate each other leading to a bcc type arrangement of the polyanions. In the dehydrated compound, a proton located in the same position as $(H_2O)_2H^+$ interacts with the four O_t atoms. Since all terminal oxygens are equivalent in the magic angle ^{17}O NMR spectrum, the proton is proposed to rapidly exchange between the four O_t atoms.[2]

Acidities of heteropolyacids in solution have been studied by conductivity,[14] Hammett acidity constants,[15] and the ^{13}C shift of mesityl oxide.[16] Based on conductivity, it is claimed that in solvents of moderate polarity like ethanol, the first and second proton of H_3PW are completely dissociated while in acetic acid, H_3PW behaves as a monoprotic acid.[11,16] In acetone, conductivity studies lead to pK_a values for the three dissociations of 1.6, 3.0, and 4.0. The pK_a values in ethanol are very similar to those in acetone. In water, the stepwise three-step dissociation of H_3PW is not detected because of the leveling influence of the solvent. However, in acetic acid, pK_{a1} is equal to 4.77.[11]

The ^{13}C shift of mesityl oxide upon reaction with H_3PW in acetic acid is interpreted to indicate that the three protons dissociate simultaneously and not consecutively.[16] Because of the size of the molecule, the negative charge of the conjugate base is claimed to be delocalized over the large Keggin structure,

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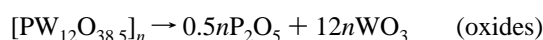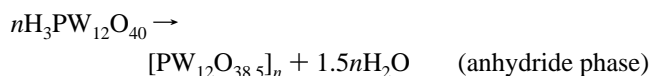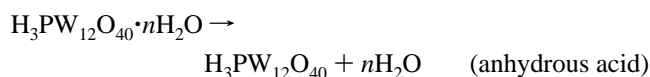[‡] Eastman Kodak Company, Rochester, New York, 14650-1907.

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1997.

(1) Okuhara, T.; Mizuno, N.; Misono, M. *Adv. Catal.* **1996**, *41*, 113.

(2) Kozhevnikov, I. V. *Catal. Rev.-Sci. Eng.* **1995**, *37*, 311.

(3) Hill, C. L.; Prosser-McCartha, C. M. *Coord. Chem. Rev.* **1995**, *143*, 407.

(4) Corma, A. *Chem. Rev.* **1995**, *95*, 559.

(5) Izumi, Y.; Urabe, K.; Onaka, M. *Zeolite, Clay, and Heteropoly Acid in Organic Reactions*; VCH: Tokyo, 1992.

(6) Pope, M. T.; Muller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34.

(7) Belanger, R.; Moffat, J. B. *Environ. Sci. Technol.* **1995**, *29*, 1681.

(8) Bélanger, R.; Moffat, J. B. *J. Catal.* **1995**, *152*, 179.

(9) Tsigdinos, G. A. *Top. Curr. Chem.* **1978**, *76*, 1.

(10) Misono, M. *Catal. Rev.-Sci. Eng.* **1987**, *29*, 269.

(11) Mateev, K. I.; Kozhevnikov, I. V. *Russ. Chem. Rev.* **1982**, *51*, 1075.

(12) Tanabe, K.; Misono, M.; Ono, Y.; Hattoni, H. *New Solid Acids and Bases−their Catalytic Properties*; Elsevier: Tokyo, 1989.

(13) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlin, 1983.

(14) Kulikov, S. M.; Kozhevnikov, I. V. *Russ. Chem. Bull.* **1981**, 348.

(15) Ghosh, A. K.; Moffat, J. B. *J. Catal.* **1986**, *101*, 238.

(16) Farcasiu, D.; Li, J. Q. *J. Catal.* **1995**, *152*, 198.

(17) Jozefowicz, L. C.; Karge, H. G.; Vasilyeva, E.; Moffat, J. B. *Microporous. Mater.* **1993**, *1*, 313.

(18) Kapustin, G. I.; Brueva, T. R.; Klyachko, A. L.; Timofeeva, M. N.; Kulikov, S. M.; Kozhevnikov, I. V. *Kinet. Catal. (Transl. Kinet. Katal.)* **1990**, *31*, 896.

(19) Lefebvre, F.; Liu-Cai, F. X.; Auroux, A. *J. Mater. Chem.* **1994**, *4*, 125.

(20) General texts for description of the Keggin structure: (a) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergmon Press: Oxford, reprinted 1994. (b) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*, 4th ed.; Harper Collins College Publishers: New York, 1993. (c) Cotton, F. A.; Wilkinson G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons: New York, 1988. For drawings of both the Keggin and the secondary structure of heteropolyacids see refs 1, 3, 4, 8, 9, 11, and 14.

and there is no charge destabilization for the second and third ionizations. In all instances, the reported studies suggest that the acidity of H_3PW is greater than that of H_2SO_4.[2,16]
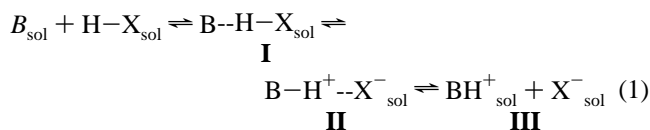
A microcalorimetric study[17] of the reaction of gaseous ammonia with solid H_3PW was carried out at 50 °C. The sample activated at 150 °C shows different behavior from one activated at 250 °C, which differs[18] from a sample activated at 300 °C and titrated at 150 °C. Another microcalorimetry study[19] at 150 °C claims that H_3PW, treated at 150 or 250 °C under vacuum, produces the anhydrous acid, whose acidity is greater than that of the anhydride prepared by vacuum drying at 400 °C. The anhydride is metastable, decomposing into constituent oxides.[19]

$$H_3PW_{12}O_{40} \cdot nH_2O \rightarrow$$
$$H_3PW_{12}O_{40} + nH_2O \qquad \text{(anhydrous acid)}$$

$$nH_3PW_{12}O_{40} \rightarrow$$
$$[PW_{12}O_{38.5}]_n + 1.5nH_2O \qquad \text{(anhydride phase)}$$

$$[PW_{12}O_{38.5}]_n \rightarrow 0.5nP_2O_5 + 12nWO_3 \qquad \text{(oxides)}$$

The exotherms from the gas−solid calorimetric titration studies of H_3PW with ammonia are complex. Initially enthalpies of 47.8 kcal mol^{-1} are reported dropping to 45 kcal mol^{-1} before 0.5 equiv of ammonia is added. This is followed by a gradual drop to 39 kcal mol^{-1} up to 2.9 equiv and a sharp drop thereafter. The three protons are reported to have comparable acidity. In the cal-ad study[21] of HZSM-5, gas−solid calorimetry at elevated temperatures was shown to contain both dispersion and acid−base components, and to average into a single step different protons whose acidities differ by 30 kcal mol^{-1}.

The conflicting reports of the acidities of H_3PW has prompted further study. With a three-step equilibrium possible, solution measurements are more easily interpreted than calorimetric studies of the solid. Enthalpies are measured as the criterion of acid strength, and they are expected to provide a temperature-independent relative acidity scale for the temperature ranges used in acid catalysis. Work from this laboratory has emphasized[22−24] using the enthalpy of adduct formation in poorly solvating solvents as the criterion for measuring donor−acceptor strength. Most of the acceptors studied to date are neutral molecules that form neutral 1:1 adducts. The strong acid H_3PW on reaction with moderately strong bases forms ionic products, and the acid is insoluble in poorly solvating solvents. These properties afford an opportunity to extend the enthalpy criterion of acid strength to new acid−base reactions but require a reevaluation of the experimental conditions that will provide the most meaningful results.

Reaction of one molecule of base with a monoprotic acid, HX, is described by the following equilibria:

$$B_{sol} + H{-}X_{sol} \rightleftharpoons B\text{-}\text{-}H{-}X_{sol} \rightleftharpoons$$
$$\mathbf{I}$$
$$B{-}H^+\text{-}\text{-}X^-_{\,sol} \rightleftharpoons BH^+_{\,sol} + X^-_{\,sol} \quad (1)$$
$$\mathbf{II} \qquad\qquad \mathbf{III}$$

where **I** is the hydrogen bond adduct, **II** is an intimate ion pair with HX behaving as a Brönsted acid, and **III** is the dissociated or solvent-separated ion pair of the Brönsted acid, HX. In the solvent-separated ion pair, the base and at least one solvent molecule are coordinated to the proton. Research leading to the Coordination Model[25] for nonaqueous solvents has shown that the position of the equilibrium between species **I**, **II**, and **III**, in different pure bases as solvent, depends on the basicity and polarity of the solvent as well as the basicity of the conjugate base X$^-$. Both strong basicity and large polarity are needed to displace the anion from the acid by a neutral base.

To establish an acidity scale, the solvent should be held constant to minimize differences from nonspecific solvation contributions to the measured enthalpy. The best solvents for studying Brönsted acids are nonprotonic and weakly basic because of the leveling effect. Basic solvents drive the equilibrium in eq 1 toward species **III** even when HX is a weak acid, i.e., those with strong conjugate bases. As a result, the enthalpy of reaction of a base with both weak and strong acids in basic solvents will be similar and will correspond to the enthalpy of the reaction (where S is a solvent molecule):

$$S_2H^+_{\,sol} + X^-_{\,sol} + B_{sol} \rightarrow BHS^+_{\,sol} + X^-_{\,sol} + S \quad (2)$$
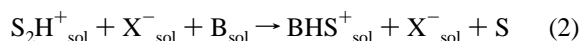
Slight differences in $-\Delta H$ may arise if the equilibrium between intimate and separated ion pairs (species **II** and **III** of eq 1) differs. Thus, weakly basic solvents must be used to discriminate the relative acidity of strong acids.

The best solvents for studying acidity should also be either only slightly polar, so the product of the reaction is species **II**, or very polar, so the only product is species **III**. In the studies reported here acetonitrile is selected as the weakly basic, polar solvent because solubility limitations of H_3PW require use of a polar solvent. When a strong, weakly polar base such as pyridine is added to H_3PW in a weakly basic polar solvent, solvent polarity will allow pyridine basicity to drive the reaction toward species **III** displacing X$^-$ from the proton. The enthalpy measured will be the net of displacing X$^-$ from the H$^+$ by pyridine plus the net nonspecific solvation of the ionic products and reactants. The nonspecific solvation is expected to be the smaller of the two contributions and relatively constant as the base is varied. Thus, in weakly basic polar solvents, relative basicities can be obtained from the enthalpies without varying contributions from the extent of ionizations of **II** to **III**. When di- and triprotic acids are studied, the above discussion for HX pertains to each step of the reaction.

With H_3PW, a series of reactions with different bases have been investigated to determine the influence of the base on the three steps of the H_3PW equilibria. The enthalpies for step 1 are correlated to the ECW model[24] to demonstrate that the basicity trends in acetonitrile toward Brönsted acids parallel those toward neutral acids in nonsolvating solvents. To compare the relative acid strength of H_3PW to other acids with this new scale, enthalpies for the reaction of pyridine with a variety of acids are also reported in CH_3CN solvent.

Experimental Section

Materials. Elemental and TGA analysis of the H_3PW, obtained from Aldrich, revealed 16 mol of water per mol of H_3PW. Acetonitrile obtained from Fisher was purified by drying over 4A molecular sieves for 24 h, and then distilled over P_2O_5. Pyridine obtained from Fisher was distilled over CaH_2. Quinuclidine, *N*-methylimidazole, *N,N*-dimethylacetamide, and triethylphosphine (Aldrich) and quinoline and dimethyl sulfoxide (Fisher) were used as supplied. Sulfuric acid (97% as calculated by standardization), *p*-toluenesulfonic acid, and benzoic acid were obtained from Fisher. Triflic acid was obtained from Aldrich.

(21) This difference is significant in light of our previous claim that gas−solid calorimetry fails to differentiate sites of different strength in HZSM-5 because the equilibrium constants are comparable at elevated temperatures. Drago, R. S.; Dias, S. C.; Torrealba, M; de Lima, L. *J. Am. Chem. Soc.* **1997**, *119*, 4449.

(22) Drago, R. S. *Struct. Bonding* **1973**, *15*, 73.

(23) Drago, R. S. *Coord. Chem. Rev.* **1980**, *33*, 251.

(24) Drago, R. S. *Applications of Electrostatic-Covalent Models in Chemistry*; Surfside Scientific Publishers: Gainesville, FL, 1994, and references therein.

(25) Meek, D. W.; Drago, R. S. *J. Am. Chem. Soc.* **1961**, *83*, 4322.

Trifluoroacetic acid and *m*-chlorobenzoic acid were obtained from Kodak. Drying and standardization procedures for the acids followed literature guidelines. Dried samples were stored in a container with 4A molecular sieves.

Thermal Treatment and Calorimetric Titration of H₃PW. H₃PW was subjected to different thermal treatments. It was heated at 128 and 162 °C in a vacuum oven. In other treatments, it was heated at 200, 300, and 400 °C under dry air flow in a tube furnace. After each treatment, the H₃PW is transported immediately to a drybox and stored under nitrogen.

Samples of H₃PW were weighed and transferred to a dewered calorimetric cell containing a stir bar. Since H₃PW is very hygroscopic, these weightings and transfers are done in a drybox. For each titration, 100 mL of acetonitrile is added to the cell. A calibrated syringe, filled with a solution of known concentration of base (e.g., 0.2 M), is inserted into the cell along with a thermistor and a heater coil. These operations are carried out in an inert atmosphere glovebag. The thermistor and heater coil are connected to an electronic circuit bridge and a computer.[26] The thermistor was calibrated with the heater coil prior or immediately after each titration. A set of 12 calibrated brass stops were used for the syringe injections. After each injection the heat evolved from reaction of the base and H₃PW is measured. The heat from adding the base solution to the solvent is negligible. Each titration was repeated three times for each base studied. Titrations of acids other than H₃PW with pyridine were repeated two times.

Spectral Analysis. A Perkin-Elmer Lambda 6 UV−vis spectrophotometer and suprasil quartz cells of 0.1 cm path length were employed. A Nicolet Model 5PC FTIR spectrophotometer and a NaCl cell of 0.1 mm path length or mull in a NaCl cell were employed.

Calculations. The heat liberated in the reaction of strong bases with H₃PW in acetonitrile is fit to the following set of equilibria, giving the respective thermodynamic parameters:

$$H_3PW + B \rightleftharpoons H_2PW^- + BH^+; \qquad K_1, \Delta H_1 \qquad (3)$$

$$H_2PW^- + B \rightleftharpoons HPW^{2-} + BH^+; \qquad K_2, \Delta H_2 \qquad (4)$$

$$HPW^{2-} + B \rightleftharpoons PW^{3-} + BH^+; \qquad K_3, \Delta H_3 \qquad (5)$$

For ease of representation, the acetonitriles attached to the protons of the H₃PW species are not shown. When base is added to a solution of H₃PW the heat liberated is given by:

$$h'_{cal} = [A]_T V(\beta_1 \Delta H_1^T R + \beta_2 \Delta H_2^T R^2 + \beta_3 \Delta H_3^T R^3)/$$
$$(1 + \beta_1 R + \beta_2 R^2 + \beta_3 R^3) \quad (6)$$

where $[A]_T$ is the total concentration of H₃PW (in mol L⁻¹); V is the volume of the titration solution (in L); β_i is the global formation constant, i.e., $\beta_1 = K_1$, $\beta_2 = K_1 K_2$, $\beta_3 = K_1 K_2 K_3$; ΔH_i^T is the global enthalpy of deprotonation of H₃PW, i.e., $\Delta H_1^T = \Delta H_1$, $\Delta H_2^T = \Delta H_1 + \Delta H_2$, and $\Delta H_3^T = \Delta H_1 + \Delta H_2 + \Delta H_3$; and $R = [B]/[BH^+]$ is the ratio of free base and protonated base concentrations (in mol L⁻¹).

K_1, K_2, K_3, the total concentration of H₃PW, and the base concentration determine the concentration of all the species in solution with use of eqs 3−5. The ratio between free base and protonated base is obtained by assuming an initial value, which allows the calculation of concentrations for all species. This routine adjusts the concentrations through a mass balance of the protons, i.e., the protons on BH⁺ must correspond to the ones lost from the acid. The calculation is repeated until the values are consistent. Knowing ΔH_1, ΔH_2, and ΔH_3 as well, eq 6 can be solved for h'_{cal}. Actually, the values of the K's and ΔH's are unknown. By using initial estimates of these parameters, an iterative program is used to calculate the final values which give the minimum of the nonweighted sum of squares of the residuals (U), of eq 7, by a nonlinear routine.

$$U(\beta_i, \Delta H_i^T) = \sum (h'_{exp} - h'_{cal})^2 \qquad (7)$$

The method of steepest descent is employed to find the best values of

β_i and ΔH_i. The first derivatives, $\delta U/\delta\beta_i$ and $\delta U/\delta H_i$, are approximated as $\Delta U/\Delta\beta_i$ and $\Delta U/\Delta H_i$, which are easily calculated to give h'_{cal} (calculated heat). By using h'_{cal} and h'_{exp} (experimental heat), the minimum of the function (eq 7) is obtained. A sample data fit is shown in Table 2.

To evaluate the adequacy of the proposed model, the experimental data are replicated. The residuals ($h'_{exp} - h'_{cal}$) were randomly distributed about the regression. A comparison between the dispersion (variance) from the regression and one obtained by replication is made. To measure dispersion on the experimental points (the external variance, σ^2_{ext}), the sum of squares of the residuals is obtained and divided by the degrees of freedom (number of measured points minus the number of fit parameters). An internal variance (σ^2_{int}) is calculated in a similar manner, but the sum of squares is based on the average of the replicates and the summation is done point to point without adding the heats. Since the heats are added up for analysis purposes, an error associated with each measurement is automatically inserted in each point. The system H₃PW−pyridine, for instance, shows $\sigma^2_{ext} = 1.4903 \times 10^{-4}$ and $\sigma^2_{int} = 1.1405 \times 10^{-4}$. Assuming that σ^2_{int} is constant for these calorimetric measurements, and the errors are normally distributed, both variances can be compared by means of an F test. The ratio $\sigma^2_{ext}/\sigma^2_{int}$ gives 1.30. At 10% probability for the F distribution ($F = 3.05$, $\phi_2 = \phi_1 = 6$), both measures of dispersion are equivalent. This test of the goodness of fit,[27] although not completely rigorous in nonlinear modeling, has at least semiquantitative value, and can tell if the model provides a good fit to the data. Applying the F test to all systems gave similar results to the example shown.

Another method for evaluating the standard deviations for the K's and ΔH's uses a variance−covariance matrix of parameters,[27] which gives errors as standard deviations. This analysis provides standard deviations that match those obtained by replicated data within ±5% of the reported value.

For all the data in Tables 1, 3, and 4, the values of the parameters are based on averaged data sets of triplicate or duplicate experiments and the errors are based on the standard deviations of the variance−covariance matrix. Since precision exceeds accuracy, interpretations of differences less than ±0.5 kcal mol⁻¹ will not be made for $-\Delta H_1$ and less than 1−2 kcal mol⁻¹ for ΔH_2 and ΔH_3.

Results and Discussion

Preparing Anhydrous H₃PW. As with any polyprotic oxyacid, drying is complicated by the conversion of dihydroxy functionality that gives rise to the Brönsted acidity to an anhydride with μ-oxo functionality. For heteropolyacids, the anhydride has been shown by gas−solid calorimetry to be a much weaker acid toward ammonia than the anhydrous acid. The hydrated acid is expected to be a weaker acid than the anhydrous acid because of the endothermic displacement of coordinated water. Thus it is critical for acidity and catalytic studies to use the anhydrous acid. In view of the conflicting reports in the literature[28−30] on the influence of pretreatment on acidity and reactivity, we decided to determine the optimal drying procedure to produce the strongest acid. The total heat released, equilibrium constants, and enthalpies from calorimetric titrations with pyridine are given in Table 1 for samples prepared by different thermal treatments.

The samples in Table 1 were analyzed by UV−vis, FTIR, XRD, DSC, and TGA. No differences in the UV−vis[31] or FTIR[32−34] spectra of acetonitrile solutions were observed,

(26) Drago, R. S.; Chronister, C. W. *J. Am. Chem. Soc.* **1993**, *115*, 793.

(27) Connors, K. A. *Binding Constants−The Measurement of Molecular Complex Stability*; John Wiley & Sons: New York, 1987.

(28) For a general comparison, see refs 17−19 and 29−33.

(29) Rocchiccioli-Deltcheff, C.; Aouissi, A.; Bettahar, M. M.; Launay, S.; Fournier, M. *J. Catal.* **1996**, *164*, 16.

(30) Payen, E.; Kasztelan, S.; Moffat, J. B. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2263.

(31) Varga, G. M., Jr.; Papaconstantinou, E.; Pope, M. T. *Inorg. Chem.* **1970**, *9*, 662.

(32) Rocchiccioli-Deltcheff, C.; Fournier, M.; Franck, R.; Thouvenot, R. *Inorg. Chem.* **1983**, *27*, 207.

An Acidity Scale for Brönsted Acids Including H₃PW₁₂O₄₀

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Table 1. Results of Calorimetric Titrations (25 ± 1 °C) with Pyridine for Different H_3PW Samples in CH_3CN Solvent

sample[a]	total heat evolved (cal)	$-\Delta H_i^b$ (i = 1, 2, 3) (kcal mol^{-1})	K_i^b (i = 1, 2, 3)
128/4	6.187	19.8	1.6×10^3
		15.3	1.1×10^2
		13.9	2.4×10^1
128/8	6.365	20.5	3.6×10^2
		9.4	6.5×10^1
		20.0	5.2×10^1
162/1	5.548	18.5	4.6×10^2
		9.2	1.2×10^2
		15.3	4.2×10^1
162/2	5.768	19.9	2.2×10^3
		9.3	1.2×10^3
		16.7	2.9×10^1
162/4	6.647	21.0	2.2×10^3
		11.8	2.4×10^2
		18.6	4.2×10^1
200/2	5.511	18.6	2.2×10^3
		10.1	5.8×10^2
		17.5	9.2
300/2	4.338	17.7	4.5×10^4
		11.1	3.2×10^3
		3.0	1.5×10^2
300/16	3.827	11.4	4.8×10^3
		7.7	8.5×10^2
		9.0	5.5×10^1
400/2	1.307	8.2	1.5×10^3
		0.3	6.4×10^2
		3.3	3.2×10^{-1}

[a] Samples of H_3PW treated at different temperature (°C)/time (h). Samples at 128 and 162 °C were evacuated and those at 200, 300, and 400 °C were calcined under air flow. Two samples of $H_3PW \cdot 16H_2O$ (as purchased) were titrated with pyridine solution providing −12.9 and −5.4 kcal mol^{-1} for ΔH_1 and ΔH_2 with errors of of 3% and 6%, respectively, and 6.8×10^3 and 1.6×10^3 for K_1 and K_2 with errors of 10% and 27%, respectively. *[b]* Based on variance−covariance matrix analysis, standard deviations are 1%, 2%, and 5% of ΔH_1, ΔH_2, and ΔH_3, and, 5%, 20%, and 25% of K_1, K_2 and K_3, respectively. Conclusions are based on a error estimate of ±0.5 kcal mol^{-1} for ΔH_1 and ±1−2 kcal mol^{-1} for ΔH_2, and ΔH_3.

confirming that the Keggin structure is intact in all samples. Powder XRD results are identical except for the sample calcined at 400 °C where a slight broadening of the lines and loss of intensity occurs. Similar XRD results[35] are reported for a sample of H_3PW calcined at 400 °C.

DSC and TGA give two endothermic peaks, corresponding to loss of water at 92 and 215 °C, and a third peak at about 550 °C. After the initial weight loss, isothermal TGA's at 150, 200, 300, and 400 °C for 2 to 4 h do not show any further change. A DTA study[36] of H_3PW reports decomposition at about 590 °C forming WO_3. TGA[35] and TPD[37] studies claim that decomposition of H_3PW results from mass loss of phosphorus, as P_2O_5, occurring at 500 °C depending on the duration of heating. Traces of green and yellow powder are seen on the surface of H_3PW for 300/2, 300/16, and 400/2 (°C/h) samples. The color changes suggest formation of anhydrous WO_3 (yellow) and reduced W_nO_{3n-1} (blue), which accounts for the green color. When WO_3 is heated in vacuum, reduction occurs forming a variety of tungsten blue materials.[20a]

The results of Table 1 clearly show that the sample treated at 162 °C for 4 h under vacuum is the strongest acid, which should be the anhydrous acid. Reported gas-phase calorimetry and TGA results also indicate that this treatment will produce
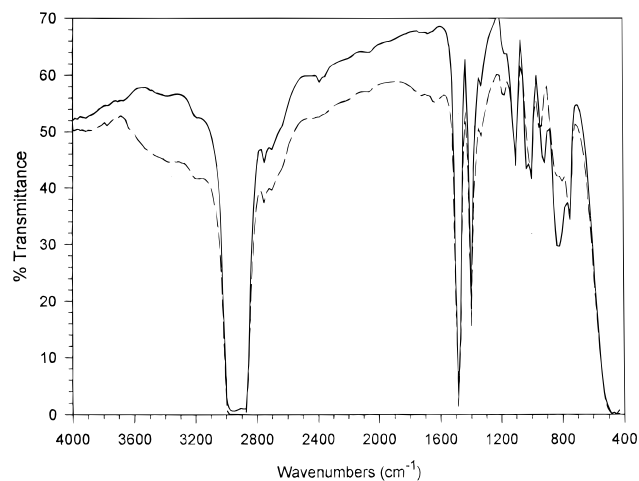
(33) Highfield, J. G.; Moffat, J. B. *J. Catal.* **1984**, *88*, 177.
(34) Southward, B. W. L.; Vaughan, J. S.; O'Conor, C. T. *J. Catal.* **1995**, *153*, 293.
(35) Hayashi, H.; Moffat, J. B. *J. Catal.* **1982**, *77*, 473.
(36) West, F. S.; Audrieth, L. F. *J. Phys. Chem.* **1955**, *59*, 1069.
(37) Hodnett, B. K.; Moffat, J. B. *J. Catal.* **1984**, *88*, 253.

Figure 1. FTIR of H_3PW in Mineral Oil. (—) H_3PW treated at 162 °C for 4 h under vacuum. (- - -) H_3PW taken from the bottle (16H$_2$O). Absorption bands of mineral oil (Aldrich, dried on 3A Molecular Sieves) are in the typical range of 2800−3000 and 1400−1600 cm^{-1}. The preparation of the mull was made in a drybox filled with nitrogen.

the anhydrous acid.[19] The FTIR of this 162/4 sample compared to the purchased sample of $H_3PW \cdot 16H_2O$, Figure 1, shows the absence of the characteristic broad absorption band for water around 3500 cm^{-1}.

To substantiate that the 162/4 (°C/h) sample produces the anhydrous acid with the data in Table 1, a calorimetric titration of the 162/4 (°C/h) sample with water as base in CH_3CN was carried out, giving a $-\Delta H_1$ of 4.2 kcal mol^{-1}. The large K indicates that any excess water in the samples of Table 1 would be coordinated to H_3PW. Since the $-\Delta H_1$ values for the vacuum-dried samples, 128/4, 162/1 and 162/2 (°C/h), are smaller than the 162/4 (°C/h) sample by an amount less than the 4 kcal mol^{-1} found for the monohydrate, we can conclude that the 128/4, 162/1, and 162/2 (°C/h) samples are partially wet. The 128/8 (°C/h) sample is almost as dry as the 162/4 (°C/h) sample, but the total heat evolved indicates a very small amount of water remains. Flowing air is not as efficient as vacuum for drying as shown by the 200/2 versus the 162/2 (°C/h) result. Since the flowing air samples 300/2, 300/16 and 400/2 (°C/h) are expected to have less water than the 200/2 sample, the lower enthalpies suggest some degree of reduction and anhydride formation consistent with the observed color changes on the surface of the solid. A large decrease in the total heat evolved for titration of sample 400/2 (°C/h) is consistent with the decreased acidity reported in the gas−solid calorimetric results[19] and illustrates the insensitivity of the XRD pattern to the changes occurring on drying. The calorimetric results in Table 1 would mitigate against use of H_3PW as an acid catalyst at or above 300 °C.

The hydrated $H_3PW \cdot 16H_2O$ was also titrated with pyridine, giving an $-\Delta H_1$ of 12.9 kcal mol^{-1}. Subtracting $-\Delta H_1$ for the reaction of H_3PW with water (4.2 kcal mol^{-1}) from 21.0 kcal mol^{-1} for the pyridine reaction with anhydrous H_3PW produces $-\Delta H_1 = 16.8$ for the reaction of the monohydrate with pyridine. Solution species of higher water molecularity in $H_3PW \cdot 16H_2O$ than in the monohydrate lead to a more endothermic water displacement. Other complications from the presence of water are evident. With all bases used in this study, properly dried H_3PW leads to the enthalpy order of $-\Delta H_1 > -\Delta H_2 < -\Delta H_3$, Table 3. In some instances, this is not observed in Table 1. Since the reactions involved in steps 2 and 3 for wet samples are not known, the possible incorrect formulation of the equilibria precludes a more detailed analysis of the results in Table 1. These experiments accomplish their

Table 2. Heat Evolved (h'_{exp})[a] Upon Addition of Pyridine to H_3PW in CH_3CN Solvent and That Calculated (h'_{cal}) from Equilibrium Analysis ([H_3PW]$_T$ = 1.39 × 10^{-3} M)

base added × 10⁴ (M)	h'_{exp} (cal)	h'_{cal} (cal)
2.43	0.499	0.504
4.54	0.932	0.936
6.74	1.377	1.372
9.05	1.827	1.813
13.6	2.624	2.621
18.1	3.325	3.341
23.5	4.146	4.147
27.1	4.690	4.683
31.7	5.374	5.372
36.1	6.011	6.012
40.6	6.458	6.459
45.2	6.647	6.648

[a] The base added and h'_{exp} values are summed giving the total base and the total heat after each addition, i.e., 4.54 × 10^{-4} M and 0.932 cal are the sums for the first two additions.

main objective by showing that the treatment at 162/4 (°C/h) produces a sample that evolves the largest total heat, gives the highest $-\Delta H_1$ comparable to that of CF_3SO_3H (vide infra), is driest, and most likely is the anhydrous acid. Unless noted otherwise, all of the results reported in the next sections of this article were obtained on H_3PW samples dried under vacuum at 162 °C for 4 h.

Solution Species. The reaction of H_3PW in CH_3CN with various bases was monitored by UV–vis spectroscopy. The absorption maximum for H_3PW in CH_3CN occurs at λ = 266 nm. The spectra are essentially unchanged when an excess of most of the bases over that required for neutralization of the three protons is added to H_3PW in acetonitrile. Quinuclidine is an exception to this behavior. With this base, the spectra are essentially unchanged up to a 1:1 ratio of base to H_3PW. A slight decrease in absorbance but no band shift is observed up to a 2:1 ratio. At the ratios of quinuclidine to H_3PW greater than 2:1, a band shift from 266 to 251 nm is observed leading to an isosbestic point at 255 nm. Different spectral behavior of H_3PW in different organic solvents has been noted.[38–41] [1]H, ^{17}O, ^{31}P, and [183]W NMR and electronic absorption spectroscopy,[40] of complexes of [DP_2H^+]$_3$[PW^{3-}] (where DP = *N*-methylpyrrolidinone (NMP), 1,1,3,3,-tetramethylurea (TMU), and 1,3-dimethyl-2-imidazolidinone (DMEU)) attribute the changes to reversible intermolecular electron donor–acceptor complexes in solution. The cause of the change with quinuclidine was not pursued in view of predominant interest in the 1:1 species in this work, vide infra.

Calorimetry. The measured amounts of heat (h'_{exp}) evolved from the calorimetric titration of H_3PW with pyridine in acetonitrile are shown in Table 2 along with the calculated values, h'_{cal}, from the data fit to a three-step equilibrium. Attempts to fit the data to a one-step equilibrium (three protons reacting with the same strength) or to a two-step equilibrium (one different and two equivalent) lead to larger sums of the squares of the deviations and meaningless parameters.

The values of K_1, K_2, and K_3 for the pyridine reaction are 2100, 240, and 41, respectively. The corresponding enthalpies, ΔH_1, ΔH_2, and ΔH_3, are −21.0, −11.8 and −18.6 kcal mol^{-1}. The thermodynamic data reveal a very interesting pattern and

(38) Hill, C. L.; Bouchard, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 5148.
(39) Prosser-McCartha, C. M.; Kadkhodayan, M.; Williamson, M. M.; Bouchard, D. A.; Hill, C. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1747.
(40) Hill, C. L.; Bouchard, D. A.; Kadkhodayan, M.; Williamson, M. M.; Schmidt, J. A.; Hilinski, E. F. *J. Am. Chem. Soc.* **1988**, *110*, 5471.
(41) Williamson, M. M.; Bouchard, D. A.; Hill, C. L. *Inorg. Chem.* **1987**, *26*, 1436.
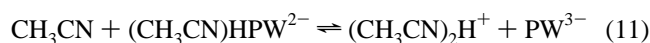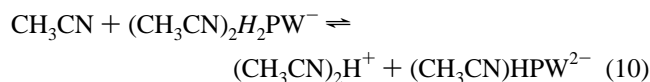
each step will be interpreted separately. The first step of the equilibria existing in solutions of H_3PW in CH_3CN is given by eq 8:

$$CH_3CN + (CH_3CN)_3H_3PW \rightleftharpoons$$
$$(CH_3CN)_2H^+ + (CH_3CN)_2H_2PW^- \quad (8)$$
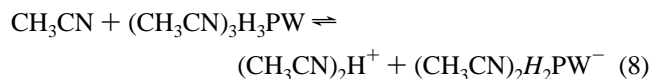
To simplify the discussion, coordination number two is assumed for the proton, anionic H_2PW^- species will be assumed to have two acetonitriles coordinated, and no attempt will be made to distinguish intimate ion-pairing from hydrogen bonding, i.e., species **I** and **II** of eq 1. The position of the equilibrium in eq 8 is unknown, but the pK_a of perchloric acid in acetonitrile[42] is 2 and the pK_{a1} for H_3PW in acetone is 1.6. Slight ionization, eq 8, is expected in acetonitrile from these comparisons, and $-\Delta H_1$ for the reaction with pyridine corresponds predominantly to displacement of $(CH_3CN)_2H_2PW^-$ to form $C_5H_5NHCH_3CN^+$ (eq 9). Both basicity and solvent polarity are needed to dissociate the anion or form a solvent-separated ion-pair.[25]

$$(CH_3CN)_3H_3PW + B \rightleftharpoons BHCH_3CN^+ + (CH_3CN)_2H_2PW^- \quad (9)$$

The second and third ionization steps for H_3PW in acetonitrile proceed to a very small extent and are given in eqs 10 and 11.

$$CH_3CN + (CH_3CN)_2H_2PW^- \rightleftharpoons$$
$$(CH_3CN)_2H^+ + (CH_3CN)HPW^{2-} \quad (10)$$

$$CH_3CN + (CH_3CN)HPW^{2-} \rightleftharpoons (CH_3CN)_2H^+ + PW^{3-} \quad (11)$$
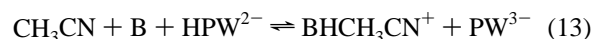
Reaction of the second proton of H_3PW with pyridine involves reaction of the species in eq 10. The lower $-\Delta H_2$ than $-\Delta H_1$ for all bases studied (e.g., 11.8 vs 21.0 kcal mol^{-1} for pyridine) clearly shows that step 2 involves a weaker acid than step 1. Had the reactions in eqs 8 and 10 gone to completion when H_3PW is added to CH_3CN, $-\Delta H_2$ would equal $-\Delta H_1$ because the titration reaction would involve displacement of CH_3CN from $(CH_3CN)_2H^+$ (eq 2) in both instances. This resolves the literature differences by showing that the first two protons removed from H_3PW are not comparable in acidity. Step 2 predominantly involves titration of $(CH_3CN)_2H_2PW^-$, shown in eq 10, giving a smaller $-\Delta H_2$ than $-\Delta H_1$ for all bases studied. The question then arises, why is a large K_2 and a small $-\Delta H_2$ observed for all bases studied (Table 3)? When base reacts with $(CH_3CN)_2H_2PW^-$, the endothermic loss of CH_3CN molecules could occur to form HPW^{2-} as shown in eq 12.

$$(CH_3CN)_2H_2PW^- + B \rightleftharpoons$$
$$BHCH_3CN^+ + HPW^{2-} + CH_3CN \quad (12)$$

With acetonitrile being bound less completely or not at all to the weaker acid HPW^{2-}, ΔS_2 increases and $-\Delta H_2$ decreases for the second step, eq 12.

Equation 12, a more accurate representation of eq 4, also accounts for the smaller K and larger $-\Delta H_3$ observed for step 3. Since endothermic CH_3CN displacement is not involved in step 3, a larger $-\Delta H$ and $-\Delta S$ results than for step 2. Equation 13 represents the equilibrium given in eq 5 for the third step.

$$CH_3CN + B + HPW^{2-} \rightleftharpoons BHCH_3CN^+ + PW^{3-} \quad (13)$$

Note that in contrast to step 1 where one pyridine coordinates, there is an enthalpy contribution from one molecule of pyridine

(42) Angelici, R. *J. Acc. Chem. Res.* **1995**, *28*, 51.

Table 3.   Thermodynamic Parameters[a] for H₃PW−Base[b] (25 ± 1 °C) in CH₃CN Solvent

	Qi	Py	M-Im	Tep	Qn[c]	H₂O	DMA	THF
K_1	4.8×10^2	2.1×10^3	1.5×10^4	3.5×10^4	1.1×10^6	1.0×10^3	6.1×10^6	9.2×10^1
	(± 9.5)	(± 4.0)	$(\pm 1.8 \times 10^2)$	$(\pm 7.4 \times 10^2)$	$(\pm 1.4 \times 10^3)$	(± 0.5)	$(\pm 5.5 \times 10^5)$	(± 1.2)
K_2	2.6×10^2	2.4×10^2	1.1×10^4	4.5×10^3	9.2×10^5	3.8×10^2	2.4×10^6	5.6×10^1
	$(\pm 3.9 \times 10^1)$	(± 3.4)	$(\pm 4.8 \times 10^3)$	$(\pm 1.7 \times 10^3)$	$(\pm 5.2 \times 10^5)$	$(\pm 6.8 \times 10^1)$	$(\pm 3.1 \times 10^5)$	$(\pm 1.7 \times 10^1)$
K_3	5.2×10^1	4.1×10^1	6.5×10^1	7.5×10^2	1.3×10^2	$7.1 \; (\pm 0.7)$	$4.7 \; (\pm 2.6)$	
	$(\pm 1.3 \times 10^1)$	(± 5.8)	(± 7.1)	$(\pm 9.9 \times 10^1)$	$(\pm 4.6 \times 10^1)$			
$-\Delta H_1$	18.1 (±0.4)	21.0 (±0.2)	29.5 (±0.4)	32.2 (±0.7)	42.6 (±2.1)	4.2 (±1.0)	13.2 (±2.0)	11.4 (±0.5)
$-\Delta H_2$	7.1 (±0.2)	11.8 (±0.3)	16.3 (±0.5)	15.3 (±0.3)	18.6 (±0.4)	0.9 (±0.5)	3.4 (±0.5)	0.3 (±0.1)
$-\Delta H_3$	15.9 (±0.7)	18.6 (±0.5)	23.4 (±0.8)	18.0 (±0.8)	26.0 (±1.1)	2.1 (±2.6)	12.0 (±1.9)	
$-\Delta G_1$	3.7	4.5	5.7	6.2	8.3	4.1	9.3	2.7
$-\Delta G_2$	3.3	3.2	5.6	5.0	8.1	3.5	8.7	2.4
$-\Delta G_3$	2.3	2.2	2.5	3.9	2.9	1.2	0.9	
$-\Delta S_1$	48.3	55.1	79.8	87.1	115.0	0.3	13.3	29.2
$-\Delta S_2$	12.9	28.8	36.0	34.7	35.1	−8.8	−18.0	−7.0
$-\Delta S_3$	45.4	55.1	70.0	47.3	77.4	3.0	37.2	

[a] ΔH_i and ΔG_i in kcal mol⁻¹. ΔS_i in cal deg⁻¹ mol⁻¹. [b] Bases are listed as quinoline (Qi), pyridine (Py), *N*-methylimidazole (M-Im), triethylphosphine (Tep), quinuclidine (Qu), *N,N*-dimethylacetamide (DMA), and tetrahydrofuran (THF). The errors are standard deviations calculated by variance−covariance matrix analysis. Deviations for ΔH_2 and ΔH_3 reflect cumulative errors on the measured heat values (h'_{exp}). Since the equilibrium constants are calculated from h'_{exp} values, small errors on these measurements cause large errors on equilibrium constants. Our main criterion for acidity is the enthalpy and these are very well determined. [c] UV−vis spectral changes indicate these data may reflect a more complex reaction.

and one of acetonitrile coordinating to the displaced proton in step 3. With weaker donors, step 3 could involve formation of a hydrogen bonded adduct instead of PW³⁻, and the equilibria would be incorrectly formulated in eq 5 of our analysis. Both steps 2 and 3 may be more complicated than shown above because of reaction of BHCH₃CN⁺ with added base to form B₂H⁺ instead of or in addition to the reactions in eqs 12 and 13. Complexes of heteropolyacids with the organic molecules with the formula [(B₂H⁺)₃][PX³⁻] (X = Mo, W) have been prepared.[38−41] X-ray studies of these complexes show that the B₂H⁺ units do not interact with the polyoxoanions. Spectral studies[38−41] also suggest that the structure of these complexes in solution are similar to those in the solid state. Because of the complications from competing reactions and extents of CH₃-CN displacement, our focus will be on step 1 for acidity comparisons and no further interpretation of steps 2 and 3 will be offered. Clearly, our analysis has accomplished the primary objective by demonstrating that the three protons of H₃PW have very different strengths.

Reactions of H₃PW with Other Bases. Calorimetric titrations were carried out with the bases quinoline (Qi), *N*-methylimidazole (M-Im), quinuclidine (Qn), triethylphosphine (Tep), tetrahydrofuran (THF), water, *N,N*-dimethylacetamide (DMA), and dimethyl sulfoxide (DMSO). The reactions described above for pyridine explain the consistent pattern of $K_1 > K_2 > K_3$ and $-\Delta H_1 > -\Delta H_3 > -\Delta H_2$ for all bases. For THF, the total heat evolved is 1.610 cal, and the exotherm virtually stops when base is added above a 2:1 mol ratio of THF to H₃PW. Therefore, K_3 and ΔH_3 cannot be determined in CH₃CN at these experimental conditions, and the data are analyzed with a two-step equilibrium. When the experimental heats (h'_{exp}) from the titration curves of DMSO are analyzed with a three-step equilibrium, meaningless equilibrium constants and enthalpies result. A reasonable fit is obtained with a 2:1 model when base additions up to a 2:1 mole ratio of DMSO to H₃PW are used. These limited data are fit to a two-step equilibrium giving values of $K_1 = 1.6(\pm 0.6)$, $K_2 = 6.6 \times 10^{-2}(\pm 4.2 \times 10^{-2})$, $-\Delta H_1 = 22.5 \; (\pm 0.3)$ kcal mol⁻¹, and $-\Delta H_2 = 9.2(\pm 4.8)$ kcal mol⁻¹, respectively.

Figure 2 shows an excellent linear relation of log K_1 to $-\Delta H_1$ for all bases except DMA, water, and DMSO. DMA and water lie above the line while DMSO falls below. DMSO and DMA also show a poor correlation of $-\Delta H_1$ to the ECW model. Discussion of the complications encountered with these donors and limitations on the interpretation of these enthalpies will be
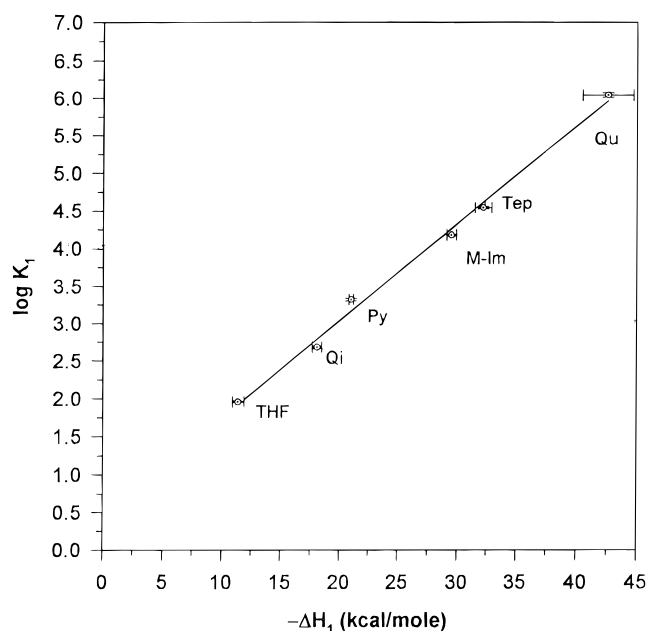

Figure 2. log K_1 versus $-\Delta H_1$ (kcal mol⁻¹) for the reaction of H₃PW with various bases in CH₃CN solvent. The bases used are quinuclidine (Qu), triethylphosphine (Tep), *N*-methylimidazole (M-Im), pyridine (Py), quinoline (Qi), and tetrahydrofuran (THF), respectively.

treated in the section on the ECW analysis. The large experimental errors for K_2 and the small range of K_3 values preclude meaningful log K vs $-\Delta H$ plots for steps two and three.

Enthalpy Analysis with the ECW Model. The ECW approach has been successfully employed[22−24] to correlate many neutral base-neutral acceptor adduct formation enthalpies to the equation

$$-\Delta H = E_A E_B + C_A C_B + W \qquad (14)$$

$E_A E_B$ and $C_A C_B$ describe electrostatic and covalent contributions for the donor (B)−acceptor (A) reaction. The W term is zero for simple donor−acceptor adduct reactions in poorly solvating media, but for a more complex reaction, it incorporates any constant contributions of a particular acid that is independent of the base it reacts with. Equation 14 has, for the most part, been applied to 1:1 adduct formation enthalpies. Recently, a successful correlation of the enthalpies of reaction of CF₃SO₃H

Table 4. Enthalpies (kcal mol⁻¹) and Equilibrium Constants (25 ± 1 °C) for the Reaction of Pyridine with Various Acids[a] in CH_3CN Solvent ($[Acid]_T = 1.39 \times 10^{-3}$ M)

acid	K_1	K_2	K_3	$-\Delta H_1$	$-\Delta H_2$	$-\Delta H_3$
H_3PW	$2.1 \times 10^3 (\pm 4.0 \times 10^1)$	$2.4 \times 10^2 (\pm 3.4 \times 10^1)$	$4.1 \times 10^1 (\pm 5.8)$	21.0 (±0.2)	11.8 (±0.3)	18.6 (±0.5)
H_2SO_4[b]	$1.5 \times 10^2 (\pm 2.0 \times 10^1)$	7.9 (±5.8)		18.4 (±0.2)	0.2 (±0.5)	
CF_3SO_3H	$6.1 \times 10^2 (\pm 5.0 \times 10^1)$			19.9 (±0.2)		
$CH_3C_6H_4SO_3H$	$2.1 \times 10^2 (\pm 5.5 \times 10^1)$			18.7 (±0.2)		
CF_3COOH	$2.8 \times 10^1 (\pm 1.2 \times 10^1)$			14.2 (±1.0)		
ClC_6H_4COOH	$2.1 \times 10^{-1} (\pm 1.0 \times 10^{-1})$			6.5 (±1.9)		

[a] Standard deviations are based on variance−covariance matrix analysis. [b] Concentrated sulfuric acid used for preparation of a standard solution of H_2SO_4 in acetonitrile was 97% w/w, calculated by standardization.

Table 5. Results of ECW Fits for Reactions of H_3PW−Bases in CH_3CN Solvent[a]

base	C_B/E_B	$-\Delta H_{exp}$	$-\Delta H_{ECW}$[b]
pyridine	1.99	21.0	21.3
quinoline	1.27	18.1	17.8
N-methylimidazole	4.24	29.5	29.9
THF	1.33	11.4	10.9
quinuclidine	8.40	42.6	42.2
triethylphosphine	19.75	32.2	32.1
acetonitrile	0.43	0.0	0.07

[a] ΔH in kcal mol⁻¹. [b] Calculated with $2.56(\pm 0.22)E_B + 7.38(\pm 0.07)C_B - 9.36(\pm 0.0)$. Values of E_B and C_B for the bases listed above can be obtained in ref 24. Parameters for triethylphosphine are $E_B = 0.28$ and $C_B = 5.53$.

with various bases[42] to form an ion-pair in dicloroethane has been reported.[43] This encouraged us to attempt a correlation of the $-\Delta H_1$ values for the ionic products of the reaction of a Brönsted acid with the bases in Table 3. The result is the excellent data fit to eq 14 shown in Table 5 for most of the bases studied, giving $E_A^* = 2.56 \pm 0.23$, $C_A^* = 7.38 \pm 0.07$, and $W = -9.36$. The E_A^* and C_A^* parameters characterize the acceptor properties of CH_3CNH^+ in acetonitrile. The W value incorporates constant net solvation energies of products and reactants and the endothermic enthalpy of dissociation of the anion from $(CH_3CN)_3H_3PW$.

The E_A^* and C_A^* values of 2.56 and 7.38 for CH_3CNH^+ compared to the reported values of E_A^* and C_A^* of 4.51 and 5.70 for CF_3SO_3H in dichloroethane suggest that the former is more covalent and much less electrostatic than CF_3SO_3H. With different C_A^*/E_A^* ratios for the different acids involved, the enthalpies of reaction for a series of different bases reacting with H_3PW in CH_3CN and CF_3SO_3H in 1,2-dichloroethane are not expected to plot linearly.

The fit of the H_3PW enthalpies to ECW is an important result for it indicates that the same base properties that correlate neutral donor−acceptor reactions in poorly solvating solvents also determine the basicity order when ionic products are formed from Brönsted acids in acetonitrile. The acid concentration should be held constant to establish basicity orders because variation in the extent of ion pairing with acid concentration will influence the enthalpy measured. The ECW fit shows that the enthalpy contribution from the basicity and polarity of acetonitrile solvent in facilitating ionization of HX is either a constant factor or linear with basicity. As a result, with the acid concentration constant, $-\Delta H$ for reaction of a base in this solvent provides a measure of the donor strength and substantiates earlier discussion on the selection of acetonitrile as a solvent for studying Brönsted acidity.

The enthalpy data for DMSO, H_2O, and DMA do not obey the ECW correlation and reveal some interesting conclusions regarding reactivity. The DMSO reaction could involve bonding to sulfur, which is expected for acceptors with a large C_A^*/E_A^*. With the E_B and C_B values reported[24] for DMSO referring

to oxygen coordination, even an equilibrium mixture of S and O coordination would give an average $-\Delta H$ larger than that predicted by ECW. Unfortunately overlap of the S=O stretching frequency with H_3PW and CH_3CN bands precludes testing this explanation. Water was not included in the ECW analysis because E_B and C_B parameters are only available for the gas-phase monomer and these cannot be used for water aggregates in solution. Solutions of heteropolyacids in DMA are reported to be photochemically redox active.[38−41] The solution resulting from our titration of H_3PW with DMA has a bluish tint, and we attribute the discrepancy with ECW to enthalpy contributions from redox reactions.

The ECW analysis is not only a correlation and predictive tool but can provide thermodynamic data for reactivity that cannot be measured directly. By using E_A^* and C_A^* with E_B and C_B for CH_3CN, the enthalpy of coordinating CH_3CN to $(CH_3CN)H^+$ in acetonitrile is calculated to be 9.4 kcal mol⁻¹. Comparing this quantity to the W value of 9.4 indicates that $(CH_3CN)H^+$ coordinates acetonitrile and $(CH_3CN)_2H_2PW^-$ with equal strength, so displacement of the anion by acetonitrile would have a zero enthalpy contribution. Alternatively, eq 8 occurs to completion producing an ion pair. Adding W of 9.4 kcal mol⁻¹ to $-\Delta H_1$ measured in acetonitrile gives $-\Delta H$ for reactions of bases with CH_3CNH^+ as an acid in acetonitrile.

An Acidity Scale in CH_3CN toward Pyridine. To provide a comparison of relative acidity, the enthalpies of reactions of a series of other acids with pyridine were measured in CH_3CN and are presented in Table 4. Since the position of the ionic equilibria in eq 1 will be concentration dependent, an acid concentration of 1.39×10^{-3} M is used in all experiments and is a defined quantity for our acetonitrile acidity scale. Because of variation in ion pairing, differences less than ±0.5 kcal mol⁻¹ are not considered significant. The $-\Delta H_1$ values furnish the following acidity order: $H_3PW > CF_3SO_3H > p\text{-}CH_3C_6H_4SO_3H \sim H_2SO_4$ (97%) $\gg CF_3COOH \gg ClC_6H_4COOH$. A plot of $\log K_1$ vs $-\Delta H_1$ for the acids studied (Table 4) is shown in Figure 3. The linear free energy−enthalpy relation supports a similar reaction type for all acids. H_3PW is the strongest acid that can be measured with this scale because an acid that is completely ionized in acetonitrile will exist as $(CH_3CN)_2 H^+$, and it was shown earlier that acetonitrile and $(CH_3CN)_2H_2PW^-$ have similar enthalpies of displacement from $(CH_3CN)H^+$.

An enthalpy for the reaction of pyridine with p-$CH_3C_6H_4$-SO_3H in acetonitrile is reported.[44] At low base concentration, a $-\Delta H$ of 18.3 kcal mol⁻¹ results from a limiting reagent estimate in good agreement with our value of 18.7 kcal mol⁻¹. When the limiting reagent approach is used with a 10-fold excess of acid, an enthalpy of 18.6 kcal mol⁻¹ is reported.[44] The $-\Delta H$ is reported to decrease with base concentration and this is attributed to a base-dependent heat of reaction. Our magnitude for K shows this behavior is expected from incomplete protonation of all the base added as a 1:1 ratio is

(43) Drago, R. S.; Joerg, S. *J. Am. Chem. Soc.* **1996**, *118*, 2654.

(44) Arnett, E. M.; Heaksma, R. A.; Chawla, H. B.; Healy, M. H. *J. Am. Chem. Soc.* **1986**, *108*, 4888.
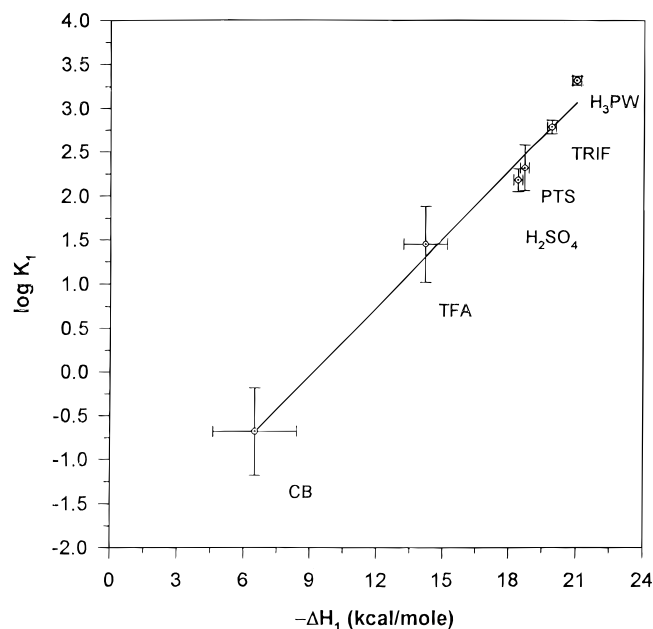
Figure 3. log K_1 versus ΔH_1 (kcal mol^{-1}) for the reaction of pyridine with various acids in CH$_3$CN solvent. The acids used are 12-tungstophosphoric (H$_3$PW), triflic (TRIF), *p*-toluenesulfonic (PTS), sulfuric (H$_2$SO$_4$), trifluoroacetic (TFA), and *m*-chlorobenzoic (CB), respectively.

approached and the true enthalpy of product formation is base concentration independent.

The reaction of pyridine with triflic acid in CH$_3$CN gives an enthalpy of 19.9 kcal mol^{-1}. In acetonitrile the enthalpy of reaction of (CH$_3$CN)H$^+$ with pyridine is calculated as -30.4 kcal mol^{-1}. The difference in the measured enthalpy and this quantity gives 10.5 kcal mol^{-1} as the enthalpy of dissociating the CF$_3$SO$_3^-$ from CH$_3$CNH$^+$ in acetonitrile compared to the W value of 9.4 for dissociating (CH$_3$CN)$_2$H$_2$PW$^-$. Assuming that all acids in the above series form (CH$_3$CN)H(C$_5$H$_5$N)$^+$, similar calculations for the other acids provide an enthalpy scale of conjugate base strengths toward this acid.

An extensive compilation of the dissociation constants (pK_a) in acetonitrile is available.[45] For the acids employed in this work, pK_a's of 7.8, 8.7, and 12.6 are given for sulfuric, *p*-toluenesulfonic, and trifluoroacetic acids, respectively. The pK_a trend is in good agreement with our enthalpy trend, which provides a direct measure of bond strength.

Comparison of Solution and Solid Calorimetric Data. Comparison of the solution enthalpies with those from gas–solid calorimetry is informative. As reported,[21] the gas–solid data contain a dispersion component not present in solution, leading to larger measured $-\Delta H$ values than those corresponding to the donor–acceptor component. Furthermore, the differential heat of gaseous ammonia adsorption at 50 °C for the solid sample treated[17] at 250 °C is claimed to show that all three protons of the solid are titrated, producing the same $-\Delta H$ of $\cong$35 kcal mol^{-1}. There is no solvent leveling or displacement in the gaseous ammonia reaction, but this cannot account for three protons of equivalent acidity. Unfortunately equilibrium constants are not measured in reported gas–solid calorimetric studies.[21] If K_1, K_2, and K_3 decrease slightly for the gas-phase reaction, simultaneous reaction of all three protons would occur, leading to averaged heat evolution and an average $-\Delta H$ of 35 kcal mol^{-1}. The $-\Delta H$ could in reality correspond to the average

(45) Izutsu, K. *Acid–Base Dissociation Constants in Dipolar Aprotic Solvents*; Chemical Data Series No. 35, Blackwell Scientific Publications: Oxford, 1990.

of large, medium, and small enthalpies with similar K's. Slightly decreasing equilibrium constants would account for a $-\Delta H$ slightly higher than 35 with 0.1 mol of NH$_3$ to 1 mol of H$_3$PW added and the small $-\Delta H$ of $\approx$20 kcal mol^{-1} based on a limiting reagent assumption for the remaining weakest site up to a 3:1 NH$_3$ to H$_3$PW mole ratio. Titration of samples with varying water content is reported,[17] but as described above (Table 1) interpretation of these measurements is difficult. Calorimetric titrations with ammonia[19] at 150 °C on samples activated at 150 and 200 °C are also reported. Reaction is practically complete for 2.89 mol of added base with the differential heat decreasing from 48 to 36 kcal mol^{-1} during the titration. At this higher temperature the step equilibrium constants, for steps with decreasing enthalpies, will be closer in magnitude than at lower temperatures. Without a knowledge of the three-step equilibrium constants, the interpretation of the results from a gas–solid enthalpy titration is ambiguous because the measured heat evolved cannot be resolved into contributions from the different steps.[21]

Solution calorimetry unequivocally shows the three protons are not strong acids of equal strength and the discussion offered in this article is relevant to measuring acidity in homogeneous systems. Solid acids have the conjugate base anion as part of the crystal lattice and proton transfer from a Brönsted site produces an intimate ion-pair. The lattice energy of the ion-pair compared to that of the solid acid contributes to $-\Delta H$. Thus, any direct comparison of enthalpies for homogeneous and heterogeneous systems should take into account the differences in the reactions involved.

Conclusions

This study provides thermodynamic parameters for the three-step equilibria of H$_3$PW reacting with a series of bases in acetonitrile solution. The results indicate that the three protons are not of equal strength as proposed from gas–solid calorimetry measurements. Only one strong proton per molecule of acid is furnished for stoichiometric or catalytic reactions in any solvent of basicity equal to or less than CH$_3$CN. Consistent with literature claims of superacidity, the enthalpies in acetonitrile show that, as a monoprotic acid toward pyridine, H$_3$PW is comparable to triflic acid and is stronger than sulfuric acid and *p*-toluenesulfonic acid.

The enthalpies of reactions for the first protonation process were successfully correlated to the ECW model, leading to substantial covalent character ($C_A^*/E_A^* = 2.88$) in the donor–acceptor reactions of the species (CH$_3$CN)H$^+$. With a database of >100 bases in the ECW correlation, enthalpies of reaction of all these bases with H$_3$PW can be predicted. Of even more significance is the ability of the solvation-minimized ECW parameters for neutral donor–acceptor interactions to predict enthalpies for the reaction of Brönsted acids in acetonitrile solvent. This justifies arguments presented for using enthalpies in acetonitrile as a Brönsted acidity scale.

The dehydration of H$_3$PW is complicated by decomposition, and it must be dried carefully to obtain the anhydrous acid. A procedure for accomplishing this is reported. The demonstrated instability of H$_3$PW at 300 °C precludes its use as an acid catalyst at this or higher temperatures.

In any acid-catalyzed reaction occurring in the condensed phase, the reactivity will depend upon the number of protons provided as well as the strength of interaction of the acid with the substrate. Hammett indicators, which provide a measure of the number of acid species supplied, do not measure the strength of the acid–substrate bond. Calorimetry at low base concentration, assuming complete complexation, can provide a

measure of the strength of the interaction for monoprotic acids or when $K_1 > K_2$ for diprotic acids. The determination of both K and $-\Delta H$ furnishes a complete characterization of the strength and amount of acid species. With a linear log K vs $-\Delta H$ plot (Figure 3), the trend in amount and strength is the same for H_3PW in acetonitrile. Thus, the calorimetric measurement of $-\Delta H$ for different acids in acetonitrile solvent provides a temperature-independent Brönsted acidity scale of relevance to homogeneous catalytic reactions in which unusual entropy effects are absent. We emphasize that this is a one-parameter scale and should be applied in a manner consistent with the limitations[46] of such a scale.

(46) Drago, R. S. *Inorg. Chem.* **1990**, *29*, 1379.