Efficient homogeneous catalysis of heteropoly acid and its characterization through etherifications of alcohol

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Abstract

A Keggin-type heteropoly acid revealed high catalytic activity for the etherification such as diethylene glycol with ethanol and cyclization of diethylene glycol in the homogeneous liquid. The catalytic activities of the heteropoly acid were much higher than those of conventional acid catalysts such as sulfuric acid, *p*-toluene sulfonic acid and phosphorous acid at the same catalyst concentrations or the same proton concentrations. On the basis of comparative measurement of electrical conductivity, acidity, and softness of anion for the solutions of acid catalysts, the efficient acid catalysis by heteropoly acid was suggested to due to be the specific properties of the heteropoly anion, which can be characterized by very weak basicity and great softness, together with the large size of the polyhedral structure. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Catalysis of Keggin-type heteropoly acid has attracted much interest since seventies. The heteropoly acid (hereafter abbreviated as HPA) possesses the dual catalytic functions of strong acidity and oxidizing ability. Onoue et al. [1] have reported that HPA catalyzed olefin hydration in a dilute aqueous solution much more efficiently than the ordinary acid such as sulfuric acid and phosphoric acid, and this knowledge led to the development of a new commercial process for the direct hydration of propene. HPA has high catalytic activity for the methyl *tert*-butyl ether synthesis [2,3] and the etherification of β-naphthol with alknols [4]. Tungstophosphoric acid has been used as a catalyst for the dehydration of 2-propanol [5]. HPA will be expected as an alternative acid catalyst to improve several organic processes which employ conventional acids [6,7].

In aqueous solution, HPA such as PW, SiW, and PMo are strong fully dissociated acids. HPA in solution is stronger than the usual mineral acids such as H_2SO_4, HCl, HNO_3, etc. [8].

The authors have recently studied homogeneous acid catalysis of HPA, in order to elucidate its catalytic features at a molecular level. Etherification of diethylene glycol with ethanol [9,10] and cyclization of diethylene glycol in the homogeneous liquid phase [11], for example, HPA revealed a catalytic activity higher than *p*-toluene sulfonic acid, sulfuric acid or phosphorous acid under conditions of identical proton concentrations and ionic strengths. It was suggested that the dissociated heteropoly anions in the aqueous phase might play a key role in accelerating the reaction. It has been reported [12] that the rates of dehydration and etherification are directly

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proportional to total acidity of heteropoly acid. HPA exhibited greater catalytic efficiency than the conventional acids for non-aqueous homogeneous reactions such as alcoholysis of epoxides [13], in which HPA worked presumably in the non-dissociated form. Such efficient acid catalysis of HPA in the non-aqueous phase also may be due to certain specific properties of the heteropoly anion.

This paper aims to characterize the homogenous acid catalysis of HPA in connection with the properties of heteropoly anion, through the examination of some etherifications in which the difference in acid catalysis between HPA and other acids can be clearly reflected.

2. Experimental

2.1. Materials

All organic reagents used were highest purity commercial products ($\geq$99%). 12-Tungstophosphoric acid ($H_3PW_{12}O_{40} \cdot 25H_2O$, containing 0.01% free water), 12-tungstosilicic acid ($H_4SiW_{12}O_{40} \cdot 26H_2O$, containing 0.01% free water), 12-molybdophosphoric acid ($H_3PMo_{12}O_{40} \cdot 28H_2O$, containing 0.01% free water), 12-molybdosilicic acid ($H_4SiMo_{12}O_{40} \cdot 12H_2O$, containing 0.01% free water), sulfuric acid (98%), phosphorous acid (85%), *p*-toluene sulfonic acid were of commercially available purity. Silver salts of HPA, sulfuric acid, phosphorous acid and *p*-toluene sulfonic acid were prepared by adding a stoichiometric amount of Ag_2CO_3 into a hot aqueous solution containing an acid.

3. Experimental method for the determination of the water content of HPA

The amount of free and structural water of HPA was determined by thermogravimetric analysis (DT-2B-type, Japan). The conditions were follows: the rate of raising temperature was 3°C/min, and the paper rate was 0.35 cm/min.

3.1. Reaction procedure

All reactions were carried out in the homogeneous liquid phase.

Cyclization of diethylene glycol proceeded in a 500 ml glass distillation flask. At first, diehylene glycol and catalyst were added in the flask, then heated for the reaction.

Etherification of diethylene glycol with ethanol proceeded in a 400 ml autoclave, with electromagnetic stirring and electric furnace heating through a temperature controller. Also, there is a sampling tube connected to the autoclave. The materials of the autoclave and sampling tube are stainless steel.

Reaction method: Diethylene glycol, ethanol and catalyst are placed into autoclave, at first, put in nitrogen to 1.7 MPa, then raise temperature up to 200°C, the pressure is up to 5.0 MPa. The reaction occurs under stirring and after 2 h, sampling and analyze it.

3.2. Product analysis

The composition and content of the product were determined with internal standard by thermal conduct detector of 1102G-type gas chromatograph made in Shanghai Analysis Instrument Factory. The chemical structure of the products was determined by GC–MS instrument made in Japan. The products were separated by distillation.

3.3. Equilibration between silver salt and sodium iodide

In order to estimate the relative softness of the heteropoly anion, equilibrium constants were measured for the reactions of sodium iodide with salts of HPA, sulfuric acid, *p*-toluene sulfonic acid and phosphorous acid in aqueous solutions at 25°C. After equilibration (6–50 h), free iodide ion in the aqueous phase was oxidized to iodate in a buffered solution with bromine. The excess bromine was reduced with sodium formate. The iodate was determined by adding iodide and acid and by titrating the liberated iodine with standard sodium thiosulfate by iodometry [14]. The procedure was as follows.

Pipette, an aliquot of the sample containing 0.2–5.0 mg of iodide, into a 500 ml wide-mouth Erlenmeyer flask and dilute to 100 ml with water, if necessary. Add 15 ml of 2 mol/l sodium acetate and 5 ml of 2 mol/l acetic acid. Add 4 ml of bromine water, or enough to produce a definite pale yellow color

Table 1
Cyclization of diethylene glycol (180°C, 40 min)[a]

Catalyst	Catalyst concentration (mol/l)	Conversion (%)	Selectivity of 1,4-dioxane (%)
$H_3PW_{12}O_{40}$	0.001	57	95
$H_4SiW_{12}O_{40}$	0.001	46	96
$H_3PMo_{12}O_{40}$	0.001	26	96
$H_4SiMo_{12}O_{40}$	0.001	32	99
H_3PO_4	1.6	7	67
H_2SO_4	1.7	10	56
TsOH	1.2	6	64

[a] $HO(CH_2CH_2)O(CH_2CH_2)OH \longrightarrow$ (1,4-dioxane) $+ H_2O.$
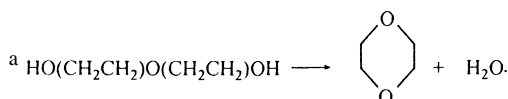
due to excess bromine. Mix the solution and allow to stand 10 min. Add 2 ml of a 25% sodium formate solution, blow out any bromine vapor from the flask, and wash the inside of the flask with water. When the bromine has been reduced, add 1 g of potassium fluoride dehydrate. In 0.5 g of potassium iodide, add 10 ml of 1:4 sulfuric acid. Titrate the liberated iodine with 0.01 mol/l sodium thiosulfate, adding a starch indicator just before the end point. Disregard any return of blue color after the end point has been reached. Determine a blank on the reagents and subtract it from the observed titration.

$$\%I^- = \frac{\text{ml } 0.01 \text{ mol/l Na}_2S_2O_3 \times 0.01 \times 0.02115 \times 100}{\text{grams of sample}}$$

4. Results and discussion

Hydrated HPA which usually contains 11–28 water molecules per Keggin unit at ambient temperature, is moderately soluble in polar organic solvents such as alcohol, ether, ketone, carboxylic acid and ester, whereas anhydrous HPA is scarcely soluble therein. It is, therefore, preferable to use a hydrated HPA for examining its homogeneous acid catalysis in organic media.
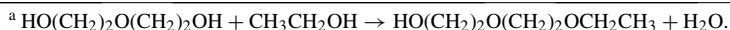
4.1. Etherifictions of the alcohol on heteropoly acid

All of the reactions were performed in the homogeneous liquid phase. The acid catalysts employed were the Keggin-type heteropoly-tungstic and -molybdic acids, *p*-toluene sulfuric acid, sulfuric acid and phosphorous acid. All of the HPA used maintained their Keggin structures in the course of the reactions, which were conformed by examining their IR spectra. At temperature above 200°C, heteropoly-molybdic acid, which has a relatively higher redox potential than heteropoly-tungstic acid, was reduced with the reacted substance, changing its color from yellow to blue.

As shown in Tables 1 and 2 and Figs. 1 and 2, the results from the cyclization of diethylene glycol and etherification of diethylene glycol with ethanol

Table 2
Etherification of diethylene glycol with ethanol at 200°C[a]

Catalyst	Catalyst concentration (10^{-3} mol/l)	Conversion (%)	Selectivity of diethylene glycol ethyl ether (%)
$H_3PM_{12}O_{40}$	1.6	60	75
$H_4SiW_{12}O_4$	1.6	56	78
$H_4SiMo_{12}O_{40}$	1.6	48	76
$H_3PMO_{12}O_{40}$	1.6	30	77
H_2SO_4	1620	18	41

[a] $HO(CH_2)_2O(CH_2)_2OH + CH_3CH_2OH \rightarrow HO(CH_2)_2O(CH_2)_2OCH_2CH_3 + H_2O.$
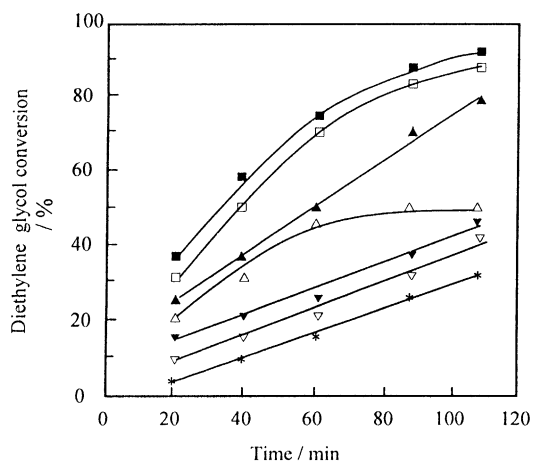
Fig. 1. Cyclizations of diethylene glycol at 180°C; diethylene glycol: 0.5 mol; (■) $H_3PW_{12}O_{40}$ (1.2×10^{-3} mol/l); (□) $H_4SiW_{12}O_{40}$ (1.2×10^{-3} mol/l); (▲) $H_4SiMo_{12}O_{40}$ (1.2×10^{-3} mol/l); (△) $H_3PMo_{12}O_{40}$ (1.2×10^{-3} mol/l); (▼) TsOH (1.2 mol/l); (▽) H_3PO_4 (1.6 mol/l); (∗) H_2SO_4 (1.7 mol/l).

indicate that HPA catalyst was far more efficient than H_2SO_4, H_3PO_4 and *p*-toluene sulfuric acid.

Regardless of the used catalysts, the normal dehydrating product was 1,4-dioxane from the cyclization of diethylene glycol at 180°C, and the normal dehydrating product was diethylene glycol ethyl ether from the etherification of diethylene glycol with ethanol at
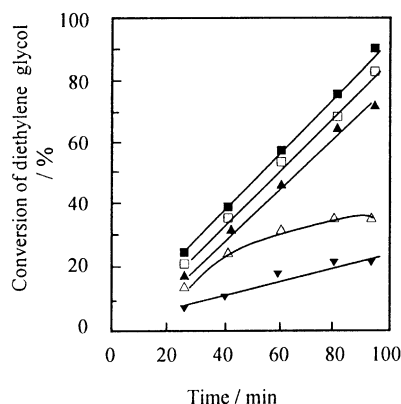

Fig. 2. Etherification of diethylene glycol with ethanol at 200°C; diethylene glycol: 0.9 mol, ethanol: 1.8 mol; (■) $H_3PW_{12}O_{40}$ (1.6×10^{-3} mol/l); (□) $H_4SiW_{12}O_{40}$ (1.6×10^{-3} mol/l); (▲) $H_4SiMo_{12}O_{40}$ (1.6×10^{-3} mol/l); (△) $H_3PMo_{12}O_{40}$ (1.6×10^{-3} mol/l); (▼) H_2SO_4 (1.62 mol/l).
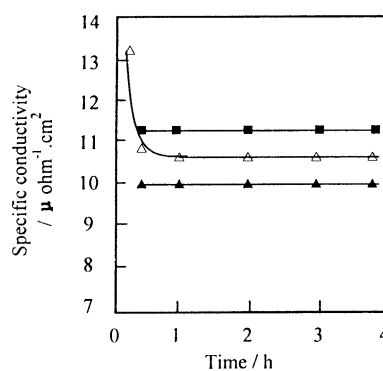

Fig. 3. Variation in specific conductivity of ethanol solutions at 200°C; (■) ethanol: 2.0 mol, diethylene glycol: 1.0 mol, $H_3PW_{12}O_{40}$ (1.6×10^{-3} mol/l); (△) ethanol: 2.0 mol, diethylene glycol: 1.0 mol, H_2SO_4 (1.62 mol/l); (▲) ethanol: 2.0 mol.

200°C. It should be noted that the catalytic activities of H_2SO_4, H_3PO_4, and TsOH were much low even though the acid concentration was 10^3 times higher than that employed for HPA (Figs. 1 and 2). It is probable due to an acidity loss resulting from the formation of sulfuric, phosphorous, and tosyl ester of alcohol. Indeed, as shown in Fig. 3, the electrical conductivity of a reaction medium containing H_2SO_4 catalyst rapidly decreased with the increase of reaction time, owing to the decrease in acidity, in contrast with no change observed with $H_3PW_{12}O_{40}$ catalyst. The decrease in catalytic activity of H_2SO_4 might closely related to the decrease in electrical conductivity. On the other hand, HPA does not form its esters with alcohol, and consequently it can easily effect the etherification. Diethylene glycol and diethylene glycol with ethanol readily underwent etherification at 180 and 200°C in the presence of HPA, respectively (Tables 1 and 2). 1,4-Dioxane and diethylene glycol ethyl ether, which are normal products of the etherification were predominantly obtained. The stability of HPA toward hydrolysis in aqueous solution follows the order: SiW > PW > SiMo > PMo. From ^{17}O NMR data, PW remains fully ionized in a 94:6 v/v AcOH–H_2O solution, the solvated protons loosely bound to the anion as a whole rather than to a certain oxygen atom in the anion. The strength of the Keggin HPA depends weakly on their composition. Yet the tungsten acids are markedly stronger than molybdenum ones. The

strongest acid in the Keggin series is PW. $SiW_{12}O_{40}{}^{4-}$ and $PW_{12}O_{40}{}^{3-}$ anions remain deprotonated even after accepting two and three extra electrons, respectively, upon polarographic reduction in aqueous solution at pH 1 [8]. The catalytic activity of PMo_{12} decreased noticeably at an earlier stage of the reaction because it was apt to decompose in the presence of alcohol at higher temperature. As illustrated in Figs. 1 and 2, 12-molybdosilicic acid was indeed more active than H_2SO_4, H_3PO_4, and TsOH at foremost stage of the reaction, but its activity gradually decreased after the turnover number (moles of converted alcohol per mole of catalyst) exceeded ∼50, and at the same time a blue insoluble solid which then changed into black was deposited in the reaction medium. Although this precipitate has not yet been identified, it seems to be an HPA that contains a few molecules of alcohol in place of some structural water of Keggin unit, since the IR spectrum of the recrystallized unknown substance showed a clear absorption peak at $1100 \, cm^{-1}$ (C–O) in addition to the characteristic absorption of the HPA.

4.2. Characterization of acid catalysis by HPA

Acidity appears to be essential to the acid catalysis of HPA in the present homogeneous etherification of alcohol, because neutral HPA salts such as $Na_3PW_{12}O_{40}$ and $Ca_2SiW_{12}O_{40}$ did not catalyze the reactions at all. The catalytic activity of HPA was much higher than sulfuric acid, phosphoric acid and TsOH on the basis of molar concentration of catalyst or the proton concentration, where HPA was assumed to behave as a tri- or tetra-basic acid. Hence, the remarkable difference in catalytic efficiency between HPA and other acids should be attributed to a certain qualitative difference in acidic properties. Although, the present study employed polyhydrated HPA, monohydrated TsOH, 85% phosphoric acid and 98% sulfuric acid as catalysts instead of anhydrous acids, because the concentration of sulfuric acid, TsOH, and phosphoric acid are 10^3 times higher than HPA throughout all reactions. The water content order of the reaction medium is following: $H_3PO_4 > H_2SO_4 > HPA > TsOH$, but the catalytic activity order is, $HPA > TsOH > H_3PO_4 > H_2SO_4$. It was conformed from separate experiments that the variation in water content between the systems of

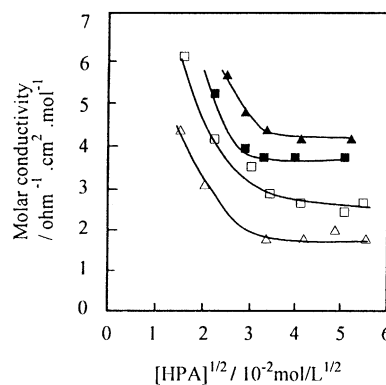Fig. 4. Molar conductivity of ethanol solutions of heteropoly acid at 28°C; (▲) $H_4SiMo_{12}O_{40}$; (■) $H_3PMo_{12}O_{40}$; (□) $H_3PW_{12}O_{40}$; (△) $H_4SiW_{12}O_{40}$.

HPA and other acids is never a critical cause for the difference in catalytic activity.

HPA, TsOH, sulfuric acid, and phosphoric acid, appear to behave as weak electrolytes in non-aqueous organic media whereas they are completely dissociated in aqueous solutions. Fig. 4 shows the dependence of the molar electrical conductivity on the HPA concentration in ethanol solution. The curvature of the phoreogram indicates that HPA exists as a weak electrolyte in ethanol. The catalytic activity must be, therefore, associated with the acidity of non-dissociated acid species in an organic medium, rather than with the concentration of dissociated proton. The acidity of HPA, H_2SO_4, H_3PO_4 and TsOH in ethanol at various concentrations were qualitatively estimated by use of Hammett indicator (Table 3). $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$ showed an acidity range in terms of H_0 function between -8.2 and -3.7 even at ≤ 0.01 mol/l, but H_2SO_4, H_3PO_4 and TsOH revealed the same range of H_0 function only at high concentration above 5.0, 4.5, and 1.1 mol/l, respectively. Thus, the strong acidity of HPA in ethanol should be responsible for its high catalytic efficiency in the etherifications.

In order to explain the difference in catalytic activity among HPA catalysts, it is necessary to compare their acidity, i.e. the basicities of the corresponding heteropoly anions. The results [15] showed that $SiMo_{12}O_{40}{}^{4-}$ anion was the strongest base. $H_4SiMo_{12}O_{40}$ should correspond to the weakest

Table 3
Acidity estimation of ethanol solution of heteropoly acid, H_3PO_4, H_2SO_4, and TsOH by Hammett indicators at $25°C^a$

Acid	Concentration (mol/l)	Bromophenol blue ($pK_a = -3.7$)	Anthraquinone ($pK_a = -8.2$)
$H_4PW_{12}O_{40}$	4.5×10^{-3}	+	−
	1.0×10^{-2}	+	−
	5.0×10^{-2}	+	−
$H_4SiW_{12}O_{40}$	4.9×10^{-3}	+	−
	1.0×10^{-2}	+	−
	5.0×10^{-2}	+	−
$H_4SiMo_{12}O_{40}$	4.0×10^{-3}	−	−
	1.0×10^{-2}	+	−
	6.0×10^{-2}	+	−
$H_4PMo_{12}O_{40}$	4.8×10^{-3}	−	−
	1.2×10^{-2}	+	−
	6.4×10^{-2}	+	−
H_3PO_4	4.9×10^{-4}	−	−
	1.1	±	−
	4.5	+	−
H_2SO_4	5.0×10^{-4}	−	−
	4.2	±	−
	5.0	+	−
TsOH	1.0×10^{-1}	−	−
	6.2×10^{-1}	±	−
	1.1	+	−

^{a} +: Acidic color; −: basic color; ±: border line.

acid among the HPA tested. Thus, the following order was found with respect to the acidity of HPA: $H_3PW_{12}O_{40} > H_3PMo_{12}O_{40} > H_4SiW_{12}O_{40} > H_4SiMo_{12}O_{40}$. This order of acidity agrees fairly well with the order of catalytic activity of HPA, except for the remarkable efficiency of $H_4SiW_{12}O_{40}$ in the etherification of the alcohol and the ineffectiveness of $H_3PMo_{12}O_{40}$ in the same reaction. The latter exception may be in part due to the decomposition of heteropoly-molybdic acid at high temperature. But the IR spectrum of heteropoly-molbdic acid which had been heated at $350°C$ in the air for 3 h did not showed the typical mark of the decomposition [9]. The reduction of $H_3PMo_{12}O_{40}$ in the etherifications also might change its acidity and the catalytic performance. IR spectrum of reduced 12-molybdophosphoric acid showed the typical remarkable decrease in absorbance at $1060 cm^{-1}$ (P–O) and $860 cm^{-1}$ (Mo–O–Mo) [12,16]. So the experimental fact that 12-molybdophosphoric acid was less active than the corresponding heteropoly-tungstic acid containing the same heteroatom may be explained by

the difference between their difference in susceptibility to reduction, their original acidity and stability.

However, another experimental fact that TsOH, sulfuric acid and phosphoric acid were quite inactive for the etherifiction in very high concentrations, as well as the exceptional catalytic behavior of $H_4SiW_{12}O_{40}$, suggests that the catalytic activity of HPA might be influenced also by certain properties besides the acidity. 'Softness' of the heteropoly anion may be one of the relevant characteristics. In fact, it is known that a heteropoly anion is a large oxide cluster ion (ca. 10 Å diameter) [17], and its surface change density is very low [18]. Such properties of a heteropoly anion imply that it may be a soft base. Table 4 summarizes the equilibrium constants (K) for the reactions between water soluble silver salts of various anions (X) and sodium iodide measured in aqueous solutions at $25°C$

$$Ag_nX + n\,Na \xrightarrow{K} n\,AgI + Na_nX$$
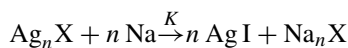
Since a soft anion is apt to interact favorably with soft silver cation(s), the smaller K values of Table 4

Table 4
Equilibrium constants for the reactions between water-soluble silver salts and NaI in aqueous solutions at 25°C

	[X] (10^{-3} mol/l)	[NaI] (10^{-3} mol/l)	K
$PW_{12}O_{40}^{3-}$	2.98	9.02	0.1
$SiW_{12}O_{40}^{4-}$	2.20	9.02	0.001
$PMo_{12}O_{40}^{3-}$	2.82	8.98	2.9
$SiMo_{12}O_{40}^{3-}$	2.22	9.01	3.8
TsO^-	9.06	9.08	148
SO_4^{2-}	4.42	9.02	498
PO_4^{3-}	5.12	9.22	412

probably represent increasing softness of the anions. The order of softness is therefore estimated as follows: $SiW_{12}O_{40}^{4-} > PW_{12}O_{40}^{3-} > PMo_{12}O_{40}^{3-} > SiMo_{12}O_{40}^{4-} > TsO^- > SO_4^{2-} > PO_4^{3-}$. Thus, the heteropoly anion, particularly $[SiW_{12}O_{40}]^{4-}$, is by far softer than the anions of ordinary protonic acids. Assuming that a soft heteriopoly anion could stabilize and activate a transient intermediate protonated cation as oxonium or oxocarbonium ion from alcohol through its intimate interaction with the cation, both the efficient acid catalysis by HPA compared with other proton acids and the exceptional catalytic behavior of $H_4SiW_{12}O_{40}$, can be reasonably explained.

5. Conclusion

The high efficiency of HPA revealed in acid catalysis to the etherification in the homogeneous liquid is mainly attributed to the specific properties of the heteropoly anion, which can be characterized by very weak basicity and probably by great softness, together with the large size of the polyhedral structure.

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