JOURNAL OF CATALYSIS **143**, 437–448 (1993)

Catalysis by Heteropoly Compounds

XXII. Reactions of Esters and Esterification Catalyzed by Heteropolyacids in a Homogeneous Liquid Phase—Effects of the Central Atom of Heteropolyanions Having Tungsten as the Addenda Atom[1]

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Received October 21, 1992; revised February 12, 1993

Decomposition of isobutyl propionate (IBP) (Reaction (1)), ester exchange of IBP with acetic acid (Reaction (2)), ester exchange of IBP with *n*-propyl alcohol (Reaction (3)), and esterification of propionic acid with isobutyl alcohol (Reaction (4)) have been studied in a homogeneous liquid phase using heteropolyacids $H_mXW_{12}O_{40}$ (X = P, Si, Ge, B, and Co) having the Keggin structure and $H_6P_2W_{18}O_{62}$ having the Dawson structure. The results clearly indicated that the catalytic behavior of heteropolyacids remarkably depended on the kind of reaction system, namely, the basicity of reactants. For Reaction (1), the catalytic activities of the heteropolyacids were 60–100 times higher than those of H_2SO_4 and *p*-toluenesulfonic acid. Among the heteropolyacids, the activity was in the order $H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} \sim H_4GeW_{12}O_{40} > H_5BW_{12}O_{40} > H_6CoW_{12}O_{40}$. This order suggests that the activity follows the order of the acid strength of the solutions of heteropolyacids, which increases with the decrease in the negative charge of the polyanion. $H_6P_2W_{18}O_{62}$ showed an activity between those of $H_5BW_{12}O_{40}$ and $H_6CoW_{12}O_{40}$. Water molecules in the system retarded Reaction (1). For Reaction (2), the activity order was similar to that for Reaction (1) in the absence of water. However, contrary to Reaction (1), the addition of water greatly accelerated Reaction (2). It was presumed that, in the presence of water, Reaction (2) proceeds via the hydrolysis of IBP to propionic acid and isobutyl alcohol, followed by the esterification of isobutyl alcohol with acetic acid. On the other hand, the difference in the activity between the heteropolyacids and H_2SO_4 was not significant for Reactions (3) and (4), for which the effective acid strength of the catalysts may level off as a consequence of the leveling effect of the reactant alcohols.

INTRODUCTION

Heteropolyacids are known to be active catalysts for both homogeneous and heterogeneous acid-catalyzed reactions (*1–6*). Several industrial processes such as hydration of olefins (*7–9*) and polymerization of tetrahydrofuran (*10*) have been operated utilizing heteropolyacids. At the same time, heteropolyacids are well-defined mixed oxides, and their acidic and redox properties can be controlled by the substitution of the constituent elements without changing the fundamental structure (*1*). Izumi *et al.* (*6*) have reported the following order of acid strength by using Pope's method (*11*): $H_3PW_{12}O_{40} > H_3PMo_{12}O_{40} > H_4SiW_{12}O_{40} \sim H_4GeW_{12}O_{40} > H_4SiMo_{12}O_{40} > H_4GeMo_{12}O_{40}$. They indicated that, in several reactions in nonaqueous solutions, the catalytic activities were related to the acidity of the solution of heteropolyacids and the softness of the polyanion (*6*). In dilute aqueous solutions, the softness becomes more important, since all of those hetero-

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[1] For part XXI, see T. Okuhara, T. Nishimura, H. Watanabe, and M. Misono, *J. Mol. Catal.* **74**, 247 (1992).

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0021-9517/93 $5.00

polyacids are almost completely dissociated (6).

However, systematic control of the acid strength of heteropolyacids as well as the quantitative relationship between acid strength and catalytic activity has not yet fully been established, while the control of acidity is of great importance for their application as acid catalysts.

In the present study, we attempted to clarify the effect of the central (or hetero) atom of heteropolyacids mainly of the Keggin type on the catalytic activity in homogeneous liquid-phase reactions. The objectives of the present study are to demonstrate the superiority of heteropolyacids in certain reactions and to discuss the factors determining the relative activity of the heteropolyacids. Because heteropolyacids containing W as the polyanion are more stable than those containing Mo in the reaction systems (*1*, *6*), we used the heteropolyacids containing a W atom. Since these heteropolyacids are soluble in polar solvents such as alcohols and esters, we chose as test reactions the decomposition of an ester, exchange of an ester with an acid or alcohol, and esterification. There are a few reports on these types of reactions using heteropolyacids as catalysts, for example, esterification of ethanol with acetic acid (*12*), exchange of ester (*3*), and decomposition of an ester (*3*).

EXPERIMENTAL

Preparation of Catalysts

Heteropolyacids having W as the addenda (or poly) atom were prepared according to the literature (*13–17*). $H_3PW_{12}O_{40} \cdot 30H_2O$ was obtained from $Na_2WO_4 \cdot 2H_2O$ (Nacalai Tesque, Inc.) and Na_2HPO_4 (Kokusan Chemicals Works, Ltd.) (*13*). $H_4SiW_{12}O_{40} \cdot 22H_2O$ was also obtained from Na_2WO_4 and $Na_2SiO_3 \cdot 9H_2O$ (Nacalai Tesque, Inc.) (*14*).

$H_4GeW_{12}O_{40} \cdot 7H_2O$ was prepared from $Na_2WO_4 \cdot 2H_2O$ (50 g) and GeO_2 (1.32 g, Yokozawa Chemical Co.) (*14*). They were dissolved in water (200 ml) at room temperature. Then an aqueous solution of HNO_3 (62%, Yanashima Chemical Co.) was added dropwise to the solution with vigorous stirring until the pH decreased to about 3. The solution was boiled for 6 h to concentrate it to about 60 ml. After the solution was cooled to room temperature, it was extracted with diethyl ether. The extractant was added to water (100 ml) and evaporated at 60°C, followed by recrystallization from water.

$H_5BW_{12}O_{40} \cdot 15H_2O$ was prepared from $Na_2WO_4 \cdot 2H_2O$ (100 g) and H_3BO_3 (150 g, Koso Chemicals Co.) (*15*). $H_6CoW_{12}O_{40} \cdot 19H_2O$ was prepared as follows (*16*). $Na_2WO_4 \cdot 2H_2O$ (99 g) and acetic acid (20 ml) were added in water (200 ml). After the solution was heated at 80°C, an aqueous solution (63 ml) of $Co(OCOCH_3)_2 \cdot 4H_2O$ (9.3 g) (Koso Chemicals Co.) was added dropwise in 24 h. The solution was concentrated to 80 ml at the same temperature. After it was cooled to room temperature, the solution was filtered. Extraction with diethyl ether of the solution and recrystallization from water gave blue crystallites.

$H_6P_2W_{18}O_{62} \cdot 32H_2O$ (Dawson structure) was synthesized according to the literature (*17*). $Na_2WO_4 \cdot 2H_2O$ (150 g) was dissolved in hot water (150 ml), and then 125 ml of an aqueous solution of H_3PO_4 (85%, Nacalai Tesque, Inc.) and 30 ml of water were added with vigorous stirring. The solution was boiled for 5 h, the volume of the solution being kept at 250 ml by adding water. To prevent reduction, a small amount of HNO_3 was added to the light yellow solution. After the solution was concentrated by boiling until thin films were formed on the surface of the solution, it was cooled to 0°C and the precipitate was separated by the filtration. Then the precipitate was dissolved in water (30 ml) and recrystallized at room temperature. It was extracted with diethyl ether. By recrystallization from water, yellow crystallites were obtained.

Water Content and IR Measurement

The content of the crystallization water was measured with a microbalance (Shimadzu TG-30) by heating the sample from room temperature to 300°C in a vacuum, assuming that the content is zero after evacuation at 300°C (*18, 19*). By evacuation at 150°C, the water content became less than 0.5 molecule per polyanion. Thus the samples prepared by evacuation at 150°C in a vacuum-oven (Model DPE-31, Yamato) for 8 h were used as anhydrous heteropolyacids. $H_3PW_{12}O_{40} \cdot 6H_2O$ was prepared by evacuation at room temperature for 6 h. *p*-Toluenesulfonic acid (abbreviated PTS) was pretreated at 105°C in the vacuum oven for 2 h. H_2SO_4 (>98%, Nacalai Tesque, Inc.) was used without further purification. Just before the reactions were carried out, the catalysts were always pretreated under the above conditions.

Infrared spectra of the heteropolyacids were recorded at room temperature using an FT-IR spectrometer (Shimadzu 8500). The powder samples were pressed into disks with KBr. The water in the reactants was removed by using a molecular sieve 5A which was pretreated at 300°C. The content of water was confirmed to be less than 0.1 mol% by using a moisture meter (Mitsubishi Chemical Ind., Model CA-D2).

Catalytic Reactions

Four different types of reactions (Reactions (1)–(4)) were examined:

$$(CH_3)_2CHCH_2OCOC_2H_5 \rightarrow (CH_3)_2C{=}CH_2 + C_2H_5COOH \quad (1)$$

$$(CH_3)_2CHCH_2OCOC_2H_5 + CH_3COOH \rightarrow (CH_3)_2CHCH_2OCOCH_3 + C_2H_5COOH \quad (2)$$

$$(CH_3)_2CHCH_2OCOC_2H_5 + n\text{-}C_3H_7OH \rightarrow C_3H_7OCOC_2H_5 + (CH_3)_2CHCH_2OH \quad (3)$$

$$(CH_3)_2CHCH_2OH + C_2H_5COOH \rightarrow (CH_3)_2CHCH_2OCOC_2H_5 + H_2O \quad (4)$$

All reactions were performed in a three-neck flask (about 50 ml) equipped with a water-cooler condensor, a thermometer, and a sampling tube. The reaction temperatures were 128 and 70°C for Reaction (1) and Reactions (2)–(4), respectively, and all reactions were performed using neat solutions. In Reaction (1), the catalyst (typical conditions: heteropolyacids, 1.50×10^{-4} mol; *p*-toluenesulfonic acid (PTS), 5.50×10^{-4} mol; H_2SO_4, 8.60×10^{-4} mol) was added to start the reaction into isobutyl propionate (IBP) (10 ml, 0.067 mol), which was kept at 128°C. All the heteropolyacids were soluble under the conditions of Reaction (1). In the case of Reaction (2), first the catalyst (heteropolyacids, 1.78×10^{-4} mol; PTS, 7.04×10^{-4} mol; H_2SO_4, 1.50×10^{-3} mol) was added to the solution of IBP (10 ml) at 70°C. Then the reaction was started by the injection of acetic acid (3.82 ml, 0.067 mol) into the solution at 70°C. While $H_5BW_{12}O_{40}$ and $H_6CoW_{12}O_{40}$ were not fully soluble under the conditions of Reaction (2), the other heteropolyacids dissolved into the solution.

In Reaction (3), catalysts (heteropolyacids, 1.94×10^{-4} mol; PTS, 5.80×10^{-4} mol; H_2SO_4, 3.86×10^{-4} mol) were added to IBP (10 ml) at 70°C, and then *n*-propyl alcohol (5 ml, 0.067 mol) was introduced into the solution at 70°C to start the reaction. All the heteropolyacids were soluble in the reactant solution. In Reaction (4), the catalyst (3.6×10^{-5} mol) was added to isobutyl alcohol (10 ml, 0.109 mol) at 70°C. After the catalysts were dissolved completely, propionic acid (5 ml, 0.067 mol) was added at 70°C, to start the reaction. All the reactions were carried out in an atmosphere of dry N_2. The solutions were stirred vigorously under the above conditions and 0.2 μl of the solution was sampled using a microsyringe at 30-min regular intervals for the analysis.

The products were analyzed with a gas chromatograph (flame ionization detector, Yanaco GC-8500) equipped with Gasukuropack 55 (GL Science, glass column, 2 m), the temperature of which was 225°C.

RESULTS

Infrared Spectra of Heteropolyacids

Infrared spectra of the heteropolyacids are shown in Fig. 1. Characteristic vibration bands due to the Keggin structure appeared in the region of 600–1100 cm^{-1} for

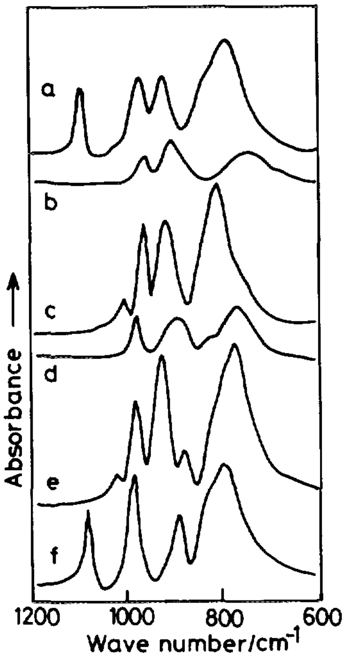


FIG. 1. Infrared spectra of heteropolyacids with Keggin and Dawson structures. The samples were pressed into KBr: (a) $H_6P_2W_{18}O_{62} \cdot 32H_2O$, (b) $H_6CoW_{12}O_{40} \cdot 19H_2O$, (c) $H_5BW_{12}O_{40} \cdot 15H_2O$, (d) $H_4GeW_{12}O_{40} \cdot 7H_2O$, (e) $H_4SiW_{12}O_{40} \cdot 22H_2O$, and (f) $H_3PW_{12}O_{40} \cdot 30H_2O$.

$H_mXW_{12}O_{40}$ (X = P, Si, Ge, B, and Co). No peaks due to impurities were detected. Dawson-type $H_6P_2W_{18}O_{62}$ obtained here also gave bands from 780 to 1090 cm^{-1}. Wavenumbers of the IR absorption are compared with those in the literature in Table 1. IR peak positions of these heteropolyacids were in agreement with those in the literature (*14, 20–22*).

Homogeneous Acid-Catalyzed Reactions

Reaction (1) took place rapidly in the presence of heteropolyacids, where all the catalysts were dissolved completely under the reaction conditions. The rate is expressed by the first-order rate equation

$$\ln [\mathrm{IBP}] = -k_1 t + B, \tag{5}$$

where k_1 and B are the first-order rate constant and $\ln[\mathrm{IBP}]_0$ ($[\mathrm{IBP}]_0$ is the initial concentration of isobutyl propionate), respectively.

Figure 2 shows the time courses and the first-order plots of Reaction (1). The first-order plots based on Eq. (5) gave straight lines, and the rate constants obtained from the slopes are summarized in Table 2. Heteropolyacids were much more active than PTS and H_2SO_4, and the differences among heteropolyacids were also large. The content of water in the heteropolyacids influenced the activity; anhydrous $H_3PW_{12}O_{40}$ was three times as active as $H_3PW_{12}O_{40} \cdot 30H_2O$. When Reaction (1) was performed using $H_3PW_{12}O_{40} \cdot 30H_2O$ (0.7×10^{-5} mol), a small amount of *tert*-butyl alcohol (about 0.6% of the initial concentration of IBP) was detected after 2 h as a byproduct. The effect of water on Reaction (1) is described in more detail in the next section.

When the rate constants per unit mole of proton (in parentheses) were compared for the anhydrous heteropolyacids, the following order was obtained: $H_3PW_{12}O_{40}$ (11.9) > $H_4SiW_{12}O_{40}$ (7.3) ~ $H_4GeW_{12}O_{40}$ (7.2) > $H_5BW_{12}O_{40}$ (5.8) > $H_6P_2W_{18}O_{62}$ (3.5) > $H_6CoW_{12}O_{40}$ (2.4). The differences are so large that the order does not change even if the rate constants are compared per unit mole of polyanion. This indicates that the rate constant greatly decreases as the negative charge of the polyanion increases.

Reactions (2) and (3) followed the second-order rate equation

$$dx/dt = k(a - x)^2 - k'x^2. \tag{6}$$

Its integrated form is

$$\ln \{[x(a - 2x_e) + ax_e]/[a(x_e - x)]\} = k\{2a(a - x_e)/x_e\}t. \tag{7}$$

where a and x_e in Eqs. (6) and (7) are, respectively, the initial concentration of the reactants and the equilibrium concentration of products (x_e = 2.51 mol · dm^{-3} for Reaction (2), x_e = 2.09 mol · dm^{-3} for Reaction (3)), and k and k' are the second-order rate constants for forward and reverse reactions, respectively.

The rate constants for Reaction (2) deter-

TABLE 1

Wave numbers of Infrared Absorption of Heteropolyacids

$H_3PW_{12}O_{40}$	$H_4SiW_{12}O_{40}$	$H_4GeW_{12}O_{40}$	$H_5BW_{12}O_{40}$	$H_6CoW_{12}O_{40}$	$H_6P_2W_{18}O_{62}$	Modes of vibration
1080^{a}					1091^{a}	
1080^{b}					1022^{e}	ν_{as}(P–O)
1080^{c}					1090^{e}	
	1018^{a}		1006^{a}			
	1020^{b}		1010^{d}	1170^{d}		
982^{a}	980^{a}	978^{a}	960^{a}	960^{a}	962^{a}	ν_{as}(W=O)
985^{b}	982^{b}	980^{b}	960^{d}	960^{d}	975^{e}	
990^{c}	981^{c}	980^{c}				
	926^{a}		914^{a}			
	930^{b}		920^{d}			ν_{as}(X–O), X=Si, B
	928^{c}					
893^{a}	878^{a}	886^{a}		895^{a}	914^{a}	ν_{as}(W–O–W)
887^{b}	885^{b}	910^{b}	902^{d}	900^{d}	916^{e}	
890^{c}	880^{c}	903^{c}				
		818^{a}				
		815^{b}				ν_{as}(Ge–O)
		818^{c}				
812^{a}	779^{a}	765^{a}	810^{a}	738^{a}	780^{a}	
807^{b}	792^{b}	775^{b}	820^{d}	740^{d}	780^{e}	ν_{as}(W–O–W)
810^{c}	785^{c}	760^{c}				
				445^{a}		
				453^{d}		ν(Co–O)

[a] Present study.
[b] Ref. (*14*).
[c] Ref. (*20*).
[d] Ref. (*21*).
[e] Ref. (*22*).

mined from the slopes of the second-order plots are summarized in Table 2. The equilibrated conversion (76%) was obtained after about 6 h with $H_3PW_{12}O_4 \cdot 30H_2O$ (2×10^{-4} mol). Even after 6 h, the formation of *tert*-butyl alcohol and isobutene was negligibly small. When the rate constant of Reaction (2) (per unit mole of H^+) was compared among anhydrous heteropolyacids, the difference was rather large and the following order was obtained: $H_3PW_{12}O_{40} \sim H_4SiW_{12}O_{40} > H_4GeW_{12}O_{40} \sim H_6P_2W_{18}O_{62}$. The order remains unchanged even if the rate constants are compared per unit mole of polyanion. Since $H_6CoW_{12}O_{40}$ and $H_5BW_{12}O_{40}$ were not completely soluble in the reaction solution, reliable data were not obtained for them. It can be seen in Table 2 that the rate constant of Reaction (2) was very sensitive to the content of water; the water appreciably accelerated the reaction. The effect of water is described in more detail in the next section. For Reaction (3), the rate constants were determined from the

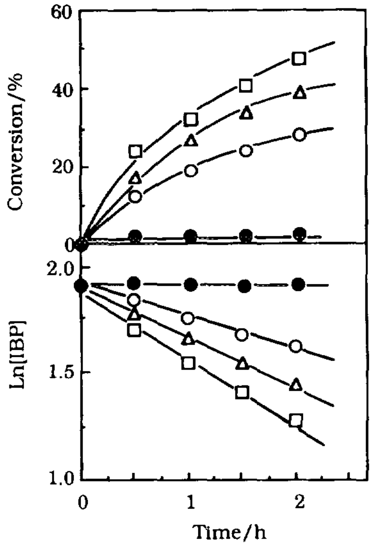


FIG. 2. Time course (upper figure; product) and the first-order plot (bottom figure) for the decomposition of isobutyl propionate (Reaction (1)) over heteropolyacids and *p*-toluenesulfonic acid at 128°C. Isobutyl propionate, 10 ml (0.067 mol); heteropolyacids, 1.5 × 10^{-5} mol; and PTS, 5.5 × 10^{-4} mol. □, $H_6P_2W_{18}O_{62}$; ○, $H_5BW_{12}O_{40}$; △, $H_4GeW_{12}O_{40}$; and ●, PTS. [IBP] shows the concentration of isobutyl propionate.

slopes of the second-order plots, as shown in Fig. 3. The equilibrium concentrations, which are necessary for the plot, were determined by the reactions in the presence of excess $H_3PW_{12}O_{40}$ (10^{-3} mol) for 8 h. The conversion reached nearly a constant value (47%) after about 5 h. The byproducts such as *tert*-butyl alcohol and diisopropyl ether were less than 0.5% of the reactant, even after 8 h.

The rate constants for Reaction (3) are given in Table 3. Contrary to Reactions (1) and (2), there were much smaller differences in the rate constants among the catalysts including H_2SO_4 and PTS.

The rate of Reaction (4) is expressed by

$$dx/dt = k(a - x)(b - x) - k'x^2$$
$$(a = 4.47, b = 7.27 \text{ mol} \cdot \text{dm}^{-3}). \quad (8)$$

Its integrated form is

$$q^{1/2}kt = \ln [x_e/(x_e - x)] \cdot \{[(k - 1)(x_e - x) + Kq^{1/2}]/[(K - 1)x_e + Kq^{1/2}]\}$$
$$(q = (a - b)^2 + 4ab/K). \quad (9)$$

Here, a, b, and x_e are the initial concentrations of reactants and the equilibrium concentration of products, respectively, and k and K are the second-order rate constant and the equilibrium constant, respectively.

The rate constants were evaluated from the slopes of the plots based on Eq. (9), where k and K were experimentally determined to be x_e = 3.6 mol · dm^{-3} and K = 4.0. The latter was determined by the reaction of propionic acid (0.067 mol) and isobutyl alcohol (0.109 mol) at 70°C for 8 h in the presence of $H_6P_2W_{18}O_{62} \cdot 32H_2O$ (3.60 × 10^{-5} mol). Under the above reaction conditions, the equilibrated conversion (53%) was obtained after about 6 h. The products other than IBP were less than 0.5% of the initial concentration of the reactant after 8 h. The rate constants obtained are also given in Table 3. Similar to Reaction (3), no significant difference in the rate constant was observed among the catalysts for Reaction (4).

Dependences of the rate constants of Reactions (1)–(4) on the concentration of the heteropolyacids are shown in Fig. 4. The

TABLE 2

Rate Constants of Reactions (1) and (2) over Acid Catalysts

	n^a	Rate constant[b]	
		Reaction (1)[c]	Reaction (2)[d]
$H_3PW_{12}O_{40}$	0	11.9	0.09
	30	3.7	0.9
$H_4SiW_{12}O_{40}$	0	7.3	0.08
	22	4.5	0.8
$H_4GeW_{12}O_{40}$	0	7.2	0.03
$H_5BW_{12}O_{40}$	0	5.8	(Insoluble)
$H_6CoW_{12}O_{40}$	0	2.4	(Insoluble)
$H_6P_2W_{18}O_{62}$	0	3.5	0.03
PTS[e]		<0.1	0.1
H_2SO_4		<0.1	0.1

[a] Number of the crystallization water, n in $H_mXW_{12}O_{40} \cdot nH_2O$.

[b] Per H^+-mol.

[c] Decomposition of isobutyl propionate at 128°C ($\text{min}^{-1} \cdot H^+\text{-mol}^{-1}$).

[d] Exchange reaction between isobutyl propionate and acetic acid ($\text{mol}^{-1} \cdot \text{dm}^3 \cdot \text{min}^{-1} \cdot H^+\text{-mol}^{-1}$).

[e] *p*-Toluenesulfonic acid.

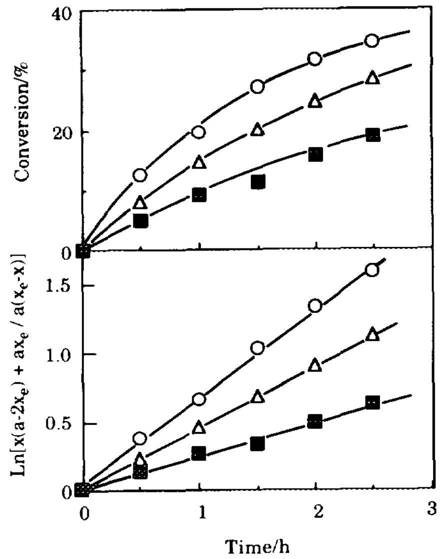


FIG. 3. Time course (upper figure; product) and the second-order plot (bottom figure) for the exchange of isobutyl propionate with *n*-propyl alcohol (Reaction (3)) over heteropolyacids and H_2SO_4. Isobutyl propionate, 10 ml (0.067 mol); *n*-propyl alcohol, 5 ml (0.067 mol); heteropolyacids, 5.8×10^{-5} mol; and H_2SO_4, 3.86×10^{-4} mol. ○, $H_6P_2W_{18}O_{62} \cdot 32H_2O$; △, $H_3PW_{12}O_{40} \cdot 30H_2O$; and ■, H_2SO_4.

TABLE 3

Rate Constants of Reactions (3) and (4) over Acid Catalysts

	n[a]	Rate constant[b]	
		Reaction (3)[c]	Reaction (4)[d]
$H_3PW_{12}O_{40}$	30	1.2	3.8
	6	1.5	4.8
	0	1.5	4.9
$H_4SiW_{12}O_{40}$	22	1.1	3.3
$H_4GeW_{12}O_{40}$	7	1.1	3.3
$H_5BW_{12}O_{40}$	15	0.8	3.2
$H_6CoW_{12}O_{40}$	19	0.7	2.3
$H_6P_2W_{18}O_{62}$	32	0.8	2.7
PTS[e]		0.8	6.4
H_2SO_4		0.5	3.2

[a] Number of the crystallization water, n, in $H_mXW_{12}O_{40} \cdot nH_2O$.

[b] Per H^+-mol.

[c] Exchange reaction of isobutyl propionate with *n*-propyl alcohol at 70°C ($mol^{-1} \cdot dm^3 \cdot min^{-1} \cdot H^+$-$mol^{-1}$).

[d] Esterification of propionic acid with isobutyl alcohol at 70°C ($mol^{-1} \cdot dm^3 \cdot min^{-1} \cdot H^+$-$mol^{-1}$).

[e] *p*-Toluenesulfonic acid.

rate constants for all reactions increased in proportion to the concentration of the heteropolyacids. It was confirmed that the rate of Reaction (1) increased linearly with the concentration of $H_4SiW_{12}O_{40}$, as in the other reactions, although the data were fewer.

Effect of Water on the Rate Constant

In Figs. 5 and 6, the effects of water on the rates of Reactions (1)–(4) catalyzed by $H_3PW_{12}O_{40}$ are given; the water concentration was changed by altering the number of the water of crystallization and by the intentional addition of water into the solutions. The rate constants for Reactions (1), (3), and (4) decreased appreciably as the water content increased. The retarding effect was Reaction (1) > (3) > (4). In contrast, the rate constant of Reaction (2) increased with the water content. The effects of water were similar also for PTS catalyst; water accelerated Reaction (2), but retarded Reactions (3) and (4).

Effect of $PW_{12}O_{40}^{3-}$ Concentration on Reaction (1)

Figure 7 shows the effect of the concentration of $PW_{12}O_{40}^{3-}$ (anion) on Reaction (1).

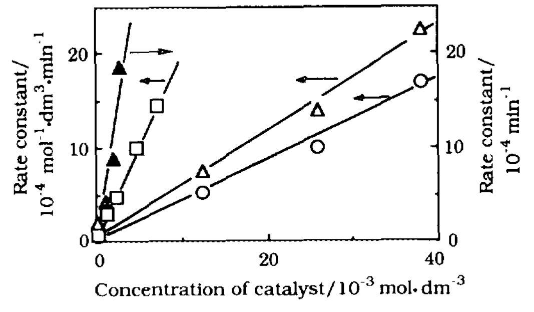


FIG. 4. Dependence of the concentration of heteropolyacids on the rate constants. ▲, Reaction (1) (decomposition of isobutyl propionate (10 ml)), $H_3PW_{12}O_{40}$, 128°C, ○, Reaction (2) (isobutyl propionate (10 ml) + acetic acid (3.8 ml); the solution contained 0.6 mol% water), $H_4SiW_{12}O_{40}$, 70°C. △, Reaction (3) (isobutylpropionate (10 ml) + *n*-propyl alcohol (5 ml)), $H_4SiW_{12}O_{40}$, 70°C, and □, Reaction (4) (isobutyl alcohol (10 ml) + propionic acid (5 ml)), $H_4SiW_{12}O_{40}$, 70°C.

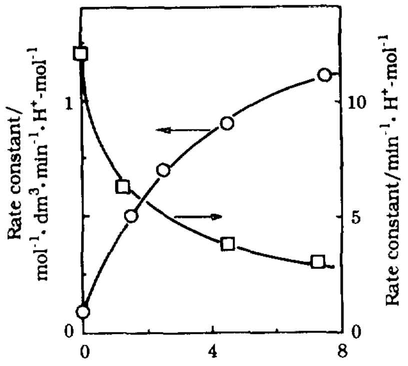


FIG. 5. Effects of water on the rate constants on Reactions (1) and (2) over $H_3PW_{12}O_{40}$. □, Reaction (1) (decomposition of isobutyl propionate (10 ml), 128°C). ○, Reaction (2) (isobutyl propionate (10 ml) + acetic acid (3.8 ml), 70°C).

The rate constant for Reaction (1) was plotted as a function of the concentration of $PW_{12}O_{40}^{3-}$, where the concentration of $PW_{12}O_{40}^{3-}$ was increased by the addition of $Na_3PW_{12}O_{40}$ to the $H_3PW_{12}O_{40}$ solution. It was observed that the rate was independent of the concentration of $PW_{12}O_{40}^{3-}$.

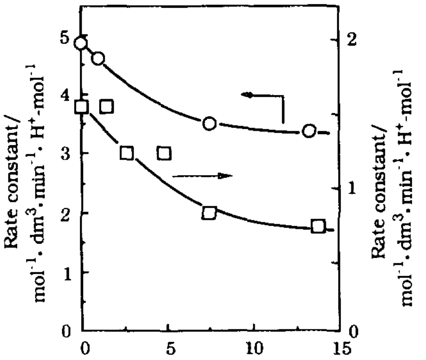


FIG. 6. Effects of water on the rate constants of Reactions (3) and (4) over $H_3PW_{12}O_{40}$. □, Reaction (3) (isobutyl propionate (10 ml) + *n*-propyl alcohol (5 ml), 70°C). ○, Reaction (4) (isobutyl alcohol (10 ml) + propionic acid (5 ml), 70°C).

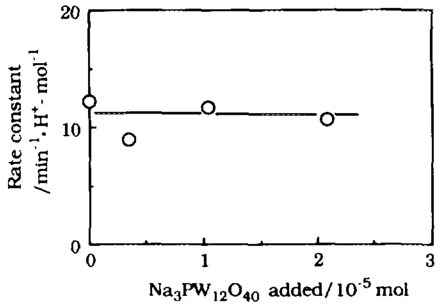


FIG. 7. Effects of the addition of $Na_3PW_{12}O_{40}$ on the rate constant of Reaction (1). $H_3PW_{12}O_{40}$, 2.1 × 10^{-5} mol; isobutyl propionate, 0.067 mol, 128°C. The reaction system was homogeneous also after the addition of $Na_3PW_{12}O_{40}$.

DISCUSSION

Efficient catalysis of heteropolyacids in a homogeneous liquid phase has been demonstrated in various organic reactions (*1*, *3*, *4*, *6*). The present study has focused on the effects of the central atom on catalysis when the Keggin structure has W as the addenda atom. One Dawson-type heteropolyacid was also examined for comparison. The main objectives of the present study are (i) to demonstrate the usefulness or superiority of heteropolyacid catalysts compared with the conventional mineral acids in certain reactions, (ii) to show how their catalytic features vary depending on the reaction systems, and (iii) to discuss the possible factors determining the activity order of the heteropolyacid catalysts.

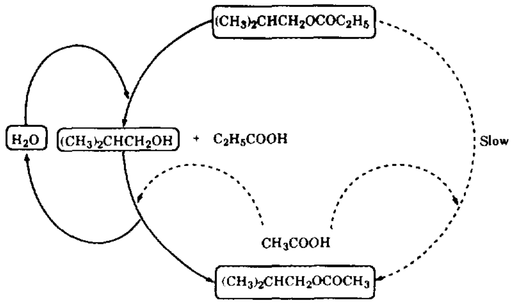
First, the effect of water on the rate is discussed, since water in the reaction solution greatly influenced the rates. Then the relative activity of the heteropolyacid catalysts to H_2SO_4 and PTS, as well as the activity patterns among the heteropolyacids, is discussed.

Effects of the Concentrations of $PW_{12}O_{40}^{3-}$ and Water

Izumi *et al.* found the activities of heteropolyacids to be higher than that of H_2SO_4 in nonaqueous solutions, and attributed this difference to the difference in the acid strength of the catalyst solution (*6*). They further inferred that the softness of the heteropolyanion plays an important role in the acid-catalyzed reactions in an aqueous solution by forming complexes with reaction intermediates, such as a complex between the isobutyl cation and the heteropolyanion (*23*) for the hydration of isobutene. Baba and Ono (*24*) also observed the promoting effect of polyanion on the rate of dehydration of 1,4-butanediol to tetrahydrofuran in an aqueous solution of $H_4SiW_{12}O_{40}$. On the other hand, they found that the rate of the same reaction in *dioxane* solution was independent of the concentration of $SiW_{12}O_{40}^{4-}$.

As shown in Fig. 7, the addition of $Na_3PW_{12}O_{40}$ had no acceleration effect on the rate of Reaction (1) in the present study, in accordance with the results of Baba and Ono (*24*), suggesting that the complexation of the polyanion is not important in these cases. The significant difference in the rate constant of Reaction (1) can likely be attributed to the difference in the acid strength of the catalyst solution of IBP. For the reactions in nonaqueous solutions, such as ether cleavage (*6*) and the decomposition of cumenyl hydroperoxide (*25*), the acid strength of the heteropolyacid solution is an important factor determining the reaction rate.

As shown in Figs. 5 and 6, the presence of water retarded Reactions (1), (3), and (4). Probably, the coordination of water to a proton reduces the acid strength of the $H_3PW_{12}O_{40}$ solutions, as has been suggested for the dehydration of 1,4-butanediol in dioxane catalyzed by $H_4SiW_{12}O_{40}$ (*24*). On the other hand, Aoshima *et al.* found that the presence of certain amounts of water ($n <$ 6) in $H_3PW_{12}O_{40} \cdot nH_2O$ accelerated the polymerization of tetrahydrofuran (*10*). These results suggest that the water acts as both a poison and a promoter depending on its content and the kind of reaction. More detailed study is necessary for the full elucidation of the role of water (in a wider sense, the solvent effect).



SCHEME 1. Reaction scheme for ester exchange of isobutyl propionate with acetic acid (Reaction (2)).

In Reaction (2), $H_3PW_{12}O_{40} \cdot 30H_2O$ was 10 times as active as anhydrous $H_3PW_{12}O_{40}$, and the intentional addition of water to the solution also enhanced the reaction (Fig. 5). From the acceleration effect of water, we propose Scheme 1 for Reaction (2), based on the results described below. In this scheme, water acts as a co-catalyst; that is, water reacts with IBP to form isobutyl alcohol and propionic acid, and then the reaction between isobutyl alcohol and acetic acid takes place to form the product, isobutyl acetate, and water. In order to verify Scheme 1, the reaction rates of the hydrolysis of IBP and the esterification of isobutyl alcohol with acetic acid were measured. In Table 4, the results are compared with that of the exchange of IBP with propionic acid (Reaction (2)) at the same initial concentrations. It was observed that the hydrolysis of IBP and the esterification of isobutyl alcohol with acetic acid were much more rapid than in Reaction (2). This strongly supports Scheme 1. Since the acceleration effect of water was also observed over PTS, Scheme 1 may be applica-

TABLE 4

Initial Rate of Hydrolysis of Isobutyl Propionate, Esterification of Isobutyl Alcohol with Acetic Acid, and Reaction (2)

Reaction[a]	Initial rate (mol · cat-mol^{-1} · min^{-1})
Isobutyl propionate + H_2O	7.0
Isobutyl alcohol + acetic acid	11.6
Reaction (2) (isobutyl propionate + acetic acid)	1.2

[a] Reactants, 0.067 mol; temperature, 70°C; catalyst, $H_3PW_{12}O_{40} \cdot 30H_2O$, 1.78 × 10^{-4} mol.

ble not only to heteropolyacids but also to the other acid catalysts.

Activity Patterns of the Reactions

It is remarkable that for Reactions (3) and (4) the catalytic activities of heteropolyacids were comparable to or slightly less than those of H_2SO_4 and PTS, while a great difference in the activity was observed for Reaction (1). Reaction (2) probably belongs to the latter class, although the reliable data are fewer. It has been reported that $H_3PW_{12}O_{40}$ completely dissociates in water, while in acetic acid, the dissociation is slight (*4, 6*). This is reasonable because acetic acid is a much weaker base than water (*26*). The following order of basicity has been reported; water > alcohols > acetic acid > ester (*26*). Thus the protons of the catalysts are almost completely transferred to the reactant alcohols in Reactions (3) and (4). In fact, it has been reported that most of $H_3PW_{12}O_{40}$ is dissociated in ethanol solution (*3, 27*). By this effect, the acid strength of the reactant solution, including the catalysts, becomes almost the same ("leveling effect" of alcohols), and consequently the activity becomes insensitive to the catalyst. The "leveling effect" of water that brings all stronger acids down to the same acidity is well known (*28*).

On the other hand, in the case of the catalyst solution of an ester, the dissociation of the heteropolyacid may be incomplete due to the weak basicity of the ester, and, therefore, the amount of protonated ester (which is considered an intermediate) increases as the acid strength of the heteropolyacid increases, thereby enhancing the reaction rate. Because heteropolyacids behave as weak electrolytes in acetic acid, Izumi *et al.* (*6*) suggested that ether cleavage with acetic acid in nonaqueous solution is catalyzed by the nondissociated heteropolyacids. We suppose that this reaction belongs to general acid catalysis. The heteropolyacids also behave as weak electrolytes in the ester (IBP). In this case, the concentration of dissociated protons is not proportional to the concentration of the heteropolyacids. Thus the fact that the rate increased linearly with the concentration of the heteropolyacid (Fig. 4) suggests general acid catalysis, but not specific hydronium-ion catalysis. The activity of anhydrous $H_3PW_{12}O_{40}$ in Reaction (1) was 100 times as high as that of PTS and H_2SO_4. The significant difference in the activity between the heteropolyacids and H_2SO_4 may be attributed to the difference in the acid strength of the catalyst solutions (i.e., pK_a of heteropolyacids < H_2SO_4, PTS). Actually, Kozhevnikov *et al.* reported that the acidities of $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ are significantly stronger than that of H_2SO_4 in acetic acid (*4*). In addition, Izumi *et al.* showed that $H_3PW_{12}O_{40}$ gave a lower value of H_0 than PTS in acetic acid at the same concentration (*6*). As discussed above, the effect of the softness of the polyanion, suggested in the literature (*6*), by the formation of a complex with a cationic intermediate may be insignificant in Reaction (1).

If the central atom changed while the polyanion structure remained unchanged, the acid strength of the heteropolyacid would increase with the decrease in the negative charge of the polyanion, as the interaction between proton and polyanion decreases. Hence, the following order of the acid strength is expected among the Keggin anions used in the present study: $H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} \sim H_4GeW_{12}O_{40} > H_5BW_{12}O_{40} > H_6CoW_{12}O_{40}$. Kozhevnikov and Matveev (*4*) determined the dissociation constants (pK_a) in acetic acid to be 4.8, 5.0, and 7.0 for $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, and H_2SO_4, respectively. Izumi *et al.* (*6*) reported the following order of the acid strength: $H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} \sim H_4GeW_{12}O_{40}$, evaluated by the NMR chemical shifts of the proton of chloral hydrate (*11*). Those results are in agreement with the expected order of the acid strength.

In Fig. 8, the rate constants for Reaction (1) as well as Reactions (3) and (4) are plotted against the negative charge of the polyanion, and the logarithms of the rate constants are plotted in Fig. 8B. The data for

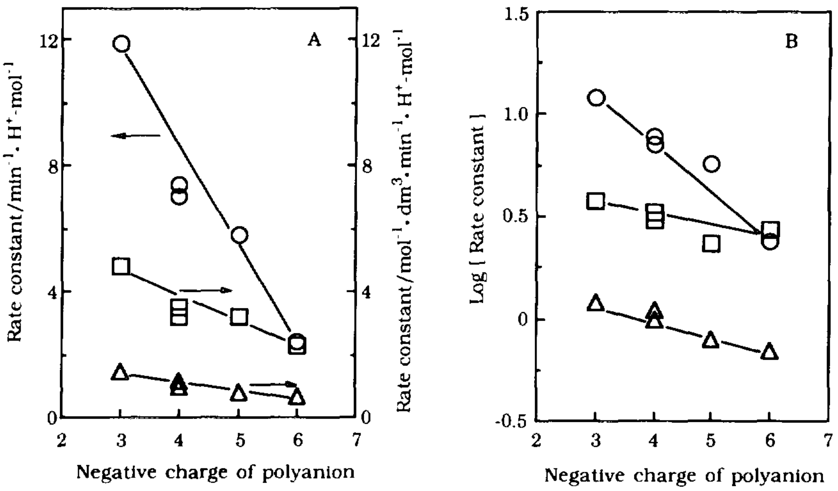


FIG. 8. The rate constants for Reactions (1), (3), and (4) as a function of the negative charge of polyanion, $XW_{12}O_{40}^{n-}$ (X = P, Si, Ge, B, and Co). ○, Reaction (1); △, Reaction (3), and □, Reaction (4). (A) Normal plot and (B) logarithm of the rate constant vs the negative charge.

Reaction (2) are not included because there are fewer reliable data. But the trend is more like that for Reaction (1). As shown in Fig. 8A, the rate constant for Reaction (1) decreased monotonically as the negative charge of the heteropolyanion increased. This activity order agrees well with that of the acid strength described above. The changes in the rate constants for Reactions (3) and (4) were much smaller than that of Reaction (1), which is presumably due to the leveling effect as discussed above.

CONCLUSION

Heteropolyacids of the Keggin type containing W in the polyanion showed remarkably high catalytic activities for certain reaction systems, "solvent effect." For the liquid-phase homogeneous decomposition of isobutyl propionate (Reaction (1)), heteropolyacid catalysts were 60–100 times more active than H_2SO_4 and *p*-toluenesulfonic acid. The catalytic activity for this reaction increased as the valency of the central atom increased. This can be attributed to the increase in the acid strength of the catalyst solution, which increases with the decrease in the negative charge of the polyanions (e.g., pK_a for $H_3PW_{12}O_{40}$ is 4.8 and that for $H_4SiW_{12}O_{40}$ 5.0 (*4*)). For reactions involving basic molecules such as alcohols, no large differences in activity among these catalysts including H_2SO_4 and *p*-toluenesulfonic acid were observed, suggesting that these catalysts were equally strong in solution due to the leveling effect of the basic reactant.

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