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Acidity of heteropoly acids with various structures and compositions studied by IR spectroscopy of the pyridinium salts

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The acidity on the "proton affinity" scale was determined by IR spectroscopy of the pyridinium salts for nineteen heteropoly acids of nine structural types (including two with the previously unknown structure) and one isopoly acid. All heteropoly acids exhibited a high acidity at the level of CF_3SO_3H and $HClO_4$. $H_3PW_{12}O_{40}$ was the strongest acid.

Key words: heteropoly acids, acidity, IR spectroscopy.

Heteropoly acids (HPA) are strong mineral acids,[1] which are widely used as acidic catalysts for organic synthesis.[2,3] Various methods were used to study the acidity of HPA in solutions and in the solid state: indicator, electroconductivity, thermodesorption of bases, calorimetry,[1,3] ^1H [4,5] and ^{13}C [6] NMR, IR spectroscopy,[7,8] kinetic method,[9,10] Cal-ad method,[11] complex formation with chloral hydrate,[12] and others. Many HPA are colored, which often make impossible the application of the common indicator method. Some methods require the use of anhydrous HPA, whereas many known HPA (for example, α-$H_6P_2Mo_{18}O_{62}$, α-$H_6P_2W_{18}O_{62}$, and $H_6P_2W_{21}O_{71}$) cannot be obtained in the anhydrous state.[1] It is still unknown whether other HPA ($H_6As_2W_{21}O_{69}$,[13] $H_{21}B_3W_{39}O_{132}$,[14] fluorine-containing HPA, *etc.*[1]) exist in the anhydrous state or not. The methods of adsorption and desorption of ammonia and organic bases are poorly suitable for the determination of HPA acidity.[15—18] Therefore, the acidity of only $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ was reliably characterized, and data for some other HPA (α-$H_6P_2W_{18}O_{62}$, $H_6P_2W_{21}O_{71}$, $H_3PMo_{12}O_{40}$, $H_4SiMo_{12}O_{40}$) are either fragmentary or need verification. At the same time, there are many HPA whose acidity is not determined.[1,14]

In this work, the acidity of nineteen HPA belonging to nine structural types (two of them were previously unknown) and one isopoly acid was studied by IR spectroscopy of the pyridinium salts. This method of determination of the "proton affinity" (*PA*) was used previously[8,19] for the study of supported $H_3PMo_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$. The application of the beforehand prepared Py salts of the acids for the determination of the acidity by this method is a methodological advantage because the stages of pyridine adsorption—desorption, which are usual in such cases, are not required and, hence, diffusion hindrances are removed.

Experimental

Synthesis of HPA and their salts. Reagents $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ (reagent grade), $HClO_4$ (60%), and CF_3SO_3H (Merck) were used as received. Commercial $H_3PMo_{12}O_{40}$ and

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$H_4SiMo_{12}O_{40}$ were purified by recrystallization from an aqueous solution. Samples of α-$H_6P_2Mo_{18}O_{62}$, α-$H_6P_2W_{18}O_{62}$, $H_6P_2W_{21}O_{71}$, $H_{10}(PW_{11}O_{39})_2Ce$, $H_4PW_{11}VO_{40}$, $H_5PW_{11}TiO_{40}$, and $H_5PW_{11}ZrO_{40}$ were prepared by electrodialysis.[20—22] According to ^{31}P NMR spectroscopy data, purity of these HPA was at least 97%. Heteropoly acid $H_3PMo_6W_6O_{40}$ was also obtained by electrodialysis and represents a mixture of the P—Mo—W-HPA compositions from $H_3PMoW_{11}O_{40}$ to $H_3PMo_{11}WO_{40}$.[22] Heteropoly acid $H_8CeMo_{12}O_{42}$ was synthesized from the ammonium salt[23] and identified by the IR spectrum.[24] Heteropoly acid $H_{21}B_3W_{39}O_{132}$ was prepared according to the previously described procedure,[14] and its purity (~100%) was confirmed by the ^{11}B NMR spectrum. Heteropoly acid $H_6As_2W_{21}O_{69}$ was obtained by the known method,[13] and the ^{183}W NMR spectrum of its solution corresponded, as a whole, to that of a solution of the rubidium salt of HPA,[25] whereas the IR spectrum of the solid HPA corresponded to that of the rubidium salt of HPA.[13] Previously unknown HPA $H_9P_2W_{20}BiO_{71}$ and $H_8P_2W_{20}SnO_{71}$ were synthesized by the interaction of a solution of the $K_{10}P_2W_{20}O_{70}$ salt[26] with $Bi(NO_3)_3 \cdot 5H_2O$ and $SnCl_2 \cdot 2H_2O$, respectively, in the presence of H_2O_2 followed by the decationation of the solution with the KU-2-8 cation-exchange resin in the H^+ form and concentrating to dryness. These HPA were characterized by IR and NMR spectra, and detailed data will be published elsewhere. A solution of the molybdenum isopoly acid was obtained by electrodialysis.[22] The IR spectrum of the Py salt precipitated from this solution is close to that of the $K_8Mo_{36}O_{112}(H_2O)_{16}$ salt prepared by a known procedure.[27] Therefore, we may assume that the prepared substance is the Py salt of isopoly acid $H_8Mo_{36}O_{112}(H_2O)_{16}$. A solution of HPA with the conventional composition $P^{3+}W_6$ was prepared by the electrodialysis of a solution containing H_3PO_3 and Na_2WO_4. A solution of HPA with the conventional composition $Se^{4+}W_9$ was prepared by the interaction of SeO_2 with a hot suspension of the freshly prepared "white tungsten acid." [28] According to the ^{31}P and ^{183}W NMR data, HPA $P^{3+}W_6$ and $Se^{4+}W_9$ are, most probably, mixtures of HPA with yet unknown structure (results of their detailed study will be published elsewhere). We attempted to synthesize pyridinium salts of other known HPA: $H_6MnMo_9O_{32}$, $H_3CrMo_6O_{24}H_6$, $H_3RhMo_6O_{24}H_6$,[29] $H_3CoMo_6O_{24}H_6$,[22,29] and $H_8TeMo_6O_{24}$.[30] According to IR spectroscopy data, mixtures of the Py salts of desired HPA and nonidentified polymolybdates were formed.

Pyridinium salts were prepared by mixing a 10% aqueous solution of pyridine neutralized with a hydrochloric acid to the neutral reaction and an aqueous solution of HPA. The amount of a pyridine solution corresponded to the calculated value for the formation of the neutral salt of HPA. The suspension of the poorly soluble salt was centrifuged, and the precipitate was twice washed with water with decanting, dried in air, and evacuated at 100 °C for 1 h. Anhydrous Py salts of HPA were obtained. Pyridinium salts of $HClO_4$ and CF_3SO_3H were prepared by the neutralization of a solution of the acid with pyridine followed by concentrating to dryness at 20 Torr and drying of the precipitate in a vacuum desiccator for 1 day. The amount of pyridine in the Py salt was determined by the weight loss after calcination at 600 °C for 1 h. For HPA presented in Table 1, the IR spectra of the Py salts correspond to those of the starting acids in the region of absorption by the HPA anions (1100—400 cm^{-1}). IR spectra of the starting HPA taken as crystal hydrates and their Py salts were recorded on a Specord IR-75 instrument in the 1100—400 cm^{-1} region in KBr pellets. ^{31}P, ^{183}W, and ^{11}B NMR spectra of solutions of HPA were recorded on a Bruker MSL-400 instrument.

Table 1. Average *PA* values for protons of heteropoly acids substituted by the pyridinium ion

Heteropoly acid	ν_{NH} /cm^{-1}	*PA* /kJ mol^{-1}	*n* (H^+)[a]	
			I [b]	II [c]
$H_3PW_{12}O_{40}$	3020	1070	4.5	3.0
α-$H_6P_2Mo_{18}O_{62}$	2940	1110	4.4	6.0
CF_3SO_3H	2900	1120	1.1	—
$H_6P_2W_{21}O_{71}$	2890	1130	5.6	6.1
$H_4SiW_{12}O_{40}$	2860	1140	3.2	4.1
$H_{10}(PW_{11}O_{39})_2Ce$	2860	1140	5.7	8.3
$H_3PMo_{12}O_{40}$	2840	1140	2.4	3.0
$H_4SiMo_{12}O_{40}$	2810	1150	5.4	4.1
$H_3PMo_6W_6O_{40}$	2810	1150	3.6	3.0
$H_9P_2W_{20}BiO_{71}$	2800	1160	6.0	7.0
$H_8CeMo_{12}O_{42}$	2800	1160	2.0	5.3
$H_4PW_{11}VO_{40}$	2760	1170	5.5	4.1
$H_{21}B_3W_{39}O_{132}$	2730	1180	10	15
$HClO_4$	2710	1180	1.07	—
$H_5PW_{11}TiO_{40}$	2700	1190	4.9	4.0
Poly-Mo	2680	1190	4.9[d]	6.6[d]
α-$H_6P_2W_{18}O_{62}$	2650	1200	6.5	6.0
$H_6As_2W_{21}O_{69}$	2630	1200	2.4	6.1
$H_8P_2W_{20}SnO_{71}$	2620	1210	5.4	6.3
$H_5PW_{11}ZrO_{40}$	2600	1210	6.1	3.5
$Se^{4+}W_9$	2600	1210	—	0.59[e]
$P^{3+}W_6$	2560	1220	—	0.25[f]
Zeolites[8]	—	1180—1260	—	—
SO_3/Al_2O_3 [8]	—	1170—1180	—	—
CF_3COOH [8]	—	1350	—	—

[a] Number of H^+ ions substituted by PyH^+.

[b] IR spectroscopy.

[c] Weight method.

[d] Calculated per $H_8Mo_{36}O_{112}(H_2O)_{16}$.

[e] Mole of Py per mole of $WO_3 \cdot 1/9SeO_2$, which is equivalent to 7.1 moles of Py/PW_{12}.

[f] Mole of Py per mole of $WO_3 \cdot 1/12P_2O_3$, which is equivalent to 3 moles of Py/PW_{12}.

Study of acidity. IR spectra of Py salts of the acids in the 1000—4000 cm^{-1} region were obtained on an IFS-113V spectrometer (Bruker) in BaF_2 pellets. In this case, ion exchange reactions between the Py salt and matrix were avoided. The resolution was 4 cm^{-1}.

The strength of proton sites of HPA were characterized by the *PA* values calculated using the equation

$$PA = [\log(3400 - \nu_{NH})]/0.0023 - 51,$$

where *PA* (kJ mol^{-1}) is the energy of proton elimination from the acid residue, 3400 (cm^{-1}) is the wave number of the band of the undisturbed N—H bond of the pyridinium ion, and ν_{NH} (cm^{-1}) is the wave number of the center of gravity of the band of the stretching vibration of the pyridinium ion, which depends on the basisity of the acid residue and determined from the contour of the ν_{NH} line in the region of 3400—1800 cm^{-1}.[8,19] In addition to the ν_{NH} band, the spectra also contained a broad band in the region of 3600—2800 cm^{-1} (especially in the spectra of nonstoichiometric HPA salts). The band is attributed to stretching vibrations of the residual OH groups. When the absorption contour of ν_{NH} was studied, this band was subtracted from the overall spectrum. The accuracy of determination of

ν_{NH} was 30 cm^{-1}, and the error of calculation of *PA* was 20 kJ mol^{-1}. A decrease in the ν_{NH} value and, correspondingly, an increase in *PA* correspond to a decrease in the acidity of the acid. The concentration of pyridinium ions (*N*) in the salts was found from the intensity of the band of the stretching vibration of the pyridinium ion with a maximum at 1540 cm^{-1} by the formula[8]

$$N = \left(\int_{1510}^{1570} a\mathrm{d}\nu\right)/A_0,\ \text{where } A_0 = 3\ \mathrm{cm}^{-1}.$$

Results and Discussion

The IR spectra of all studied salts contain a band at 1540 cm^{-1} indicating the Brönsted type of acidity,[8] and bands in the region of 1400—1440 cm^{-1} corresponding to aprotic sites or physically adsorbed pyridinium are virtually absent. The profile of the spectrum in the 3400—1800 cm^{-1} region was almost the same in all cases, differed only by the position of the center of gravity, and was similar to that for supported HPA.[8,19]

Taking into account that the applied method is similar to that for the determination of the acidity of solid systems, we can conclude that the obtained results (see Table 1) give an insight into the acidity of the studied HPA in the solid form in the anhydrous state. For both the nonstoichiometric and stoichiometric salts, these data reflect the weighed mean acidity of protons, which formed the pyridinium ions ignoring their possible differentiation.

On the *PA* scale, basic substances occupy the region of $PA > 1500$ kJ mol^{-1}, amphoteric substances occupy 1400—1500 kJ mol^{-1}, and acids lie in $PA < 1400$ kJ mol^{-1}.[8] Based on the *PA* values, we can conclude that all the studied HPA are strong acids at a level of CF_3SO_3H and $HClO_4$; approximately a half of them are more acidic than zeolites and sulfated alumina. The structure of the HPA anion has almost no effect on the HPA acidity. HPA $H_3PW_{12}O_{40}$ is the strongest acid, which agrees well with the data obtained for solid HPA and their solutions by other methods.[1—7,12,31,32] For the similar Keggin HPA, we can write the acidity sequence

$$H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} > H_4PW_{11}VO_{40} >$$
$$> H_5PW_{11}TiO_{40} > H_5PW_{11}ZrO_{40},$$

corresponding to the previously found[3,12,31] regularity. According to this, the acidity of HPA normally decreases with an increase in the anion charge. At the same time, the acidities of $H_3PMo_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$ differ slightly. For the Keggin HPA, W-HPA are stronger acids than Mo-HPA, whereas for the Dowson HPA (α-$H_6P_2M_{18}O_{62}$) this dependence is inverse, which is also confirmed by the method of complex formation with chloral hydrate.[12]

The results of determination of the amount of proton acidic sites by IR spectroscopy (see Table 1) showed that this method is satisfactorily (with an accuracy of 7—10%) appropriate for studying simple acids, such as CF_3SO_3H and $HClO_4$. In the case of HPA, the data scatter is high toward both decreasing and increasing amount of pyridine in the salt. Underestimated values can be due to the known[8] effect of disappearance of the band at 1540 cm^{-1} when the Py—H$^+$—Py complexes are formed instead of the PyH$^+$ ions; we failed to explain the cases of overestimated values. The systematic deviation of the IR spectroscopy data from the results of weight analysis can form grounds for the elucidation of the specificity of pyridine interaction with HPA.

Thus, the application of the method of studying acidity by the *PA* scale enabled the estimation of the acidity of HPA with various structures and compositions, which was impossible for many of them by other methods. The results obtained agree, as a whole, with the previously published data and suggest that the high acidity is the common property of all HPA.

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