1186 © 1994 The Chemical Society of Japan **NOTES** Bull. Chem. Soc. Jpn., 67, 1186—1188(1994) [Vol. 67, No. 4

Acid Strength of Heteropolyacids and Its Correlation with Catalytic Activity

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(Received October 25, 1993)

Synopsis. UV spectrophotometry of a Hammett indicator revealed that the acid strength of the Keggin-type heteropolyacids having W as addenda atoms increased as the valency of the central atom increased (Co<B<Si, Ge<P). The catalytic activity for the decomposition of isobutyl propionate in a homogeneous system was correlated well with the acid strength.

Heteropolyacids are excellent catalysts for acid-catalyzed reactions in both homogeneous and heterogeneous systems.[1—5] Since solid $H_3PW_{12}O_{40}$ has an acid strength of $H_0 < -13.16$, it is a superacid.[6] The acid strength of heteropolyacid depends on the constituent element. The following order of acid strength was previously reported by Izumi et al.:[7] $H_3PW_{12}O_{40} > H_3PMo_{12}O_{40} > H_4SiW_{12}O_{40} > H_4SiMo_{12}O_{40} > H_4GeMo_{12}O_{40}$.

We reported that the catalytic activities increased as the valency of the central atom of the heteropolyacids having W as addenda atoms decreased, and speculated that the acid strength also increased as the valency of the central atom decreased.[8,9] However, there was no direct evidence for the change in the acid strength due to a substitution of the central atom of $H_\alpha XW_{12}O_{40}$ (X=P, Si, Ge, B, Fe, and Co).

Here, we wish to report that the acid strength of the heteropolyacids was determined by UV spectroscopy of a Hammett indicator, and that the catalytic activity in the liquid phase was well correlated with the acid strength.

Experimental

Heteropolyacids ($H_\alpha XW_{12}O_{40}$) were synthesized according to a method described in the literature,[8] and were pretreated at 150 °C in a He flow for 2 h to remove the crystallization water. The Keggin structure for all heteropolyacids was retained after the pretreatment.[9] *para*-Toluenesulfonic acid (abbreviated as PTS, Nakalai Tesque) was used as a reference sample. Heteropolyacids were added to acetonitrile, which was dried with a molecular sieve 3A to obtain a nominal proton concentration(defined as $\alpha \times$concentration of heteropoly anion) of 4.86×10^{-3} mol dm^{-3}. Dicinnamylideneacetone (Tokyo Kasei Co.) was used as an indicator whose pK_a value is -3.0,[10] where K_a is the dissociation constant of the protonated indicator (p$K_a = -\log K_a$).

The UV spectra were measured with a quartz cell (L= 1 cm) by use of a Hitachi 340 Spectrophotometer in the 190—850 nm region. The concentration of the indicator was 3.5×10^{-5} mol dm^{-3}.

Results and Discussion

The Hammett acidity function (H_0) is a measure of the acidity of a solution or solid, and is defined by $H_0 = \mathrm{p}K_a - \log [BH^+]/[B]$ (Eq. 1), when equilibrium given by $BH^+ \rightleftharpoons B + H^+$ (Eq. 2) is maintained. $[BH^+]$ and $[B]$ are the concentrations of the protonated and neutral forms of the indictor, respectively.

Figure 1 shows the UV spectra from dicinnamylideneacetone (indicator) in the acetonitrile solution. As shown in Fig. 1A, the indicator in acetonitrile gave a broad peak at about 362 nm, which is due to the neutral form of the indicator. When $H_3PW_{12}O_{40}$ was added to the solution, the absorbance of the peak at 362 nm decreased (Fig. 1A-b), and a new band appeared at 540 nm, which was due to the protonated form (Fig. 1B-b). Figure 1B shows that the peak intensities of the protonated form changed greatly, depending on the central atom: $P^{5+} > Si^{4+} > Ge^{4+} > B^{3+} > Fe^{3+} > Co^{2+} >$ (PTS). It was confirmed that the intensities of the protonated

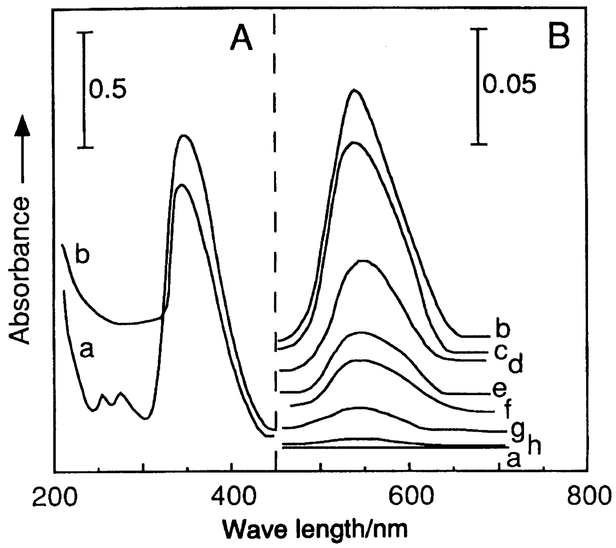

Fig. 1. Absorption spectra from dicinnamylideneacetone in acetonitrile. (A) Spectra of the neutral form of dicinnamylideneacetone in acetonitrile (a) and in $H_3PW_{12}O_{40}$–acetonitrile solution (b). The reference was acetonitrile for (a) or acetonitrile solution of $H_3PW_{12}O_{40}$ for (b). (B) Spectra of the protonated form of dicinnamylideneacetone in acetonitrile solution of (a) without acid, (b) $H_3PW_{12}O_{40}$, (c) $H_4SiW_{12}O_{40}$, (d) $H_4GeW_{12}O_{40}$, (e) $H_5BW_{12}O_{40}$, (f) $H_5FeW_{12}O_{40}$, (g) $H_6CoW_{12}O_{40}$, (h) PTS.

form increased linearly as the proton concentrations of all the solutions of heteropolyacids increased in the range from 0.5×10^{-3} to 4.86×10^{-3} mol dm^{-3}, which is reasonable because the equilibrium of Eq. 2 lies to the right in these cases.

From a quantitative comparison of the decrease in the absorbance in the neutral form (362 nm), and the increase in the acid form (540 nm) (Fig. 1), the ratio of the extinction coefficient of the two forms was estimated to be 1.3. By using this ratio of $[BH^+]/[B]$, the heteropolyacid solutions were determined. H_o was then calculated according to Eq. 1 and summarized in Table 1.

The H_o value of the acetonitrile solution of $H_3PW_{12}O_{40}$ was -2.14 at a concentration (polyanion) of 1.63×10^{-3} mol dm^{-3}. It has been reported that the H_o value of the acetic acid solution of $H_3PW_{12}O_{40}$ was about -3.0 at a concentration of 5×10^{-4} mol dm^{-3},[5] and that H_o of its aqueous solution was $+0.16$ at 5×10^{-2} mol dm^{-3}.[11] Thus, H_o for $H_3PW_{12}O_{40}$ is: in acetic acid < in acetonitrile < in water. This order is understandable, since the proton affinity (basicity) decreases in the order $H_2O \gg$ acetonitrile > acetic acid,[12] and shows that the obtained H_o value in the present study is reasonable.

Table 1 demonstrates that the H_o value increases regularly as the valency of the central atom increased from +2 (Co) to +5 (P), while Si^{4+} and Ge^{4+} as well as B^{3+} and Fe^{3+} gave a slightly different acidity in spite of the same valency. The change with the valency is reasonable because the interaction between the proton and polyanion would decrease as the negative charge of polyanion decreases, or the valency of the central atom increases. While the difference between Si^{4+} and Ge^{4+} or B^{3+} and Fe^{3+} is not clear at present, it may not influence the above conclusion.

In Fig. 2, the logarithms of the first-order rate constants (per unit mole of proton) for the decomposition of isobutyl propionate in homogeneous system (without solvent) are plotted against the H_o values of the heteropolyacids.[8] Since the reaction very likely belongs to general acid catalysis,[8] the rate constant per unit mol of the proton can be used to discuss the catalytic activity. As can be seen in Fig. 2, the rate constant is well correlated with the H_o value, indicating that the catalytic activity of heteropolyacid is principally determined by its acid strength. The general trend does not change, even if the rate constants per unit mol of polyanion are compared.

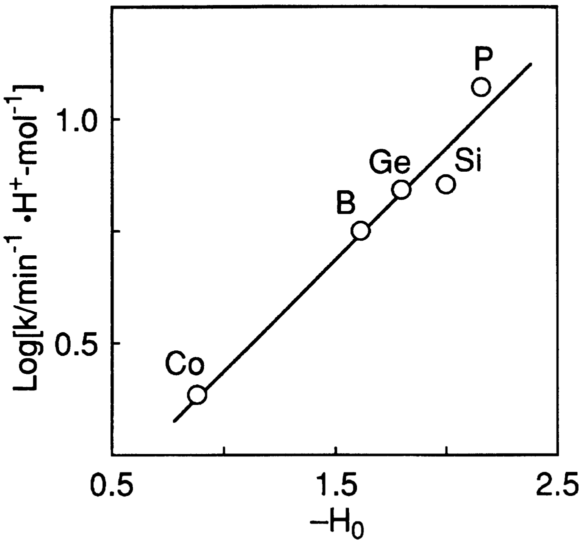

Fig. 2. Logarithms of the rate constants (per unit mol of proton) for the decomposition of isobutyl propionate versus the H_o values of acetonitrile solutions.

Table 1. H_o Values of Acetonitrile Solution of Heteropolyacids and PTS

Catalyst	H_o
$H_3PW_{12}O_{40}$	−2.14
$H_4SiW_{12}O_{40}$	−1.98
$H_4GeW_{12}O_{40}$	−1.69
$H_5BW_{12}O_{40}$	−1.55
$H_5FeW_{12}O_{40}$	−1.48
$H_6CoW_{12}O_{40}$	−0.88
PTS	−0.30

The proton concentration of the acid in acetonitrile was 4.86×10^{-3} mol dm^{-3}. The concentration of dicinnamylideneacetone ($pK_a=-3.0$) was 3.5×10^{-5} mol dm^{-3}.

We previously found that the catalytic activities for both the alkylation of 1,3,5-trimethylbenzene with cyclohexene and decomposition of cyclohexyl acetate in liquid–solid reaction system were also greatly affected by the central atom of heteropolyacids.[9] This result is also explained by the difference in the acid strength of the heteropolyacids.

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