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The Solid Acidity of 12-Tungstophosphoric Acid

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The solid acidity of 12-tungstophosphoric acid (H_3PW) has been measured using slurry calorimetry in cyclohexane with pyridine as the probe. Analysis by the Cal-ad method, pyridine adsorption slurry calorimetry coupled with a pyridine adsorption isotherm, shows the protons of solid H_3PW have different strengths. The two different types of acidic protons (sites) in H_3PW have populations, n, and enthalpies of interaction, ΔH, with pyridine in a cyclohexane slurry of $n_1 = 0.08$ mmol g^{-1}, $\Delta H_1 = -32.7$ kcal mol^{-1}, and $n_2 = 0.16$ mmol g^{-1}, $\Delta H_2 = -19.6$ kcal mol^{-1}. The total number of protons titrated (0.24 mmol g^{-1}) confirms that not all of the available protons of H_3PW (1.04 mmol g^{-1}) react with pyridine. These results suggest that the total number of protons titrated could be assigned to the number of protons in every even plane of the lattice ($E00$). The different protons were assigned to the face (n_1) and edge (n_2) positions in the unit cell of H_3PW. The greater number of protons titrated with pyridine (0.24 mmol g^{-1}) than the number of surface protons (0.008 mmol g^{-1}) for H_3PW illustrates penetration of pyridine into the lattice. X-ray diffraction results demonstrate expansion of the H_3PW lattice in which sites 1 and 2 are titrated with pyridine. The observation of single-peak resonances in ^{31}P magic-angle spinning NMR of H_3PW–pyridine adducts demonstrates that proton mobility distributes the anionic charge throughout the sample. The acid sites of H_3PW are confirmed as Brønsted type by Fourier transform infrared spectroscopy. The enthalpies of the most acidic proton measured for solid H_3PW (-32.7 kcal mol^{-1}) and for H_3PW dissolved in acetonitrile (-30.4 kcal mol^{-1}) are in good agreement. © 1999 Academic Press

Key Words: **Cal-ad; heteropolyacids; catalysis; solid acidity; X-ray diffraction; ^{31}P nuclear magnetic resonance.**

INTRODUCTION

Heteropoly acids have attracted interest due to their use as homogeneous and heterogeneous catalysts for redox and acid-catalyzed reactions (1–7). The heteropoly acid 12-tungstophosphoric acid, $H_3PW_{12}O_{40}$ (abbreviated as H_3PW), is the strongest known heteropoly acid. H_3PW has been characterized recently as a superacid in solution by calorimetry (8) resolving conflicting reports from NMR (9), IR (10–13), UV–vis (14), thermal methods (thermogravimetry, differential scanning calorimetry, temperature-programmed reaction, temperature-programmed desorption) (15–17), microcalorimetry with ammonia absorption (18–20), Hammet acidity constants (21), conductivity (22), and the ^{13}C shift of mesityl oxide (23).

The crystal structure of H_3PW (24, 25), determined by X-ray and neutron diffraction (26), is a hexahydrate. The structure can be divided into two parts: a primary part composed of the Keggin anion, and a secondary portion composed of protons and water. The Keggin anion consists of a central PO_4 tetrahedron surrounded by 12 WO_6 octahedra. The WO_6 octahedra are arranged in four groups of three edge-shared W_3O_{13}. These groups, called W_3 triads, link together through shared corners and have a common oxygen vertex to the central phosphorus (27). The structure has an overall T_d symmetry as shown in Fig. 1. The crystal structure of H_3PW shows that the Keggin anions are close packed on a body-centered lattice with the central anion turned 90° to its eight neighbors. Four types of oxygen atoms exist in the structure (terminal, corner-sharing, edge-sharing, and internal), which give rise to four of the fingerprint bands of the Keggin anion in the IR spectrum (13).

The acidic protons and water molecules, which form the secondary structure, contain quasi-planar $H_5O_2^+$ ions hydrogen-bonded to the terminal oxygens of four polyanions. It has been reported that the protons in the hexahydrate rapidly exchange with water (27). In more hydrated heteropoly anions, $H(H_2O)_4^+$ connects the four Keggin anions. On dehydration, a proton occupies the same position as the $H_5O_2^+$ ion and interacts with the four terminal oxygens (2).

It has been found that the Keggin structure of crystalline H_3PW is maintained in solution (27). An earlier report (8) measured the thermodynamic constants describing the acidity of H_3PW in acetonitrile solution by calorimetric titration. The strength and behavior of the solvated H_3PW are thought to be similar to those of solid H_3PW because of the persistence of the Keggin anion in solution.

An additional feature of the solid hydrates is high proton conductivities. The proton conduction in solid H_3PW

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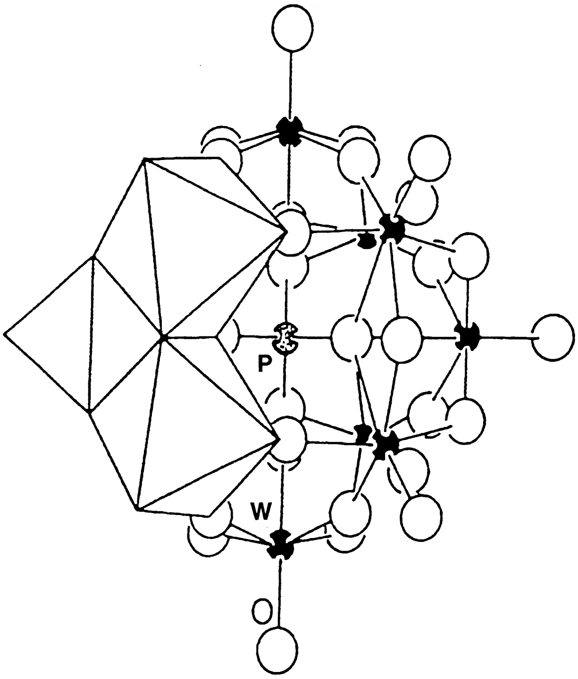

FIG. 1. H_3PW Keggin anion.

is comparable to the proton conduction of water. The low activation energies for conductance (3.3 kcal mol^{-1}) are attributed to the location of waters of crystallization and hydrated protons in the interstices of the large, globular anions (28–30).

This report characterizes the acidity of solid H_3PW using the Cal-ad method. The Cal-ad method uses combined measurements from a calorimetric tiration and adsorption isotherm (31–34). A multiple-site Langmuir equation is used to solve both measurements simultaneously and calculates the number of sites (n_i), equilibrium constants (K_i), and enthalpies (ΔH_i) for different acid sites on these solids. These values allow for a total characterization of solid acid strength and furnish enthalpies for different sites to provide a temperature-independent acidity scale. In addition, differences in the reactivity of solid H_3PW and acetonitrile solutions of this acid are described.

METHODS

Materials

Elemental and TG analysis of the H_3PW (purchased from Aldrich) revealed 16 mol of water per mole of H_3PW. Cyclohexane (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. Dried samples were stored in a container with 4A molecular sieves.

Drying Procedures

H_3PW was dried under vacuum for 4 h at 162 and 200°C. We have shown (8) that treatment of H_3PW in that range of temperature yields the anhydrous acid. Both treatments give similar total heats of reaction with pyridine in cyclohexane. The Cal-ad analysis of H_3PW with pyridine was made in samples treated under vacuum for 4 h at 162°C.

The drying apparatus consisted of a glass fixed-bed reactor with two stopcocks at the ends to close the system. An external small opening under the reactor bed contains a wire thermocouple to control and measure the temperature of the reactor. The sample was weighed, placed into the reactor, and evacuated. The reactor was filled with argon and evacuated two times during the drying period to remove equilibrium water vapor. After 4 h, the sample was cooled to room temperature, and the reactor, filled with argon, was transported to an inert atmosphere box. The samples were stored in vials in a dry box until used. The same apparatus has been successfully used to dry zeolites (34).

Spectral Analysis

A Perkin–Elmer Lambda 6 UV–vis spectrophotometer and quartz cells of 1.0-cm path length were employed for the adsorption experiment. Infrared spectra were obtained with a Nicolet Model 5PC FTIR spectrophotometer in nujol (Aldrich) mulls on NaCl plates. Mulls of dried samples were prepared under an inert atmosphere. The powder X-ray diffraction data were obtained with a Siemens General Area Detector (XRDS) with X-ray tube power at 50 kV and 40 mA (adding time of 10,000 s).

The ^{31}P magic-angle spinning (MAS) NMR spectra of H_3PW and the Py-H_3PW adducts were taken on a Varian Unity 500 NMR spectrometer operating at 202.2640 MHz. The magic angle was tuned using $K^{79}Br$. A recycle delay of 2 s was used. The acquisition time was set to 0.02 ms. Signals were indirectly referenced to 85 wt% phosphoric acid. At least 10 min of signal averaging was allowed for all spectra.

Calorimetric Titrations and Adsorption Measurements

For solid acids, a dilute pyridine solution in anhydrous cyclohexane was added to a slurry of the solid in anhydrous cyclohexane. The choice of cyclohexane was made because it is a nonsolvating solvent in which H_3PW is insoluble. The heat evolved and the equilibrium amount of base in solution were determined in two independent experiments. The calorimetric data generate an isotherm of total heat evolved versus the total moles of base added. Calorimetry, however, does not account for the amount of base in solution. An adsorption measurement provides this information, producing an isotherm of moles of base adsorbed versus moles of base in solution. Additionally, time-dependent UV adsorption was used to ensure that equilibrium of the pyridine with H_3PW was achieved in the time scale of the calorimetric titration. It is important that the concentrations of base added and the ratio (V/g) between the volume of solution (V) and the mass of solid used (g) be the same in both calorimetric and adsorption experiments to interchange the data. Samples were weighed and transferred to an insulated calorimetric cell containing a stir bar. For each titration, 100 ml of cyclohexane is added to the cell. A calibrated syringe, filled with a solution of known concentration of pyridine (e.g., 0.1 mol liter^{-1}) is inserted into the cell along with a thermistor and a heater coil. All these operations are carried out in an inert atmosphere glove bag. The thermistor and heater coil are connected to an electronic bridge and a computer (32). The thermistor is calibrated with the heater coil prior to or immediately after each titration. A set of 12 calibrated brass stops are used for the syringe additions. After each addition the heat evolved from reaction of the base with the sample is measured. The heat from adding the basic solution to the solvent is negligible. Each titration was repeated at least two times.

The adsorption experiments are carried out using 1.0 g of solid, weighed inside a dry box and added to a sealed three-neck round-bottom flask with 100 ml of cyclohexane. The same syringe and calibrated brass stops used in the calorimetric experiment are used for addition of pyridine in this experiment. After each addition of base, at least 3 min is allowed for equilibrium to be reached. Then, a 1-ml sample of solution is removed from the flask and placed into a quartz cell of 1-cm path length and 1-ml volume. One milliliter of cyclohexane is added back into the flask to maintain a constant volume. The absorbance of pyridine is measured at 251 nm to determine its equilibrium concentration in solution. Since the amount of pyridine added is known, the amount of base adsorbed by the solid is calculated by difference. Each adsorption experiment was repeated three times.

Cal-ad Calculations

The Cal-ad analysis is based on simultaneously solving data from calorimetric and adsorption experiments (31–34). The model employs multiple-site equilibrium for the different acid sites present in a solid acid. A Langmuir-type equation is summed over all sites of the solid, according to the equation

$$h/g = \sum (n_i K_i[\mathrm{B}]/(1 + K_i[\mathrm{B}]))\Delta H_i, \qquad [1]$$

where h is the sum of the heat evolved (cal) from the calorimetric titration, g is the mass of solid (g), [B] is the concentration of base in solution at equilibrium (mol liter^{-1}), n_i is the number of each different site, K_i is the equilibrium constant for each site, and ΔH_i is the enthalpy of reaction for each site on the solid.

A Simplex routine is used to calculate the parameters. The data adjusted to the model consist of the moles adsorbed and equilibrium concentration in solution (adsorption) and the sum of the heat and equilibrium concentration in solution (calorimetry). As the calorimetric titration does not measure the equilibrium concentration in solution, this information is obtained through a polynomial series, according to the expression

$$(V/g)[\mathrm{T}] = x^n[\mathrm{B}]^n + x^{n-1}[\mathrm{B}]^{n-1} + x^{n-2}[\mathrm{B}]^{n-2} + x^{n-3}[\mathrm{B}]^{n-3} + \cdots, \qquad [2]$$

where V/g is the ratio of the volume of solution (liters) to the mass of solid (g), [T] is the total concentration of base added for each addition in the calorimetric experiment (mol liter^{-1}), and [B] is the equilibrium concentration of base in solution (mol liter^{-1}). The polynomial is one degree higher than the number of sites (e.g., a third-degree polynomial for two sites, etc.). The x^n terms have the following meaning for a two-site adjustment: $x^3 = K_1K_2(V/g)$; $x^2 = n_1K_1K_2 + n_2K_1K_2 - (V/g)K_1K_2[\mathrm{T}] + (V/g)K_1 + (V/g)K_2$; and $x = n_1K_1 + n_2K_2 - (V/g)K_1[\mathrm{T}] - (V/g)K_2[\mathrm{T}] + (V/g)$. Estimates of n and K values are obtained from a Langmuir analysis of the adsorption data using the equation

$$S_\mathrm{T}B = \sum n_i K_i[\mathrm{B}]/(1 + K_i[\mathrm{B}]), \qquad [3]$$

where $S_\mathrm{T}B$ is the total number of moles of base adsorbed per gram of solid. Cal-ad has been successfully applied for calculation of K, n, and ΔH values for the solid acids silica gel (32), ZSM-5 (34), titania silicalite (35), sulfated tungsten oxide supported on silica gel (36), and sulfated zirconia (37).

RESULTS AND DISCUSSION

Spectroscopic Results of FTIR, ^{31}P MAS NMR, and XRD for H_3PW

Fourier transform infrared (FTIR) spectra of H_3PW were taken before and after reaction with pyridine. The reaction of H_3PW with pyridine does not change the characteristic Keggin bands. However, the region between 1700 and 1500 cm^{-1} shows the pyridinium ion through the presence of well-characterized bands at 1540 and 1485 cm^{-1} (38). Bands attributed to pyridine coordinated to a metal center or hydrogen bonding to a proton were not observed (Fig. 2). This is consistent with the literature (39) and the Cal-ad results (see later) which assign H_3PW as a Brønsted-type acid.

The ^{31}P NMR spectra of H_3PW and several Py-H_3PW species with different mole ratios of pyridine to the total number of acid sites were obtained. Phosphorus-31 NMR of H_3PW shows a single peak at −12.0 ppm (Fig. 3a), corresponding to literature values of −10.9 ppm (40), −12.4 ppm (41), and −11.1 ppm (9) for the anhydrous structure. The

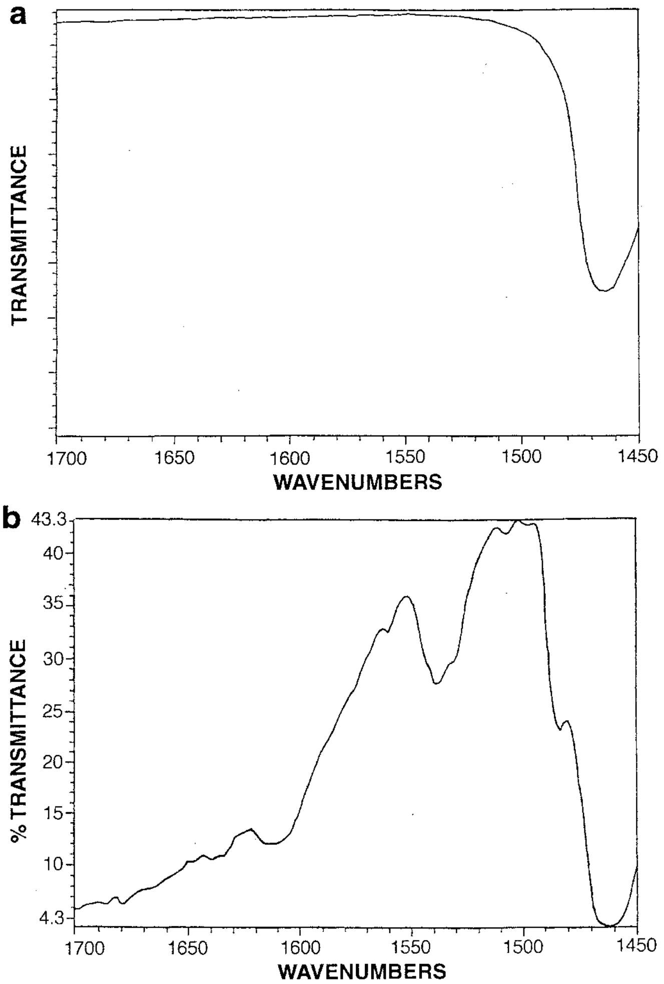

FIG. 2. FTIR spectra of (a) anhydrous H_3PW and (b) H_3PW after reaction with pyridine in cyclohexane (1 : 0.24 mole ratio of H_3PW to pyridine). The intense peaks at 1540 and 1485 cm^{-1} in (b) indicate the presence of pyridinium (H–Py^+) showing H_3PW to be a Brønsted acid.

product spectrum of the first two sites titrated with pyridine (Fig. 3b), 1.04 : 0.24 mole ratio of H_3PW to pyridine, gives only a single resonance at −17.5 ppm. Proton conduction will act to distribute the anionic charge throughout the structure, making the electron density on all the Keggin units similar on the time scale of the NMR experiment. Spectra of 1.04 : 0.08 and 1.04 : 0.12 mole ratio of H_3PW to pyridine also show a single peak at −17.5 ppm, providing further evidence that the protons are mobile in the structure.

The X-ray diffraction (XRD) spectra of H_3PW gives a pattern similar to that reported in the literature (Fig. 4a) (42). The main peaks, related to the strongest reflections, are present at $2\theta = 10.4$, 25.4, and 33.5. The broader peaks indicate loss of crystallinity, as reported for H_3PW dried under different conditions (43, 44). The XRD spectrum for the product attained from the reaction of 1.04 mmol of H_3PW with 0.24 mmol of pyridine shows a few new peaks (Fig. 4b). The most intense peak at $2\theta = 10.4$ splits up into two less intense shoulders at $2\theta = 10.30$ and 10.52. Two new reflections at $2\theta = 9.27$ and 9.98 are present in the powder pattern. These smaller angle reflections indicate a larger *d* spacing in the unit cell to accommodate the pyridine molecules attached to the protons. Other reflections shifted slightly with significant changes in intensity. No large-scale change was observed in the XRD pattern when 0.08 mmol of pyridine was adsorbed on 1.04 mmol of H_3PW (site 1 of Cal-ad analysis, see later).

Cal-ad Analysis of Solid H_3PW

The results of the calorimetric titration and adsorption experiments for pyridine reacting with a slurry of H_3PW in cyclohexane are shown in Fig. 5. The heat evolved from the reaction indicates that only a fraction of the 1.04 mmol of protons in 1 g of H_3PW is titrated. After 0.24 mmol of pyridine was added (about 24% of the moles of protons in a gram of solid), heat evolution essentially stopped, along with the adsorption of pyridine by the solid. The

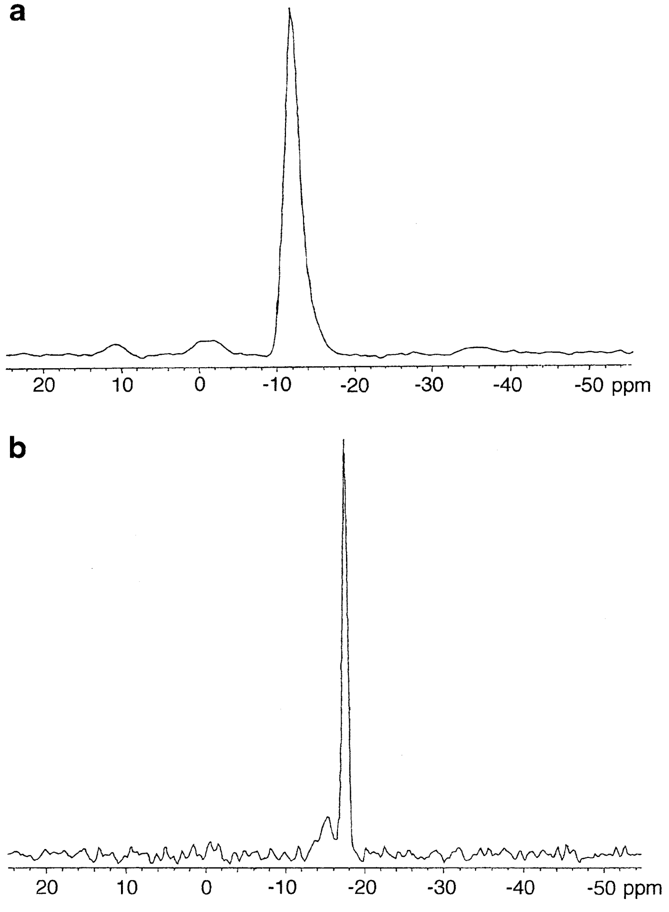

FIG. 3. ^{31}P MAS NMR spectra of (a) 12-tungstophosphoric acid, $\delta^{31}P = -12.0$ ppm, and (b) 1.04 : 0.24 mole ratio H_3PW to pyridine (sites 1 and 2 completely titrated), $\delta^{31}P = -16.5$ ppm.

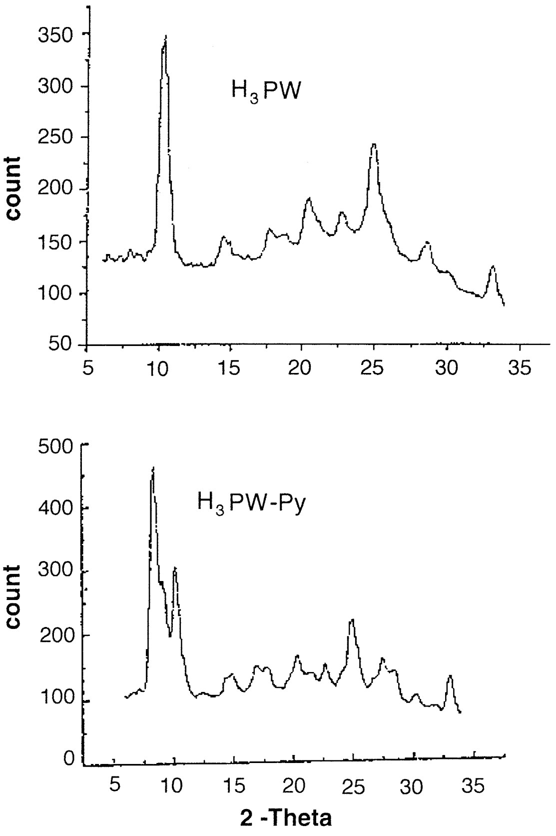

FIG. 4. XRD patterns of (a) H_3PW (dried at 162°C for 4 h under vacuum) and (b) product of reaction of 1.04 mmol of H_3PW with 0.24 mmol of pyridine.

number of surface protons reported (45) for solid H_3PW is 0.008 mmol g^{-1}, and the amount estimated from its surface area (5 $m^2\ g^{-1}$) and the diameter of the Keggin anion (10 Å) is 0.0079 (assuming a spherical molecule). Thus, in addition to reacting with the surface protons, pyridine also penetrates into and reacts with the bulk solid. This result is consistent with reports (46) that the adsorption of polar molecules by H_3PW leads to catalytic reactions in the bulk of the crystal as well as on the surface. This behavior is analogous to that of a concentrated solution and is described as a pseudoliquid phase (6), where nonpolar molecules are not absorbed.

To make sure that the incomplete reaction was not caused by formation of a layer of product on the surface that could not be penetrated by pyridine, a sample of the same calcined solid was ground to finer particles inside the inert atmosphere box and titrated with pyridine. An identical isotherm resulted demonstrating that diffusion due to restrictions of particle size is not a problem and suggesting that pyridine is not able to access certain protons in the tertiary structure.

In the tertiary structure, the protons are located at the center of each edge and face, while the Keggin anions are arranged in a cubic body-centered manner. The unit cell consists of a total of two anions (eight anions at the vertices and one anion in the center of a cube) and six protons (six positioned on the center of the faces and twelve at the edges). The ratio of anions to protons (2 : 6) corresponds to the molecular formula. The Cal-ad results suggest that the total number of protons titrated (0.24 mmol/g) could be assigned to the number of protons in every even plane of the lattice (*E*00) (Fig. 6). The Cal-ad-determined first site

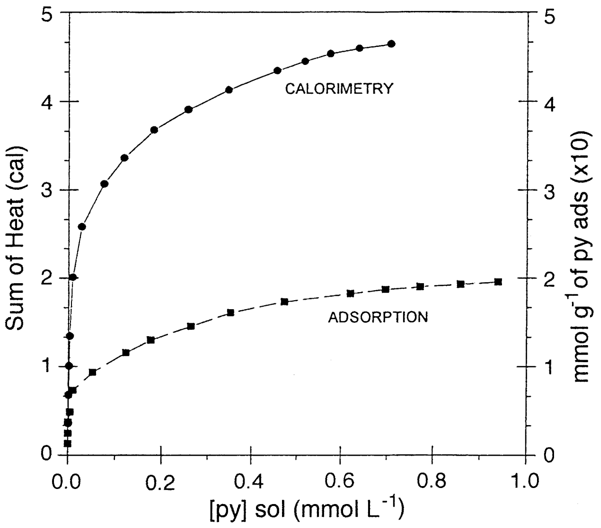

FIG. 5. Isotherms of calorimetry and adsorption of H_3PW titrated with pyridine in cyclohexane.

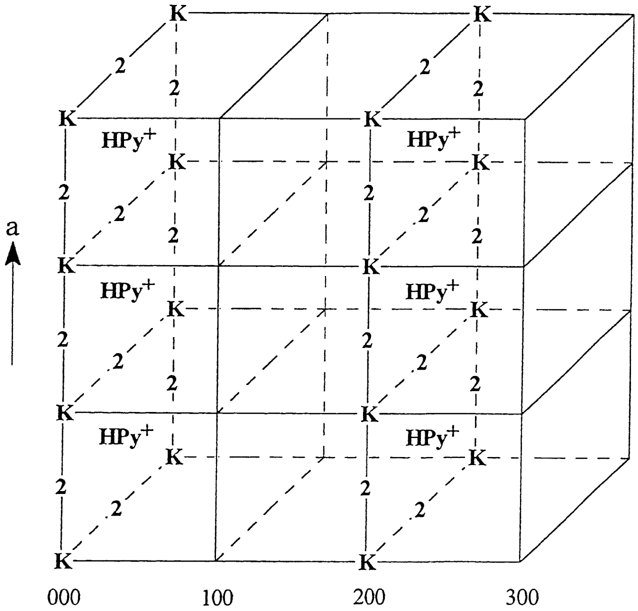

FIG. 6. Structure of the H_3PW–pyridine adduct with site 1 completely titrated. Only the constituents of the even planes are shown for clarity. The face-centered protons of every even plane (*E*00) have reacted with an incoming pyridine molecule to form pyridinium, HPy^+. K represents the Keggin units, and the site 2 protons are represented by 2.

TABLE 1

Comparison of the Cal-ad Site Populations to the Position of the Protons in the Crystal Structure of H_3PW

	Bulk crystal[a]	Even planes[a] ($E00$)	Cal-ad population[c]
Site 1 (mmol g^{-1})[b]	0.35	0.08	0.079 ± 0.002
Site 2 (mmol g^{-1})[b]	0.69	0.16	0.16 ± 0.05

[a] Site 1 for the bulk crystal and the even planes are the face-centered protons. Site 2 represent the edge protons.

[b] To convert from mmol site (g H_3PW)$^{-1}$ to mmol site (mmol H_3PW)$^{-1}$ multiply each value by 2.880 g mmol^{-1} H_3PW.

[c] The units for Cal-ad population are the number of acid sites of a particular type that interact with the probe molecule pyridine for an average gram of material.

would be the face-centered proton, corresponding to about 8% of the total protons in the cell. Summing over all the unit cells in 1 g of H_3PW would yield 0.08 mmol of protons for this site. The second site closely corresponds to the edge protons in this plane. These edge protons represent 16% of the protons of each unit cell. Again, summing over all the unit cells in 1 g of H_3PW would yield 0.16 mmol of sites. Both the individual components and the total number of moles determined in this manner correspond to the Cal-ad results of $n_1 = 0.08$ mmol g^{-1} and $n_2 = 0.16$ mmol g^{-1} (Table 1).

The best model for the Cal-ad acidity of H_3PW is found to be a two-site fit, i.e., two protons with different strengths (Table 2). The results obtained are $\Delta H_1 = -32.7 \pm 0.3$ kcal mol^{-1}, $n_1 = 0.079 \pm 0.002$ mmol g^{-1}, $\Delta H_2 = -19.6 \pm 4.8$ kcal mol^{-1}, and $n_2 = 0.16 \pm 0.05$ mmol g^{-1}. The two-site fit gives a good sum of squares and the deviations on the calorimetry are close to the sum of the squares of the experimental error (1.65×10^{-2}). This model also gives a value for the sum of sites 1 and 2 that is in complete agreement with the estimate of the moles of pyridine reacted from the calorimetric and adsorption experiment. Fitting the data to only one site results in parameters that do not match the calorimetric data. The population of the acid site for this one-site model is only 0.185 ± 0.005 mmol g^{-1}, while experimental results indicate the reaction of 0.24 mmol of pyridine per gram of H_3PW. The three-site fit has a fourfold improvement in the sum of the squares compared with the two-site fit, but the improvement in the deviations in the data fit is not significant compared with experimental error. Within experimental error a three-site fit cannot be distinguished from the two-site fit. This leads to a choice of the two-site fit.

TABLE 2

Cal-ad Results for Three Different Fits to the Data from the Reaction of H_3PW with Pyridine in Cyclohexane

	One-site fit	Two-site fit	Three-site fit
n_1 (mmol g^{-1})[a]	$1.86 \pm 0.05 \times 10^{-1}$	$7.9 \pm 0.2 \times 10^{-2}$	$8.1 \pm 0.2 \times 10^{-2}$
K_1 (M^{-1})	$3.5 \pm 0.81 \times 10^4$	$3.7 \pm 0.02 \times 10^5$	$3.6 \pm 0.02 \times 10^5$
$-\Delta H_1$ (kcal[b] mol^{-1})	25.6 ± 1.1	32.7 ± 0.3	32.1 ± 0.3
n_2 (mmol g^{-1})[a]		0.16 ± 0.05	0.08 ± 0.05
K_2 (M^{-1})		$2.9 \pm 1.0 \times 10^3$	$3.0 \pm 2.6 \times 10^3$
$-\Delta H_2$ (kcal[b] mol^{-1})		19.6 ± 4.8	25.0 ± 5.6
n_3 (mmol g^{-1})[a]			0.09 ± 0.08
K_3 (M^{-1})			$2.5 \pm 1.9 \times 10^3$
ΔH_3 (kcal[b] mol^{-1})			15.1 ± 12.2
U[c]	1.60×10^{-1}	6.59×10^{-3}	1.65×10^{-3}

[a] To convert from mmol g^{-1} to mmol site (mmol H_3PW)$^{-1}$ multiply each value by 2.880 g mmol^{-1} H_3PW.

[b] Conversion: 1 kcal = 4.184 kJ.

[c] The quantity U is the sum of squares of residuals, calculated for calorimetry as $\sum(h'_{\text{exp}} - h'_{\text{cal}})^2$.

The results from Cal-ad using pyridine as a probe differ from those of the microcalorimetry of gaseous ammonia adsorption (18–20). In the ammonia studies, all of the protons in H_3PW react and the enthalpy decreases from −48 to −39 kcal mol^{-1} over the titration. These enthalpies contain both donor–acceptor and dispersion contributions. The donor–acceptor enthalpies of reaction of H_3PW with pyridine indicate that only 24% of the available protons react and these have different strengths (−32.7 and −19.6 kcal mol^{-1}). These differences are attributed to the small size and stronger basicity of ammonia. The smaller NH_3 molecule is able to occupy the position originally allocated to water in the hydrate without appreciable change in lattice dimensions or energy.

The assignment of the protons that can react with pyridine to the faces and edges of the unit cell accounts for the two sites found in the titration of H_3PW. The unit cell of this preparation is thought to be identical to that of the hexahydrate, bcc. Pyridine initially reacts with one of the six available face protons, producing site 1 of the titration. This reaction has an enthalpy of $\Delta H_1 = -32.7$ kcal mol^{-1} and n_1 of 0.08 mmol g^{-1} (about 1 of the 6 face protons available in the unit cell). With one equivalent of pyridine attached to the structure, additional pyridine is in effect titrating $(C_5H_5NH)^+H_2PW^-$. The second site has an enthalpy of $\Delta H_2 = -19.6$ kcal mol^{-1} and consists of $n_2 = 0.16$ mmol g^{-1} (about 4 of the total 12 edge protons in the unit cell). Considering the fraction that each proton shares in the unit cell, the ratio of face protons to edge protons (1 : 2) titrated by pyridine gives the Cal-ad ratio of n_1 to n_2 (1 : 2). The sum of the n_1 and n_2 values from Cal-ad, 0.24 mmol g^{-1}, confirms that protons have reacted that are located inside the solid as well as on the surface.

Comparison of Acidity of H_3PW in the Solid State and in Solution

The acidity of H_3PW was measured calorimetrically in a solution of CH_3CN (8). In a homogeneous system of a solvent of equal or weaker basicity than acetonitrile, the first proton of H_3PW behaves as a strong acid with the other remaining protons partially dissociated. This behavior is different from that reported for H_3PW in acetic acid solution (23). According to ECW analysis (8), the first proton has an enthalpy of -30.4 kcal mol^{-1} in a reaction with pyridine. The value obtained in this work (-32.7 kcal mol^{-1}) is in good agreement with Ref. (8). This correlation demonstrates that enthalpies can be used to compare neutral donor–acceptor interactions and ionic products in low-polarity solvents, such as acetonitrile, as well as nonpolar solvents, such as cyclohexane. This comparison is possible only if the contribution of solvation of the polar solvent can be quantified. By using the ECW model, an estimate of the enthalpy of dissociation of the anion from $(CH_3CN)_3H_3PW$ and the net solvation energies of the products and reactants was obtained (8).

As previously reported (8), equilibrium exists between the completely dissociated ion pair and hydrogen bonding species for the H_3PW in acetonitrile:

$$B_{sol}+H\text{–}X_{sol} \rightleftharpoons \underset{(a)}{B\text{--}H\text{–}X_{sol}} \rightleftharpoons \underset{(b)}{B\text{–}H^{+}\text{--}X^{-}_{sol}} \rightleftharpoons \underset{(c)}{BH^{+}_{sol}+X^{-}_{sol}}. \qquad [4]$$

The first proton of H_3PW is likely to be completely dissociated (c); however, the second and third protons are believed to spread between species similar to (a) and (b). The solvent may influence the association, proton transfer, and dissociation steps. The main factor that determines the position of a Brønsted acid–base equilibrium in Eq. [4] is the differential solvation of the covalent and the ionic hydrogen-bonded complexes (a) and (b). For H_3PW in CH_3CN, the other steps were interpreted as possible mixtures between species (b) and (c). Those steps require a more detailed model of calorimetric data to better determine the thermodynamic parameters of deprotonation.

There are fewer complications related to the cyclohexane solvent. Cyclohexane has no specific interactions with solute molecules. It has a low dielectric constant, and therefore only adducts and ion pairs are expected in solution [products analogous to (a) and (b) from Eq. [4]]. H_3PW is a strong Brønsted acid and formation of an ion-pair product, where the proton is completely transferred to the base [product (b)], is anticipated. Unfortunately, not all protons of H_3PW could be probed by pyridine in cyclohexane. Comparison of the second enthalpy in cyclohexane ($\Delta H_2 = -19.6$ kcal mol^{-1}) with that obtained in CH_3CN ($\Delta H_2 = -11.8$ kcal mol^{-1}) is only speculative, because the enthalpy of solvent dissociation of the anion $(CH_3CN)_2H_2PW^-$ is not accurately known. If this enthalpy is in the same order of magnitude (8) as that of the dissociation of acetonitrile from $(CH_3CN)_3H_3PW$ ($\Delta H = -9.7$ kcal mol^{-1}), there is a close agreement between the acidity measured by both experiments ($\Delta H_{2\ ACN} = -21.5$ kcal mol^{-1} after correcting for the displacement of CH_3CN from $[(CH_3CN)_2H_2PW^-]$.

CONCLUSIONS

This work provides thermodynamic constants for H_3PW reacting with pyridine in cyclohexane slurry. The Cal-ad method indicates that solid H_3PW has two different strength acid sites and that the first site is significantly stronger than the second. Both sites are Brønsted-type as confirmed by FTIR spectroscopy. This achievement disagrees with previous claims by gas–solid calorimetry that all protons on solid H_3PW are equivalent. The large number of sites (0.24 mmol g^{-1}) titrated compared with the number of surface protons (0.008 mmol g^{-1}) demonstrates penetration of the solid by pyridine. XRD results confirm the opening of the lattice as pyridine absorbs on sites 1 and 2. Mobility of the protons is seen using ^{31}P MAS NMR spectra of H_3PW–pyridine adducts showing single peaks for different ratios of acid to pyridine. The conduction of the protons serves to spread the charge throughout the structure, lowering local charge buildup and facilitating the high acidity observed. Comparison of the enthalpy of interaction of pyridine with H_3PW measured in acetonitrile solution to that of solid H_3PW measured in cyclohexane slurry shows close agreement between the acidities measured by both experiments.

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