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Acidity of Solutions of Heteropoly Acids with Various Structures and Compositions

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Abstract—Hammett acidity functions H_0 of solutions of heteropoly acids $H_5PW_{11}XO_{40}$ (X(IV) = Ti, Zr), $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_6P_2W_{21}O_{71}$, and $H_{21}B_3W_{39}O_{132}$, as well as $HClO_4$ and CF_3SO_3H, in water and 90% aqueous acetone and acetonitrile, are measured at 20°C by the indicator method. In aqueous solutions all acids under study have the same strength, and in organic solvents their acidities differ. A correlation between the catalytic activity and acidity of the solution is found for the condensation of acetone to mesityl oxide.

INTRODUCTION

Heteropoly acids (HPAs) are strong Brønsted acids, which are used broadly as acid catalysts in homogeneous and heterogeneous catalysis [1, 2]. The acidity of HPA solutions was studied by various techniques, including the measurement of the Hammett acidity function H_0 by the indicator method. This method for the study of solution acidity is often criticized because only the equilibrium concentration of the nonionized indicator is in fact measured, whereas the concentration of the protonated indicator is calculated from the material balance equation, which is not always valid [3]. Nevertheless, the indicator method remains popular and it is used to compare the acidities of acid solutions. The method was successfully used in detailed studies of the solutions of $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ heteropoly acids for which the H_0 values in water, 40% dioxane, 90% acetone, and aqueous acetic acid have been found [4–6]. The acidity series of Keggin-type heteropoly acids for dilute solutions in acetonitrile with the same proton concentration was found by the indicator method

$$H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} > H_4GeW_{12}O_{40}$$
$$> H_5BW_{12}O_{40} > H_5FeW_{12}O_{40} > H_6CoW_{12}O_{40}.$$

This series agrees with a theoretically predicted decrease in the acid strength with an increase in the anion charge [1].

The H_0 values were also found for aqueous solutions of $H_6P_2W_{21}O_{71}$. At the same molar concentration of HPA, the solutions of $H_6P_2W_{21}O_{71}$ are more acidic than the solutions of $H_3PW_{12}O_{40}$, but their acidities are very close at the same concentration of protons [7].

In this work, we used the indicator method to find the H_0 values in water and 90% aqueous acetone and acetonitrile for the solutions of HPA with different structural types: $H_6P_2W_{21}O_{71}$, $H_{21}B_3W_{39}O_{132}$, $H_3PW_{12}O_{40}$ (Keggin structure), $H_4SiW_{12}O_{40}$, and $H_5PW_{11}XO_{40}$, where X(IV) = Ti and Zr. We find a correlation between the acidity and the reaction rate of acetone coupling.

EXPERIMENTAL

Reagents. Heteropoly acids $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ (chemically pure) were additionally purified by recrystallization from water, $H_6P_2W_{12}O_{71}$ and $H_5PW_{11}XO_{40}$ were synthesized by the electrochemical method using published procedures [7, 8], and $H_{21}B_3W_{39}O_{132}$ was prepared as recommended in [9]. The purity of HPAs was monitored by ^{31}P and ^{11}B NMR on an MSL-400 Bruker instrument. The amount of hydrated water in HPAs was determined by the weight loss after calcination at 500°C. The reagents CF_3SO_3H (98%, Merck), $HClO_4$ with a concentration of 60.6% (chemically pure), acetone (chemically pure), and acetonitrile (reagent grade) were used as received. Indicators, *ortho*- and *para*-nitroanilines, doubly recrystallized from ethanol were used to determine the Hammett acidity function H_0.

Procedure of H_0 determination. The H_0 values were calculated by the formula

$$H_0 = pK_{BH^+} - \log([BH^+]/[B]),$$

where K_{BH^+} is the protonation constant of the indicator, and $[BH^+]$ and [B] are the molar concentrations of the protonated and nonprotonated forms of the indicator, respectively. The concentration [B] was measured by the spectrophotometric method at 20°C. The absorbance of solutions was determined relatively to the equimolar solutions of HPAs without an indicator on a Specord UV–VIS M-40 in constant-temperature cells. The absorption bands of indicators and acids were not completely resolved. The error of H_0 determination was at most ±0.05.

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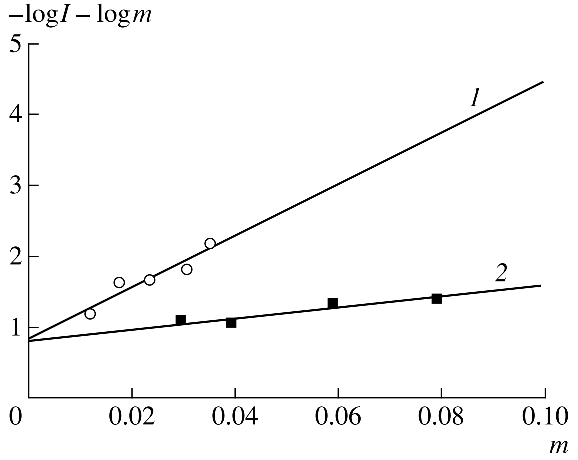

Fig. 1. Determination of pK_{BH^+} of *para*-nitroaniline in water–organic solutions of $HClO_4$: (*1*) in 90% acetonitrile and (*2*) in 90% acetone.

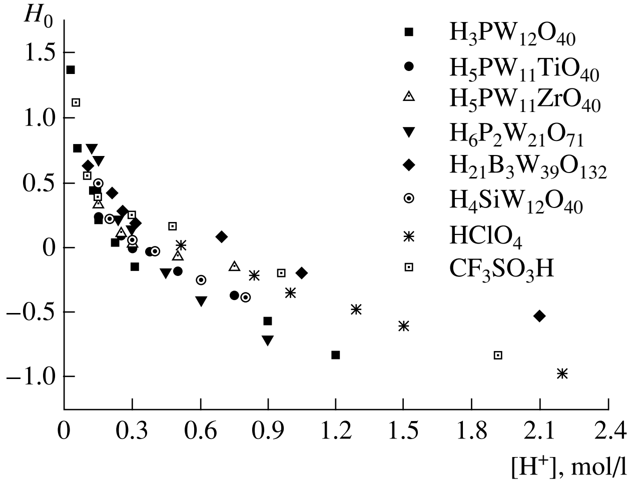

Fig. 2. A plot of the Hammett acidity function vs. acid concentration in an aqueous solution at 20°C.

Calculation of pK_{BH^+}. The pK_{BH^+} values of *para*-nitroaniline in mixed solvents were found by Paul's method [10, 11] and extrapolation of the relation ($-\log I - \log m$), where $I = C_B/C_{BH^+}$, C_{BH^+} and C_B are the molal concentrations of the protonated and nonprotonated forms of the indicator, respectively, and m is the molal concentration of $HClO_4$, to the zero concentration of $HClO_4$ (Fig. 1). The state of an infinitely dilute solution of $HClO_4$ in the specified mixed solvent was taken as a standard.

The pK_{BH^+} value for *ortho*-nitroaniline was calculated by the formula [11]:

$$pK_{BH^+} - pK_{CH^+} = \log(C_C/C_{CH^+}) - \log(C_B/C_{BH^+}),$$

where pK_{BH^+} and pK_{CH^+} are the protonation constants of *para*- and *ortho*-nitroaniline; C_B, C_{BH^+}, C_C, and C_{CH^+} are the concentrations of the nonprotonated and protonated forms of *para*- and *ortho*-nitroaniline, respectively.

Kinetic measurements. Acetone condensation was carried out in the presence of 10% water at 50°C in a glass reactor equipped with a magnetic stirrer and a reflux condenser. The yield of mesitylene oxide was determined by GLC (a column 2 m × 3 mm packed with the Carbowax 20M phase on Chezasorb AW–HMDS) [6].

RESULTS AND DISCUSSION

Tables 1 and 2 and Fig. 2 presents the results of H_0 determination are. The data for aqueous $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ solutions agree with the data reported in [4, 5]. The data for the aqueous solutions of $H_6P_2W_{12}O_{71}$ coincide with those reported in [7]. The H_0 values found by us for acetone solutions of $H_3PW_{12}O_{40}$ differ somewhat from those reported in [6] probably because pK_{BH^+} of the indicators used in [6] differ from ours. Unfortunately, the authors of [6] did not present their pK_{BH^+} values.

Our results indicate (Table 1) that the series of HPA acidity in dilute and concentrated aqueous solutions (the HPA concentration calculated per acid) do not coincide. The HPA strength in dilute solutions ([HPA] < 0.05 M) decreases in the series

$$H_{21}B_3W_{39}O_{132} > H_5PW_{11}TiO_{40} > H_5PW_{11}ZrO_{40}$$
$$> H_6P_2W_{21}O_{71} > H_3PW_{12}O_{40} > H_4SiW_{12}O_{40}.$$

However, in concentrated solutions the acidity series is different

$$H_{21}B_3W_{39}O_{132} > H_6P_2W_{21}O_{70} > H_5PW_{11}TiO_{40}$$
$$> H_3PW_{12}O_{40} \approx H_4SiW_{12}O_{40} > H_5PW_{11}ZrO_{40}.$$

This is probably because the acidity of concentrated solutions is determined by salt effects that depend on the composition and structure of HPAs [5] rather than by the dissociation constants of acids, as in the case of dilute solutions.

The H_0 values for aqueous solutions of the acids with the same proton concentration differ slightly (Fig. 2, Table 2). Therefore, all HPAs studied by us are almost equally strong acids, viz, at a level of $HClO_4$ and CF_3SO_3H or even somewhat stronger. Equimolar aqueous solutions of $H_{21}B_3W_{39}O_{132}$ and $H_6P_2W_{21}O_{71}$ have a higher acidity than the Keggin-type HPAs, $HClO_4$, and CF_3SO_3H probably due to higher proton concentrations. The difference in the acidity of aqueous solutions of HPA disappears when their weight concentrations become equal (Table 2) and is stronger in water–organic solvents. For example, 90% aqueous acetone

Table 1. Hammett acidity functions for HPA solutions

Water		Acetonitrile (90 vol %)		Acetone (90 vol %)	
[HPA], mol/l	H_0^{a}	[HPA], mol/l	H_0^{b}	[HPA], mol/l	H_0^{c}
		$H_3PW_{12}O_{40}$			
0.0104	$+1.37^{d}$	0.01	+0.47	0.050	+2.17
0.0207	$+0.77^{d}$	0.0129	+0.34	0.100	+1.59
0.0415	$+0.44^{d}$	0.0165	+0.29	0.150	+1.08
0.050	+0.22	0.0188	+0.27	0.200	+0.60
0.075	+0.05	0.0375	+0.22		
0.103	–0.15	0.050	+0.14		
0.15	–0.25	0.075	+0.01		
0.20	–0.38	0.100	-0.11^{e}		
		0.150	-0.19^{e}		
		$H_4SiW_{12}O_{40}$			
0.0375	$+0.05^{d}$	0.05	+0.46	0.050	+1.36
0.050	$+0.22^{d}$	0.075	+0.34	0.075	+1.17
0.075	+0.06	0.10	+0.12	0.10	+0.94
0.10	–0.03	0.15	-0.11^{e}	0.15	+0.51
0.15	–0.25	0.20	-0.30^{e}	0.20	+0.23
0.20	–0.38				
		$H_5PW_{11}TiO_{40}$			
0.030	+0.23	0.00625	+0.57	0.00625	+2.57
0.050	+0.10	0.0125	+0.48	0.0150	+2.01
0.060	+0.01	0.0250	+0.29	0.030	+1.77
0.075	–0.03	0.0375	+0.24	0.050	+1.31
0.100	–0.09	0.050	+0.06	0.10	+1.02
0.150	–0.36	0.100	-0.06^{e}	0.15	+0.65
		0.150	-0.12^{e}		
		$H_5PW_{11}ZrO_{40}$			
0.030	$+0.35^{d}$	0.0093	+0.46	0.00625	+2.82
0.050	+0.11	0.0187	+0.40	0.015	+2.54
0.060	+0.03	0.0275	+0.22	0.030	+2.02
0.100	–0.03	0.055	-0.09^{e}	0.050	+1.43
0.150	–0.15	0.100	-0.18^{e}	0.100	+0.91
		0.150	-0.22^{e}	0.150	+0.63
		$H_6P_2W_{21}O_{71}$			
0.02	$+0.78^{d}$	0.00625	-0.20^{e}	0.00625	+1.41
0.025	$+0.68^{d}$	0.009375	-0.23^{e}	0.0150	+0.75
0.040	+0.22	0.0250	-0.36^{e}	0.025	+0.38
0.050	+0.15	0.0375	-0.50^{e}	0.030	+0.35
0.075	–0.18	0.050	-0.58^{e}	0.050	$+0.11^{f}$
0.100	–0.40	0.075	-0.70^{e}	0.075	-0.25^{f}
0.150	–0.70	0.100	-0.80^{e}	0.100	-0.60^{f}
		$H_{21}B_3W_{39}O_{132}$			
0.005	$+0.64^{d}$	0.00625	+0.35	0.005	+1.67
0.007	$+0.46^{d}$	0.01250	+0.08	0.010	+1.45
0.00995	$+0.43^{d}$	0.0250	-0.14^{e}	0.020	+1.07
0.0125	+0.29	0.0375	-0.32^{e}	0.040	+0.50
0.0150	+0.19	0.050	-0.55^{e}	0.050	+0.21
0.033	+0.09	0.075	-0.80^{e}		
0.050	–0.19				
0.100	–0.52				

Notes: [a] *ortho*-Nitroaniline, 6.25×10^{-4} mol/l; $\varepsilon_0 = 14545$ l mol^{-1} cm^{-1}; $pK_{BH^+} = -0.30$ [10, 12]; λ = 378–385 nm.

[b] *para*-Nitroaniline, 10^{-3} mol/l; $\varepsilon_0 = 44753$ l mol^{-1} cm^{-1}; $pK_{BH^+} = 0.82$; λ = 385–389 nm.

[c] *para*-Nitroaniline, 8.02×10^{-4} mol/l; $\varepsilon_0 = 8894$ l mol^{-1} cm^{-1}; $pK_{BH^+} = 0.85$; λ = 403–407 nm.

[d] *para*-Nitroaniline, 6.25×10^{-4} mol/l; $\varepsilon_0 = 4250$ l mol^{-1} cm^{-1}; $pK_{BH^+} = 1.0$ [10, 12]; λ = 416–435 nm.

[e] *ortho*-Nitroaniline, 5×10^{-4} mol/l; $\varepsilon_0 = 5122$ l mol^{-1} cm^{-1}; $pK_{BH^+} = -0.71$; λ = 407–412 nm.

[f] *ortho*-Nitroaniline, 5.92×10^{-4} mol/l; $\varepsilon_0 = 1197$ l mol^{-1} cm^{-1}; $pK_{BH^+} = -0.61$ [10, 12]; λ = 374–378 nm.

exhibits the following acidity series (calculated per proton):

$$H_6P_2W_{21}O_{71} > H_{21}B_3W_{39}O_{132} > H_5PW_{11}TiO_{40},$$

$$H_5PW_{11}ZrO_{40} > H_3PW_{12}O_{40}, H_4SiW_{12}O_{40}.$$

A different series is observed for 90% acetonitrile

$$H_6P_2W_{21}O_{71} > H_3PW_{12}O_{40}, H_5PW_{11}ZrO_{40},$$

$$H_5PW_{11}TiO_{40} > H_{21}B_3W_{39}O_{132} > H_4SiW_{12}O_{40}.$$

Thus, both HPAs with different structures and compositions and isostructural (Keggin-type) HPAs manifest their specificity in organic solvents. The acidity of water–organic solutions of sulfuric acid is known to be in an inverse proportion to the basicity of the organic solvent [13]. Similar relations were found for all Keggin-type HPAs. The basicity of solvents decreases in the series [13]

acetone > acetonitrile > water.

The acidity of solutions of $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_5PW_{11}TiO_{40}$, and $H_5PW_{11}ZrO_{40}$ changes in the inverse order. The solutions of $H_6P_2W_{21}O_{71}$ and $H_{21}B_3W_{39}O_{132}$ do not obey this relationship, which is possibly associated with the influence of the structure of the HPA anion on the acid properties.

The data allow us to expect that HPAs with different structures and compositions differ slightly in the catalytic activity in homogeneous acid-catalyzed reactions in water. However, considerable distinctions can be observed in organic media, and activity series may differ in different solvents or for different substrates, which was observed for HPA-catalyzed ether decomposition [14].

Khankhasaeva *et al.* [6] showed for acetone condensation to mesitylene oxide in the presence of $H_3PW_{12}O_{40}$ that the catalytic activity of HPA can be predicted by the acidity function H_0:

$$\log w = \alpha H_0 + \text{const},$$

where w is the reaction rate at a low conversion of acetone. We observed a satisfactory linear relationship between the catalytic activities of HPAs with different structures and the solution acidities a found by the indicator method (Fig. 3). At temperatures above 40°C, $H_{21}B_3W_{39}O_{132}$ is rapidly reduced and looses its activity. Thus, for at least this reaction, the Hammett acidity function can be used to predict the catalytic activity of HPAs with different structures and compositions.

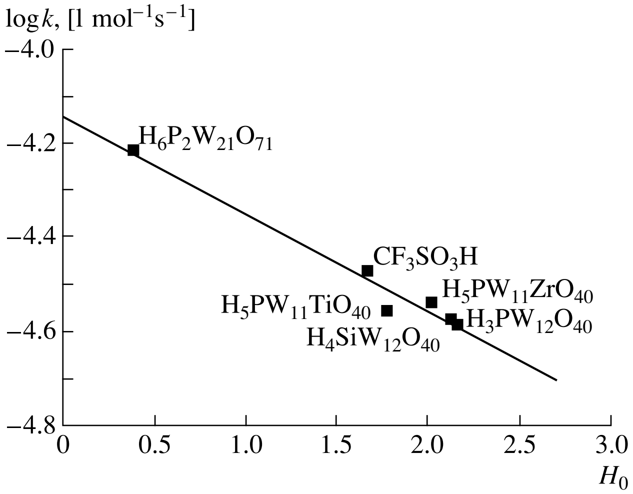

Fig. 3. A plot of the logarithm of the rate constant of acetone dimerization vs. Hammett acidity function (for all acids $[H^+] = 0.15$ mol/l).

Table 2. Hammett acidity functions for solutions of acids with the same molar and weight concentration or with the same proton concentration

Acid	Water			Acetone (90%)		Acetonitrile (90%)	
	H_0^a (0.1 mol/l)	H_0^b (0.3 mol/l)	H_0^c (288.2 g/l)	H_0^a (0.05 mol/l)	H_0^b (0.15 mol/l)	H_0^a (0.05 mol/l)	H_0^b (0.15 mol/l)
$H_{21}B_3W_{39}O_{132}$	–0.52	+0.21	+0.11	+0.21	+1.55	–0.55	+0.35
$H_6P_2W_{21}O_{71}$	–0.40	+0.15	+0.04	+0.11	+0.38	–0.58	–0.36
$H_5PW_{11}TiO_{40}$	–0.18	+0.01	–0.06	+1.31	+1.77	+0.06	+0.17
$H_3PW_{12}O_{40}$	–0.05	–0.05	–0.05	+2.17	+2.17	+0.14	+0.14
$H_5PW_{11}ZrO_{40}$	–0.07	+0.03	–0.05	+1.43	+2.02	–0.03	+0.20
$H_4SiW_{12}O_{40}$	–0.03	+0.06	–0.03	+1.36	+2.13	+0.46	+0.60
$HClO_4$	+0.81	+0.36	–0.71	+2.32	+1.80	+0.86	+0.66
CF_3SO_3H	+0.56	+0.25	–0.83	+2.00	+1.66	+0.77	+0.62

[a] At the same molar acid concentration.
[b] At the same proton concentration.
[c] At the same weight acid concentration.

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