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Acidity Measurements on a Heteropolyacid Hydrate in Acetic Acid Solution: A Case of Three Hydrons Ionizing Independently, Rather Than Consecutively

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Acidity measurements by ^{13}C NMR spectroscopy with mesityl oxide (2) as indicator (the $\Delta\delta$ method) have been conducted on phosphotungstic acid, $H_3PW_{12}O_{40}$ (1) at various levels of hydration, $H_3PW_{12}O_{40} \cdot xH_2O$ (1b) in concentrated solution in acetic acid. Extrapolation to infinite dilution of indicator allowed the determination of the H_0 acidity function. A comparison with the strong acids, sulfuric and perchloric, indicate that even in this solvent of low basicity the three hydrons of 1 dissociate independently, rather than consecutively as considered previously. The molecule of the heteropolyacid is thus equivalent to three molecules of strong acid in solution and behaves in essence like the solid acids, having acid sites of the same strength. Comparison with other acids has to be made at triple concentration of the latter and shows that the complex acid 1 is significantly stronger than perchloric acid, which in turn is stronger than sulfuric acid, as already known.

INTRODUCTION

There are in the literature a large number of publications on heteropolyacids, especially in connection with the study and application of their catalytic properties. A combination of acid and redox properties, solubility in both water and organic solvents, and good activity in the solid state as well, explain the sustained interest of many research groups in these compounds (1).

The acidity of heteropolyacids has been studied by conductimetry (2) and potentiometric titration (3) in very dilute solutions in water as well as in organic solvents. HPAs are polybasic acids but only one dissociation constant could be determined in the experiments; the dissociation constants of the remaining hydrons[1] (4) were estimated. The ratio $K_1 : K_2 : K_3$ for $H_3PW_{12}O_{40}$ (1) was thus reported as 1 : 0.04 : 0.004; similar ratios were listed for other HPAs (1c).

In other studies, the acidities of concentrated solutions (up to 60%) of HPA in water and in acetic acid (AcOH) were measured by the Hammett indicator method (5). In water, an undetermined amount of doubly dissociated acid was considered to be formed, whereas in acetic acid it was considered that the acidity reflects the first dissociation step of the HPA (6). Based on those measurements, it was concluded that at these concentrations two HPA-s, $H_3PW_{12}O_{40}$ (1) and $H_4SiW_{12}O_{40}$ are of the same strength and are 10 to 30 times stronger than sulfuric or perchloric acid (1c, f, 6).

The compositions of the samples used for the acidity measurements reported in literature were not described satisfactorily. Thus, it was indicated that the HPA used contained water of hydration, but the amount of water was not given. Moreover, the acids used contained "no more than 10%" Na ions, which means that the first hydron was neutralized up to 10% (6b). The acidity measured must have been significantly lower than that of the pure acids: contrary to the claim of the previous authors (6b) we have found that addition of very small amounts of base to an acid changes significantly the extent of hydronation of the indicator, which is a measure of the strength of the acid (7). Also, the acid strength of solutions of **1** with concentration expressed in mole/liter was compared (6b) with the strength of sulfuric acid at concentrations numerically equal, but in units of molal concentrations (8).

We undertook to examine the strength of a HPA, **1**, using the ^{13}C NMR method of acidity measurement (7). This method has been used for establishing the relative hydronating abilities (7) of strong acids and superacids (9) and more recently for determination of the acidity function of simple acids like sulfuric, perchloric, and phosphoric (7, 10), as well as complex acids (11) and even samples of industrial strong acid catalysts (7). Information about the structure of and reactions occurring within complex acids has also been obtained from these measurements (11b, c). We present here the results of our study

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[1] The name "hydron" has been recommended for the positive ion of hydrogen of natural isotopic distribution, to be distinguished from the isotopically pure "proton," "deuteron," and "triton" (4).

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of **1** by this approach, with an unsaturated ketone, mesityl oxide (**2**), as indicator.

EXPERIMENTAL

Materials. Phosphotungstic acid x-hydrate was obtained from Aldrich and used as such. The lot used had met the following specifications: ≤0.005% NH_4^+, ≤0.005% heavy metal cations (Pb), ≤0.003% Fe, and ≤0.01% Na (12). The level of hydration, $x = 22$, (**1a**) was determined by thermogravimetric analysis (TGA). Commercial mesityl oxide (**2**, min. 98% purity) and glacial acetic acid were also used as purchased. The latter was titrated as 99.2%; the water it contained was included in the amount indicated in the composition of solutions given below. The required concentrations of perchloric and sulfuric acids were obtained by addition of distilled water to commercial 71% $HClO_4$ and 96% H_2SO_4, respectively, and checked by titration (7). Phosphoric acid was available from previous work (11c).

Procedures. For acidity measurements the ^{13}C NMR spectra of the indicator **2** in solutions of the concentrations indicated in the tables were recorded at 75.468 MHz on a Bruker MSL 300 instrument, at 22.5°C. A number of 16-K points both in the time domain and for the Fourier transform gave a digital resolution of 0.03 ppm. An inverse gated decoupling program was used, with quadrature phase cycling, decoupling during acquisition (49 ms), and a decoupling preirradiation of 1.5 s to establish NOE between the recycling delay (8 s) and the excitation pulse (9 μs, 90° pulse) (7).

The TGA experiments were run under nitrogen (40 ml/min), on a Hi-Res TGA 2950 analyzer from TA Instruments. The analysis comprised heating at 10 deg/min from 24 to 100°, maintaining at 100° for 10 min, heating at 10 deg/min to 280°, maintaining there for 5 min, and heating at 10 deg/min to 550°.

RESULTS AND DISCUSSION

The hydronation of the indicator **2** is presented in Eq. 1. Because the acid–base reaction of Eq. [1] is fast, the chemical shifts of the C-13 NMR signals for the mixture of **2** and **3** are the weighted average of the values for the two species and are a measure of the extent of hydronation (ratio **3**:**2**). As explained previously, most of the positive charge in the conjugate acid **3** is localized in the β position; the α position carries little charge. Therefore, our method uses the chemical shift difference between the signals for C(β) and C(α) (Δδ, Eq. [2]) as a measure of the extent of hydronation free of solvent effects (7, 10, 13). It was also found that this quantity varies linearly with the total concentration of indicator (7, 14). An acidity function can be derived by the use of the chemical shift difference at infinite dilution (Δδ°), obtained by a short extrapolation of the linear correlation of Δδ with the total concentration of indicator (Eq. [3]) (7, 10). The slope of this correlation, *s*, depends upon acidity, being the most negative in the medium where the concentrations of **2** and **3** are equal (7). A calibration of Δδ° with the Hammett acidity H_0 of sulfuric acid solutions allows the determination of this acidity function for any other acids (7, 11).

TABLE 1

Acidity Comparisons Based on Chemical Shift Differences (Δδ) of Mesityl Oxide

No.	Mixtures and their molar ratio	Conc. of **1** (*m*)	Δδ	Slope
1	$H_3PW_{12}:H_2O = 1:165$	0.062	35.46	
		0.045	35.42	
		0.024	35.40	
		0.0	35.43[a]	0.0
2	$H_3PW_{12}:H_2O:AcOH = 1:23.14:42.77$	0.218	38.62	
		0.072	38.92	
		0.037	38.99	
		0.0	39.06[a]	−2.0
3	$H_2SO_4:H_2O:AcOH = 1:22.94:42.39$	0.285	34.81	
		0.148	34.83	
		0.066	34.84	
		0.0	34.84[a]	0.0
4	$HClO_4:H_2O:AcOH = 1:22.78:42.43$	0.276	34.91	
		0.149	34.94	
		0.066	34.91	
		0.0	34.92[a]	0.0

[a] Δδ°.

$$\underset{\mathbf{2}}{\text{Me-CO-}\overset{\alpha}{\text{C}}\text{H}{=}\overset{\beta}{\text{C}}\text{Me}_2} + AH \rightleftarrows \underset{\mathbf{3}}{\text{Me-C(OH)}{=}\overset{\alpha}{\text{C}}\text{H-}\overset{\beta}{\text{C}}{}^{+}\text{Me}_2} + A^- \tag{1}$$

$$\Delta\delta = \delta C(\beta) - \delta C(\alpha) \tag{2}$$

$$\Delta\delta = s([B] + [BH^+]) + \Delta\delta°. \tag{3}$$

Mesityl oxide (**2**) in a 49.14% solution of **1** in water had a Δδ° value (Table 1, entry 1) between those reported earlier (7) for acetic acid (H_0 0.0, (5c)) and dichloroacetic acid (H_0 − 0.75 (5c)). This strength is below the acidity range for which ketone **2** can be used with confidence for determination of acidity functions (7). Indeed, the Δδ values do not change with concentration of **2**, indicating that the latter is not hydronated in this medium. We examined, therefore, the spectra of **2** at three concentrations in a 56% solution of a hydrate 1.22 H_2O (**1a**) in acetic acid. The pertinent chemical shift differences are shown in Table 1, entry 2. The acidity of the system judged from the Δδ° value is also low, but the nonzero value of the slope s in Eq. 3 indicates that the observed change in chemical shifts comes from a partial, low level, hydronation, rather than from hydrogen bonding (7).

The molar ratio HPA : H_2O : AcOH in the solution of **1a** was 1 : 23 : 43. Such a ratio corresponds to 20% aqueous sulfuric or perchloric acid dissolved in acetic acid. At this dilution all equally concentrated solutions of strong acids consist of the equivalent amount of hydronium ions and have the same strength. Indeed, sulfuric and perchloric acid in water–acetic acid 1 : 23 : 43 exhibit the same $\Delta\delta°$ (Table 1, entries 3 and 4), because the concentration of hydronium ions in solution, equal to the analytical concentration of acid, is the same in both cases. The slope s of the correlation with Eq. [3] is near zero, indicating very little protonation. If the hydrons in the HPA solution were produced by the first step of dissociation of the latter, their concentration in solution should be the same as for the other two acids, because each molecule would produce one hydronium ion and the analytical concentration of the acid was the same in the three cases. The same acid strength should then be manifested by all three acids. The significantly greater level of hydronation of the indicator observed in that medium (Table 1, entry 2) would require that the first hydron of **1** dissociate more than 100%!

There is a simple way, however, to rationalize these results. Because of the size of the molecule, the three hydrons of **1** ionize as if coming from different molecules. The negative charges are delocalized in the Keggin structure (1a, b) such that there is no electrostatic or electronic destabilization introduced by the second and the third ionization. It was suggested that HPAs are normally fully dissociated including the third step in aqueous solution (1e) (see, however, the different conclusion reached by the same authors elsewhere (6)). We see now that the three hydrons of **1** dissociate independently, rather than consecutively, even in a solvent of low basicity, like acetic acid. In order to evaluate the strength of an acid site on the HPA molecule in solution one should compare the latter with a solution three times as concentrated of perchloric or sulfuric acid. Thus, the behavior of the HPA molecule is similar to that of an inorganic solid acid, for instance a zeolite, in which acid sites of similar strength exist on the surface of the crystal. Considering the issue from the opposite direction, we can observe that the increase in the number of acid sites beyond a certain point should introduce a heterogeneity in the acid strengths on such a surface even if the structure of the sites is identical, because the negative charge created by ionization of one site hinders the ionization of closely located adjacent sites. At this point the crystal starts resembling a molecule of a polybasic acid. What is the site density for which the centers would start interacting should depend upon the structure of the material. For the Keggin structure of **1**, the three "sites" are in terms of relative acid strength still "infinitely separated." It can be noted that microcalorimetric measurements indicated that the heat of adsorption of ammonia on solid **1** is similar for the three steps (15).

Compositions with less water of crystallization than **1a**, $H_3PW_{12}O_{40} \cdot xH_2O$ (**1b**, $x < 22$) were prepared by drying **1a**. It has been known that six water molecules are bonded strongly to the phosphotungstic acid (1e). Indeed, mild drying of a higher hydrate forms a hexahydrate (16). A combination of X-ray and neutron diffraction analyses showed that this material is best represented as an ionic structure $HPA^{3-} \cdot (H_5O_2^+)_3$ (17). Our TGA analysis showed that **1a** loses 16 out of the 22 molecules of water to 100° (maximum at 75–85°). We obtained the same hexahydrate (**1b**, $x = 6$) upon heating a sample of **1a** for 2 h in a bath of 100°, under vacuum. Further heating removes the other 6 molecules of water to 280° (maximum at 180–185°). Thus, our experiments corroborate the earlier report that about six molecules of water are strongly retained and are lost upon heating to 320° (1d), rather than the report that only about one molecule of water is retained by this HPA at 100° (16). Another 1.5 molecule of water is removed in the TGA to 550° (a not-well-defined maximum at 465–480°) with the decomposition of the HPA, in agreement with the literature data (1d, 16). The temperatures of the maxima for the second and third step are somewhat dependent upon the rate of heating.

We found that the hexahydrate is not soluble in AcOH to give a ratio of HPA : AcOH of 1 : 43. The other solutions were most conveniently prepared by dissolving in AcOH a mixture of **1a** and hexahydrate in the appropriate ratio. The most concentrated solution obtained had $x = 7.15$.

Solutions of **1b** at various levels of hydration ($7 < x < 22$) in acetic acid at two ratios **1** : AcOH were examined and are shown in Table 2. Their composition is described both in terms of moles of water and acetic acid per mole of HPA (column 2) and in terms of moles of water and acetic acid per mole of acid sites on HPA (column 3). It is the latter description which is used to compare the HPA with solutions of sulfuric acid and perchloric acid in AcOH shown in Table 3 and Fig. 1. A solution of phosphoric acid in AcOH was also studied (last entry of Table 3), but this acid was too weak to warrant further investigation. We preferred to express the compositions in mole ratios for all acids, but in order to allow a comparison with the measurements reported in the literature (6), the density of a few mixtures was determined and their molar concentrations are given in the footnotes of Table 2.

Values for the H_0 acidity function calcuated from the $\Delta\delta°$ parameter are also given in Tables 2 and 3. Because our earlier work provided well calibrated $\Delta\delta°$ values only for acids stronger than $H_0 - 3$, the values more positive than that are uncertain and are given in parentheses. The results indicate that in acetic acid–water mixtures **1** is

TABLE 2

Chemical Shift Differences (Δδ) for Mesityl Oxide Hydronated by Phosphotungstic Acid on Acetic Acid

No.	$H_3PW_{12}:H_2O:AcOH$	$H^+/H_2O/AcOH$	Conc. of **1** (*m*)	Δδ	Slope	Ho
1	1 : 23.14 : 42.77	1 : 7.71 : 14.26	0.218	38.63		
			0.072	38.87		
			0.037	39.01		
			0.0	39.06[a]	−2.03	
2	1 : 19.09 : 42.40[b]	1 : 6.36 : 14.13	0.166	41.09		
			0.087	41.47		
			0.039	41.73		
			0.0	41.92[a]	−5.06	(−1.55)
3	1 : 17.55 : 42.88	1 : 5.85 : 14.29	0.181	41.21		
			0.080	41.67		
			0.036	41.89		
			0.0	42.05[a]	−4.66	(−1.59)
4	1 : 16.81 : 42.80	1 : 5.60 : 14.27	0.185	41.96		
			0.094	42.41		
			0.043	42.74		
			0.0	42.95[a]	−5.40	(−1.90)
5	1 : 15.83 : 42.71	1 : 5.28 : 14.24	0.155	42.25		
			0.073	42.74		
			0.036	42.99		
			0.0	43.20[a]	−6.21	(−1.98)
6	1 : 14.85 : 42.77[c]	1 : 4.95 : 14.26	0.176	42.70		
			0.069	43.29		
			0.038	43.64		
			0.0	43.82[a]	−6.46	(−2.20)
7	1 : 13.66 : 42.88	1 : 4.55 : 14.29	0.157	43.45		
			0.085	44.00		
			0.036	44.42		
			0.0	44.69[a]	−8.00	(−2.50)
8	1 : 12.65 : 42.67	1 : 4.22 : 14.22	0.176	44.39		
			0.085	45.10		
			0.041	45.52		
			0.0	45.84[a]	−8.30	(−2.80)
9	1 : 11.42 : 42.72[d]	1 : 3.81 : 14.24	0.162	45.94		
			0.084	46.75		
			0.036	47.20		
			0.0	47.57[a]	−10.02	−3.26
10	1 : 10.44 : 42.68	1 : 3.48 : 14.23	0.166	47.04		
			0.086	48.04		
			0.042	48.56		
			0.0	49.08[a]	−12.25	−3.37
11	1 : 9.31 : 42.74	1 : 3.10 : 14.25	0.163	49.04		
			0.096	49.79		
			0.048	50.31		
			0.0	50.83[a]	−10.97	3.63
12	1 : 7.15 : 42.64[e]	1 : 2.38 : 14.21	0.186	52.38		
			0.093	53.83		
			0.043	54.72		
			0.0	55.40[a]	−16.29	−3.93
13	1 : 24.18 : 62.97[f]	1 : 8.06 : 20.99	0.181	38.27		
			0.089	38.43		
			0.045	38.53		
			0.0	38.61[a]	−1.89	
14	1 : 16.70 : 62.97[g]	1 : 5.57 : 20.99	0.181	40.47		
			0.099	40.86		
			0.045	41.09		
			0.0	41.29[a]	−4.52	(−1.34)
15	1 : 11.67 : 62.44[h]	1 : 3.89 : 20.08	0.173	44.13		
			0.087	44.90		
			0.038	45.36		
			0.0	45.70[a]	−9.08	(−2.76)
16	1 : 7.68 : 62.62	1 : 2.56 : 20.87	0.180	49.57		
			0.085	50.73		
			0.047	51.37		
			0.0	51.89[a]	−13.02	−3.75

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[a] Δδ°.

[b] 0.320 *M* **1** in 88.10% AcOH.

[c] 0.329 *M* **1** in 90.56% AcOH.

[d] 0.335 *M* **1** in 92.57% AcOH.

[e] 0.346 *M* **1** in 95.21% AcOH.

[f] 0.230 *M* **1** in 89.70% AcOH.

[g] 0.240 *M* **1** in 92.63% AcOH.

[h] 0.246 *M* **1** in 94.69% AcOH.

TABLE 3

Chemical Shift Differences (Δδ) for Mesityl Oxide Hydronated by Strong Acids in Acetic Acid

No.	Acid (HA)	HA : H_2O : AcOH	Conc. of **1** (*m*)	Δδ	Slope
1	H_2SO_4	1 : 8.45 : 10.47	0.256	35.78	
			0.131	35.81	
			0.078	35.84	
			0.0	35.87[a]	−0.35
2	H_2SO_4	1 : 16.79 : 14.42	0.274	34.97	
			0.128	35.00	
			0.059	35.04	
			0.0	35.05[a]	−0.29
3	H_2SO_4	1 : 11.93 : 14.27	0.266	35.17	
			0.130	35.23	
			0.063	35.19	
			0.0	35.22[a]	−0.17
4	H_2SO_4	1 : 7.82 : 14.17	0.271	35.46	
			0.139	35.49	
			0.057	35.52	
			0.0	35.54[a]	−0.30
5	H_2SO_4	1 : 5.38 : 14.33	0.259	35.72	
			0.129	35.81	
			0.061	35.84	
			0.0	35.89[a]	−0.67
6	H_2SO_4	1 : 4.09 : 14.19	0.249	36.10	
			0.119	36.16	
			0.071	36.17	
			0.0	36.20[a]	−0.38
7	H_2SO_4	1 : 9.31 : 42.59	0.271	34.97	
			0.122	35.00	
			0.063	35.04	
			0.0	35.05[a]	−0.29
8	H_2SO_4	1 : 2.93 : 42.61	0.259	35.88	
			0.130	35.94	
			0.077	36.04	
			0.0	36.08[a]	−0.82
9	H_2SO_4	1 : 1.16 : 42.63	0.261	37.04	
			0.134	37.40	
			0.072	37.43	
			0.0	37.63[a]	−2.16
10	$HClO_4$	1 : 16.65 : 14.27	0.272	35.29	
			0.138	35.33	
			0.071	35.36	
			0.0	35.38[a]	−0.31
11	$HClO_4$	1 : 11.89 : 14.37	0.281	35.62	
			0.132	35.65	
			0.061	35.68	
			0.0	35.70[a]	−0.29
12	$HClO_2$	1 : 7.75 : 14.22	0.239	36.45	
			0.136	36.49	
			0.057	36.52	
			0.0	36.54[a]	−0.38
13	$HClO_4$	1 : 5.25 : 14.15	0.262	37.40	
			0.131	37.42	
			0.058	37.46	
			0.0	37.47[a]	−0.30
14	$HClO_4$	1 : 4.05 : 14.23	0.277	38.72	
			0.139	38.95	
			0.064	39.08	
			0.0	39.18[a]	−1.67
15	$HClO_4$	1 : 4.33 : 14.22	0.259	38.43	
			0.194	38.57	
			0.062	38.77	
			0.0	38.88[a]	−1.70
16	$HClO_4$	1 : 2.89 : 14.23	0.275	40.96	
			0.136	41.41	
			0.064	41.64	
			0.0	41.84[a]	−3.23
17	$HClO_4$	1 : 11.77 : 21.33	0.252	35.52	
			0.111	35.55	
			0.055	35.58	
			0.0	35.60[a]	−0.31
18	H_3PO_4	1 : 0.52 : 19.35	0.325	35.10	
			0.170	35.17	
			0.101	35.23	
			0.0	35.27[a]	−0.55

[a] Δδ°.

significantly stronger than perchloric acid. Thus, the mixture with a ratio ($\frac{1}{3}$ **1**) : H_2O : AcOH of 1 : 3.10 : 14.25 (Table 2, entry 11) had an H_0 value of −3.63, whereas for the similar mixture containing perchloric acid (1 : 2.89 : 14.23, Table 3) H_0 is approximately −1.50. One could use this observation to conclude that **1** is a superacid, but that would be presumptuous, because the heteropolyacid would crystallize out of solution before the concentration at which superacidity were manifested could be achieved.

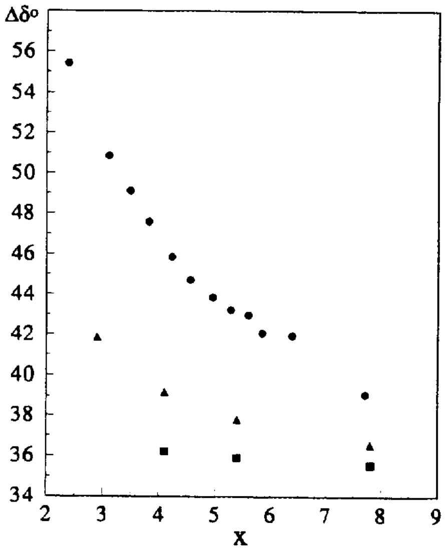

FIG. 1. Acid strength (Δδ°) toward mesityl oxide (**2**) in acetic Acid of Acids $AH \cdot xH_2O \cdot 14.33AcOH$. $AH = \frac{1}{3}(H_3PW_{12}O_{40})$ (●), $HClO_4$ (▲), and H_2SO_4 (■).

It has been found that the acid strength of solids is much lower than expected based on the acid strength of structurally similar liquid acids (18).

Table 3 and Fig. 1 also show that for low acid to water ratios perchloric acid is stronger than sulfuric acid, a result in agreement with measurements using other methods (19).

It has been reported that in a solvent of low dielectric constant like acetic acid the relative acid strength of two acids might not be the same for different bases (20). At the same time, however, the rates of several strong acid-catalyzed reactions in acetic acid were well correlated with H_0 values in the same solvent (19). Also, the solutions studied here contain significantly larger amounts of water in the solvent than in the earlier work, which used 99.65% AcOH (20). Thus, for the lowest level of hydration in **1b**, $x = 7.15$, the solvent of **1** corresponds to 95.4% AcOH. We have to consider, nonetheless, that the strength ratios found here might vary for other bases and in other solvents, but the fact that most of the positive charge in the conjugate acid **3** is concentrated at a carbon atom should make the indicator **2** a good model for carbon bases encountered in catalytic reactions.

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