Cyclotrimerization of Aliphatic Aldehydes Catalysed by Keggin-type Heteropoly Acids and Concomitant Phase Separation

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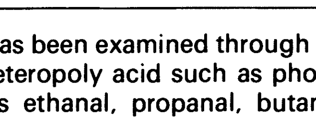
The acid-catalysed cyclotrimerization of aliphatic aldehydes has been examined through comparison of heteropoly acids with other acid catalysts. A Keggin-type heteropoly acid such as phosphomolybdic acid catalyses the cyclotrimerization of aldehydes, such as ethanal, propanal, butanal, 2-methylpropanal, 2,2-dimethylpropanal, hexanal, octanal, and decanal, to produce the respective 2,4,6-trialkyl-1,3,5-trioxanes in high yields. Catalyst turnover number of the heteropoly acid is more than 10 000 for propanal cyclotrimerization. In addition to the high catalytic activities, the reaction mixture spontaneously separates into two phases, a product phase and a catalyst phase, at high conversions of aldehyde. For propanal cyclotrimerization, the reaction mixture separates into two liquid phases, and the recovered catalyst phase may be repeatedly applied to the reaction without additional care in isolation of the catalyst. The phase separation phenomenon has been concluded to be caused by the insolubility of the heteropoly acid coordinated with propanal in the product 2,4,6-triethyl-1,3,5-trioxane.

Keggin-type[1,2] heteropoly acids such as phosphomolybdic acid, phosphotungstic acid, and silicotungstic acid are attractive catalyst materials, since they have shown characteristic catalytic activities not only for oxidation reactions but also for acid-catalysed reaction.[3–19] They have been used industrially for several types of acid-catalysed reaction such as the hydration of propylene[3] or isobutene[4,5] and the polymerization of tetrahydrofuran.[6,7] Further utilization of heteropoly acids has been examined for the production of commodity chemicals such as trioxane,[8] methyl *tert*-butyl ether,[9] bisphenols,[10] and alkylated aromatics.[11,12] These catalytic features are explained by both the strong Brønsted acidity[13,14] and the softness of the heteropoly anion.[15] The heteropoly acids also exhibit the dual catalytic function of strong acidity and oxidizing ability.[19] In addition to their acidic and redox properties, the heteropoly acids have characteristic solubility in various solvents; they are usually soluble in polar solvents, but insoluble in nonpolar solvents. A poor solubility of heteropoly acid in product media, however, improves product selectivity, owing to the phase transfer separation of reactant and product.[6]

There have been few studies on the cyclotrimerization of aliphatic aldehydes, except for methanal and ethanol. Cyclotrimerization of aldehydes has been catalysed by acids to produce 2,4, 6-trialkyl-1,3,5-trioxane.[20–26] Both protonic acids such as sulfonic acid[20,24,26] and phosphoric acid,[25] and Lewis acids such as antimony pentachloride[20] and zinc chloride,[25] were used as catalysts. The cyclic trimer of aldehyde, 2,4,6-trialkyl-1,3,5-trioxane, is also formed as a by-product in cationic polymerization[21] and aldol condensation.[22] Hashimoto *et al.* studied the equilibrium cyclotrimerization of butanal by using boron trifluoride etherate as catalyst.[23] Cyclotrimerization of aldehydes is thermodynamically favoured compared to their polymerization. Among various substituted trioxanes, 2,4,6-tris(1-methylethyl)-1,3,5-trioxane and 2,4,6-tris(1,1-dimethylethyl)-1,3,5-trioxane have been developed as flavouring materials for food[26] or carriers for scents, repellents, deodorants,[27] and insecticides.[28] As far as 2,4,6-tris(1-methylethyl)-1,3,5-trioxane is concerned, phosphomolybdic acid has been reported to catalyse the cyclotrimerization of 2-methylpropanal in the patent literature.[29]

We have previously reported on the cyclotrimerization of propanal catalysed by several heteropoly acids and its convenient recyclable use of catalyst.[18] In the present work, an acid-catalysed cyclotrimerization of aliphatic aldehydes, such as propanal, butanal, 2-methylpropanal, 2,2-dimethylpropanal, hexanal, octanal, and decanal, was examined through comparison of several heteropoly acids with other more usual acids. This paper also aims to characterize the phase separation phenomenon for propanal cyclotrimerization in connection with the solubility of heteropoly acids in organic solvents.



R = methyl, ethyl, propyl
1-methylethyl
1,1-dimethylethyl
pentyl, heptyl
and nonyl

Experimental

Keggin-type heteropoly acids of phosphotungstic acid ($H_3PW_{12}O_{40}$), phosphomolybdic acid ($H_3PMo_{12}O_{40}$), and silicotungstic acid ($H_4SiW_{12}O_{40}$), containing *ca.* 30 eq. of crystal water, were of commercially available purity. Toluene-*p*-sulfonic acid, and anhydrous aluminium chloride, iron(III) chloride and zinc chloride were also of commercially available purity. All organic reagents were highest purity commercial products (>98%), and used for the reaction without further purification.

A catalyst was placed in a 50 cm^3 flask containing neat aldehyde (Tables 1 and 2) or a solution of aldehyde (Table 3). All catalytic runs were carried out in air under the conditions described in the Tables. After either the reaction mixture or the separated product phase had been neutralized with sodium hydrogen carbonate, product compositions were determined by GLC using a column of PEG HT (1 m). The major products were isolated by either recrystallization or column chromatography using Wakogel C-200, and identified by NMR and IR spectroscopy, and GC–MS. Small amounts of by-products were speculated to be linear-trimers and linear-tetramers by GC–MS.

Table 1 Cyclotrimerization of aldehydes catalysed by heteropoly acids[a]

Aldehyde	(g)	Catalyst	(g)	Time/ h	Yield (%)	Phase[b]
CH_3CHO[c]	10	$H_3PMo_{12}O_{40}$	0.5	0.1	94.0	Not separated
CH_3CH_2CHO	10	$H_3PMo_{12}O_{40}$	0.5	1	81.9	L/L
$CH_3(CH_2)_2CHO$	10	$H_4SiW_{12}O_{40}$	0.5	1	76.9	L/L
$(CH_3)_2CHCHO$	3	$H_4SiW_{12}O_{40}$	0.015	1	99.9	S/L
$(CH_3)_3CCHO$	3	$H_4SiW_{12}O_{40}$	0.05	2.5	100	S/L
$CH_3(CH_2)_4CHO$	3	$H_4SiW_{12}O_{40}$	0.015	1	80.9	L/S
$CH_3(CH_2)_6CHO$	3	$H_4SiW_{12}O_{40}$	0.2	3.5	31.1	L/S
2nd run	3	recycle		1	90	S/S
3rd run	3	recycle		1	87.5	S/S
$CH_3(CH_2)_8CHO$	3	$H_4SiW_{12}O_{40}$	0.15	1	63.2	S/S

[a] Reacted at room temperature. [b] The feature of phase separation (product/catalyst), where L and S are liquid and solid phase, respectively. [c] Reacted at 0 °C.

IR spectra were recorded on a JASCO IRA-1 spectrometer. NMR spectra were measured with an Hitachi R-600 instrument. *J*-Values are in Hz. GC–MS spectra were recorded on a Shimadzu QP-1000EX.

2,4,6-*Trimethyl*-1,3,5-*trioxane*. This was identified by comparison with the GLC retention times of authentic samples.

2,4,6-*Triethyl*-1,3,5-*trioxane*. ν_{max}/cm^{-1} 1100, 1170 (C–O–C); δ 0.97 (t, 9 H, *J* 7.4, $-CH_3$), 1.66 (m, 6 H, *J* 7.4, $-CH_2-$), 4.81 (t, 3 H, *J* 4.8, –CH=); *m*/*z* 173 (M − H).

2,4,6-*Tripropyl*-1,3,5-*trioxane*. ν_{max}/cm^{-1} 1096, 1155 (C–O–C); δ 0.93 (t, 9 H, *J* 7.2, $-CH_3$), 1.00–2.20 [m, 12 H, *J* 7.4, $-(CH_2)_2-$], 4.86 (t, 3 H, *J* 4.7, –CH=); *m*/*z* 216 (M^+).

2,4,6-*Tris*(1-methylethyl)-1,3,5-*trioxane*. M.p. 57.5 °C; ν_{max}/cm^{-1} 1149 (C–O–C); δ 0.93 (d, 18 H, *J* 6.6, $-CH_3$), 1.80 (m, 3 H, –CH=), 4.63 (d, 3 H, *J* 5.4, –CH=); *m*/*z* 215 (M − H).

2,4,6-*Tris*(*tert*-butyl)-1,3,5-*trioxane*. M.p. 86.2 °C; ν_{max}/cm^{-1} 1100, 1200 (C–O–C); δ 0.93 (s, 27 H, $-CH_3$), 4.38 (s, 3 H, –CH=); *m*/*z* 257 (M − H).

2,4,6-*Tripentyl*-1,3,5-*trioxane*. ν_{max}/cm^{-1} 1103, 1143 (C–O–C); δ 0.90 (t, 9 H, *J* 5.3, $-CH_3$), 0.59–2.10 [m, 24 H, $-(CH_2)_4-$], 4.87 (t, 3 H, *J* 4.9, –CH=); *m*/*z* 299 (M − H).

2,4,6-*Triheptyl*-1,3,5-*trioxane*. M.p. 31–33 °C; ν_{max}/cm^{-1} 1113, 1160 (C–O–C); δ 0.88 (t, 9 H, *J* 4.8, $-CH_3$), 0.63–1.91 [m, 36 H, $-(CH_2)_6-$], 4.85 (t, 3 H, *J* 4.8, –CH=); *m*/*z* 215 [M − (C_7H_{15} + CO)].

2,4,6-*Trinonyl*-1,3,5-*trioxane*. M.p. 40.5 °C; ν_{max}/cm^{-1} 1108, 1150 (C–O–C); δ 0.90 (t, 9 H, *J* 4.4, $-CH_3$), 0.48–1.98 [m, 48 H, $-(CH_2)_8-$], 4.86 (t, 3 H, *J* 4.4, –CH=); *m*/*z* 313 (M − (C_9H_{19} + CO)].

Results and Discussion

Cyclotrimerization of Aliphatic Aldehydes Catalysed by Heteropoly Acids. Table 1 summarizes typical results of the cyclotrimerization of several aliphatic aldehydes catalysed by heteropoly acids without using solvent. All of the aldehydes examined were selectively converted into the respective 2,4,6-trialkyl-1,3,5-trioxane. When aliphatic aldehydes, except for ethanal, were reacted with heteropoly acids, the reaction mixture was homogeneous in the initial stage of reaction and then separated into two phases with increased conversion of aldehyde. For example, using propanal and butanal, the reaction mixture was separated into two liquid phases. The separated bottom phase contained the majority of heteropoly acid used. For 2-methylpropanal and 2,2-dimethylpropanal, the reaction mixture was separated into liquid and solid phases. The solid phase consisted of 2,4,6-trialkyl-1,3,5-trioxane crystals, and the liquid phase was mainly heteropoly acid. For hexanal and octanal, on the other hand, the reaction mixture separated into a solid catalyst phase and a liquid product phase. Since the heteropoly acid did not dissolve in nonpolar solvents such as hexane. it was readily recovered from the separated catalyst phase. For decanal, the reaction mixture separated into two solid phases. The separation behaviour was clearly observed with yellow $H_3PMo_{12}O_{40}$: the coloured solid heteropoly acid was precipitated together with the solidifying reaction mixture; the yellow catalyst was dispersed in the product crystals. For ethanal, however, the reaction mixture remained homogeneous, while ethanal was converted into 2,4,6-trimethyl-1,3,5-trioxane in high yield.

Table 2 summarizes the results for several aldehydes which produced liquid cyclic trimers, and shows the difference in catalytic activities between heteropoly acids and the other acids. For the cyclotrimerization of ethanal, heteropoly acid catalysts exhibited high conversion of ethanal and high selectivity to 2,4,6-trimethyl-1,3,5-trioxane at −12 °C. In contrast to the heteropoly acid catalysts, such acids as zinc chloride and toluene-*p*-sulfonic acid showed poor selectivity because of the formation of ethanal tetramer, metaldehyde, which precipitated in the reaction mixture. Unfortunately, no catalyst-phase separation was observed with any catalyst tested for ethanal cyclotrimerization.

For cyclotrimerization of propanal, butanal and hexanal, heteropoly acid catalysts were more active than the other acid catalysts, as previously reported[18] with regard to propanal cyclotrimerization. For propanal cyclotrimerization, phase separation was observed in each case, while gel-like precipitates was formed by using a large amount of catalyst for aluminium chloride and ferric chloride.[18] Fig. 1 shows the recycle-run activity using the bottom catalyst phase. The bottom catalyst phase, separated by using a separatory funnel, was used for the repeated reaction without isolation of catalyst. The recycle-run activity of heteropoly acid reacted for 2 h remained unchanged even after the fifteenth run, whereas that of toluene-*p*-sulfonic acid decreased with the number of recycles. The recycle-run activity of $H_3PMo_{12}O_{40}$ decreased with the number of recycles after the fifteenth run. In the nineteenth run, however, the reaction of propanal for 24 h attained the initial level of conversion. The decrease is caused by gradual increase of water in the reaction mixture, rather than by gradual catalyst losses into the upper product phase, depending upon the partition coefficient of the catalyst in the product trioxane. This will be discussed later in connection with a result in Fig. 6. Another catalyst recycle test was done for octanal (Table 1). For octanal, the reaction mixture separated into solid catalyst phase and liquid product phase. The solid phase, separated by washing with hexane, was able to be repeatedly used for the reaction; the conversion was increased for the second and third runs, and the reaction mixture separated into two solid phases. The product phase solidified owing to the high conversion of octanal.

Table 2 Cyclotrimerization of various aliphatic aldehydes

Aldehyde	Catalyst	Amount/ mmol	Conversion (%)	Selectivity[a] (mol%)	TON[b]
Ethanal[c]	$H_3PMo_{12}O_{40}$	0.004	90.8	99.7	38 000
	$H_3PW_{12}O_{40}$	0.003	88.0	100	53 000
	$H_4SiW_{12}O_{40}$	0.003	92.5	100	56 000
	$ZnCl_2$	0.073	16.3	44.0	180
	p-TsOH	0.053	73.2	79.7	2 000
Propanal[d]	$H_3PMo_{12}O_{40}$	0.004	93.4	94.1	35 000
	$H_3PW_{12}O_{40}$	0.003	74.7	90.9	39 000
	$H_4SiW_{12}O_{40}$	0.003	56.4	86.3	28 000
	$AlCl_3$	0.075	21.0	76.7	370
	$FeCl_3$	0.062	46.8	80.4	1 000
	p-TsOH	0.053	59.9	87.8	1 700
Butanal[e]	$H_3PMo_{12}O_{40}$	0.013	27.2	93.7	820
	$H_3PW_{12}O_{40}$	0.009	84.0	99.4	3 900
	$H_4SiW_{12}O_{40}$	0.009	81.5	99.0	3 700
	$ZnCl_2$	0.22	32.9	86.9	54
	p-TsOH	0.16	75.4	98.3	190
Hexanal[e]	$H_3PMo_{12}O_{40}$	0.013	83.4	97.8	1 900
	$H_3PW_{12}O_{40}$	0.009	83.2	98.0	2 700
	$H_4SiW_{12}O_{40}$	0.009	69.1	96.7	2 200
	p-TsOH	0.16	76.3	97.5	140

[a] Selectivity to 2,4,6-trialkyl-1,3,5-trioxane. [b] Turnover number (molar ratio of aldehyde converted into trioxane to catalyst). [c] Reacted at −12 °C for 0.5 h, 0.01 g of catalyst to 8 g of ethanal. [d] Reacted at room temperature for 48 h, 0.01 g of catalyst to 10 g of propanal. [e] Reacted at room temperature for 2 h, 0.03 g of catalyst to 3 g of the reactant aldehyde.

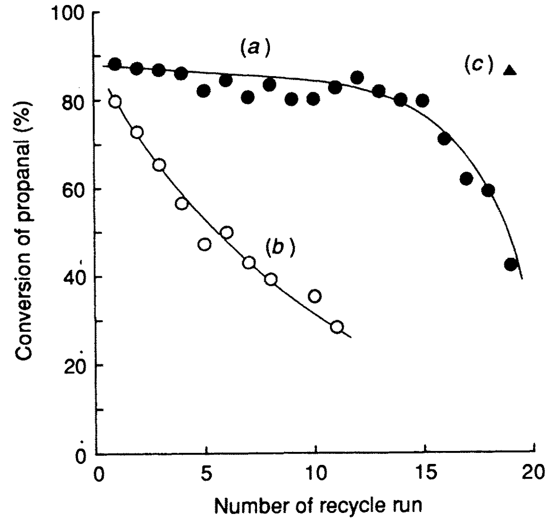


Fig. 1 Recycle of catalyst for cyclotrimerization of propanal. Each catalytic run was repeated by using 10 g of propanal with regard to a recovered catalyst phase containing 1 g of catalyst at room temperature for 2 h. (*a*) catalysed by $H_3PMo_{12}O_{40}$; (*b*) toluene-*p*-sulfonic acid; (*c*) the reaction catalysed by $H_3PMo_{12}O_{40}$ was continued for 24 h.

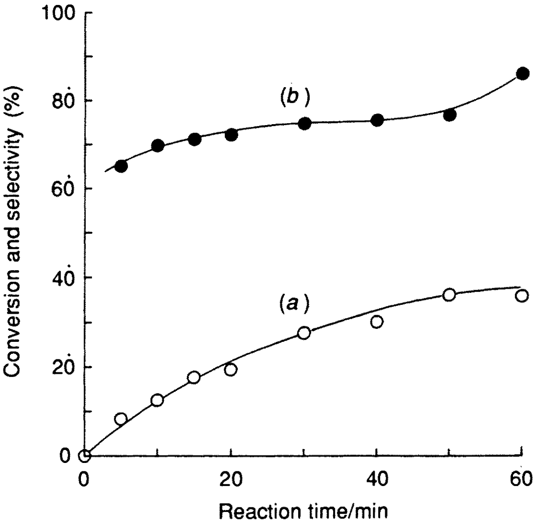


Fig. 2 Changes in conversion of propanal catalysed by $H_3PMo_{12}O_{40}$ with process time at 0 °C. The reaction was carried out by using 10 g of propanal with regard to 0.1 g of $H_3PMo_{12}O_{40}$. (*a*) conversion of propanal; (*b*) selectivity to 2,4,6-triethyl-1,3,5-trioxane.

Since the reaction mixture was separated into liquid catalyst and crystal product phases for 2-methylpropanal, the solvent effect on the phase separation was examined (Table 3). In hexane used as a solvent, $H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, and toluene-*p*-sulfonic acid gave 2,4,6-tris(1-methylethyl)-1,3,5-trioxane with 60% conversion and high selectivity. For heteropoly acid, the reaction mixture separated into two liquid phases: phase separation occurred in such non-polar solvents as toluene, methylene dichloride, and hexane. For toluene-*p*-sulfonic acid, however, the reaction mixture remained still homogeneous. On the other hand, the catalytic activities of $H_3PMo_{12}O_{40}$, $H_4SiW_{12}O_{40}$, zinc chloride, and toluene-*p*-sulfonic acid were depressed in diethyl ether. Since $H_3PW_{12}O_{40}$ is, however, the strongest of these poly acids,[15] it was active even in ether. Furthermore, the reaction mixture remained homogeneous: phase separation did not occur in polar solvents such as diethyl ether, acetone, and ethanol. When alcohol was used as a solvent, acetal was formed as a major product.[19]

The cyclotrimerization of propanal will be described in greater detail below, from the standpoint of the reaction kinetics and the phase separation behaviour.

Effect of Reaction Temperature.—The effect of reaction temperature was examined for propanal cyclotrimerization. Fig. 2 shows the change in catalytic activities with reaction time at 0 °C. Propanal was converted into 2,4,6-triethyl-1,3,5-trioxane with a selectivity of about 70%. The selectivity increased with reaction time, and attained more than 90% after 2 h. Although the reaction proceeded faster at 45 °C than at 0 and

Table 3 Cyclotrimerization of 2-methylpropanal[a]

Solvent	Catalyst	Amount/ mmol	Conversion (%)	Selectivity[b] (mol%)	TON[c]
Hexane	$H_3PMo_{12}O_{40}$	0.013	64.3	98.0	2000[d]
	$H_3PW_{12}O_{40}$	0.009	61.7	99.7	2800[d]
	$H_4SiW_{12}O_{40}$	0.009	42.7	89.6	1800[d]
	$ZnCl_2$	0.22	10.2	96.7	19[e]
	p-TsOH	0.16	60.5	89.2	140[e]
Diethyl ether	$H_3PMo_{12}O_{40}$	0.013	21.9	96.2	680[e]
	$H_3PW_{12}O_{40}$	0.009	50.8	87.5	2100[e]
	$H_4SiW_{12}O_{40}$	0.009	0.76	100	35[e]
	$ZnCl_3$	0.22	0.77	0	0[e]
	p-TsOH	0.16	4.34	92.7	10[e]

[a] Reacted at room temperature for 2 h, 0.03 g of catalyst was used in 3 g of 2-methylpropanal and 3 g of solvent. [b] Selectivity to 2,4,6-tris-(1-methylethyl)-1,3,5-trioxane. [c] Turnover number (molar ratio of aldehyde converted into trioxane to catalyst). [d] Reaction mixture was separated into two liquid phases. [e] Not separated.

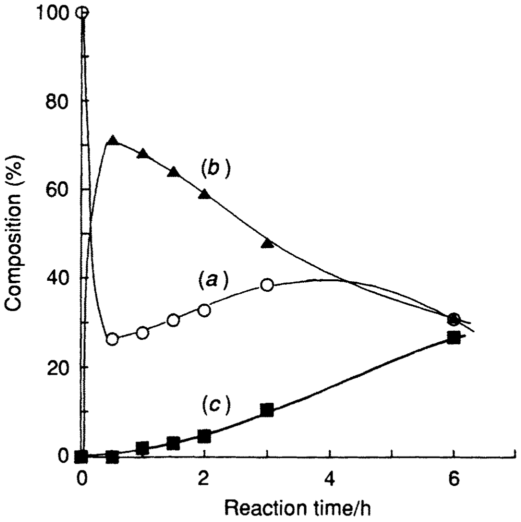


Fig. 3 Cyclotrimerization of propanal catalysed by $H_3PMo_{12}O_{40}$ at 45 °C: (*a*) composition of propanal, (*b*) 2,4,6-triethyl-1,3,5-trioxane, (*c*) linear tetramer (based on mol% of reactant propanal)

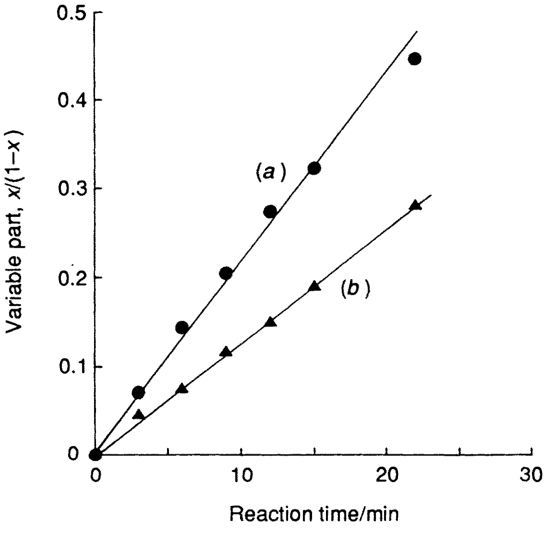


Fig. 4 Test of second-order rate equation by integral method for cyclotrimerization of propanal at 27 °C. Each catalytic run was carried out by using 10 g of propanal with regard to 0.1 g of (*a*), $H_3PMo_{12}O_{40}$; (*b*) *p*-toluenesulfonic acid.

25 °C, the produced 2,4,6-triethyl-1,3,5-trioxane reacted further to give propanal and tetramers of propanal (Fig. 3). Calculated from the Arrhenius plot over a temperature range of 0–25 °C, apparent activation energies for $H_3PMo_{12}O_{40}$ and toluene-*p*-sulfonic acid were found to be 20.8 and 16.7 kJ mol^{-1}, respectively.

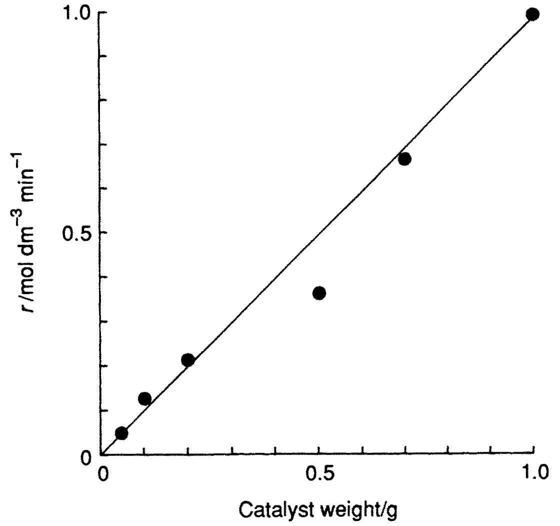


Fig. 5 Change in reaction rate for cyclotrimerization of propanal with concentration of $H_3PMo_{12}O_{40}$ at 0 °C

Reaction Kinetics and Phase Separation.—In order to estimate the reaction rate, changes in conversion with reaction time was examined for the cyclotrimerization of propanal at 27 °C in the range of reaction time within 30 min. Conversion data obtained were analysed by using the conventional integral formulae of various reaction rate equations. We have consequently found that the data obeyed good second-order kinetics. The integral form of second-order kinetics is $x/(1-x) = knCt$, where x, k, n, C, and t are conversion of propanal, reaction rate constant, amount of catalyst, concentration of propanal, and reaction time, respectively, and the plot gave a straight line (Fig. 4). So, the rate of 2,4,6-triethyl-1,3,5-trioxane formation is second-order with respect to the concentration of propanal. The rate constant, k, for $H_3PMo_{12}O_{40}$ is 45.7 dm^3 mol^{-1} min^{-1} mol-cat^{-1} at 27 °C, and is much larger than that for toluene-*p*-sulfonic acid, 1.8 dm^3 mol^{-1} min^{-1} mol-cat^{-1}. Moreover, the rate of 2,4,6-triethyl-1,3,5-trioxane formation was directly proportional to the concentration of catalyst (Fig. 5). Although it is known that the reaction rate is affected by the heteropoly anion, for example, the dehydration–cyclization of 1,4-butanediol to tetrahydrofuran,[17] the reaction rate for the cyclotrimerization in this work did not change on increasing the concentration of heteropoly anion by adding heteropoly acid

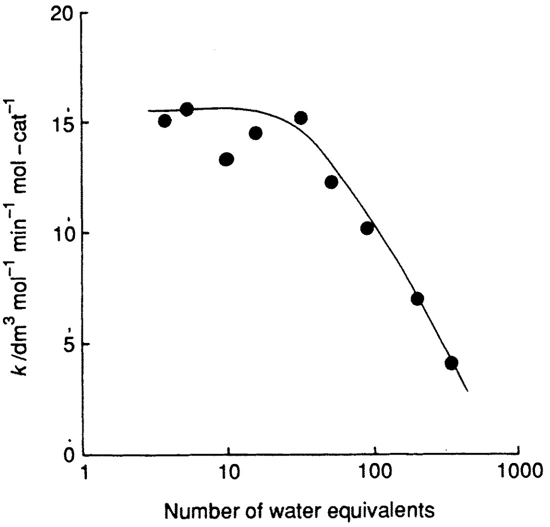


Fig. 6 Effect of number (n) of equivalents of water on reaction rate constant for cyclotrimerization of propanal catalysed by $H_3PMo_{12}O_{40}$–nH_2O system at 0 °C

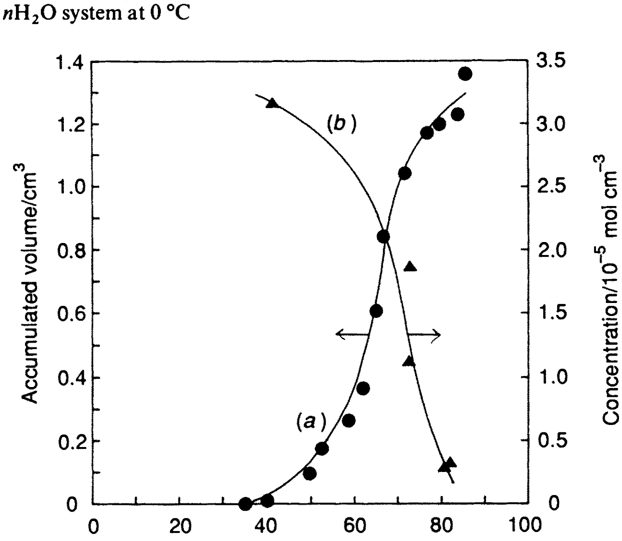


Fig. 7 Change in both volume of catalyst phase and concentration of catalyst in product phase for propanal cyclotrimerization catalysed by 1 g of $H_3PMo_{12}O_{40}$ for 10 g of propanal at room temperature: (a) accumulated volume of catalyst phase; (b) concentration of $H_3PMo_{12}O_{40}$ in product phase

Table 4 Extraction of organic compounds from the catalyst phase with benzene[a]

Number of extraction	Extraction time/min	Extracted propanal/g	Extracted 2,4,6-triethyl-1,3,5-trioxane/g
1	10	0.180	0.255
2	10	0.034	0.017
3	20	0.006	0
4	60	0.003	0
5	120	0.001	0
Total		0.224	0.272

[a] The catalyst phase (*ca.* 2 g) was separated from the reaction mixture containing propanal (10 g) and $H_3PMo_{12}O_{40}$ (1 g) for 2 h at conversion of 89%. The extraction of organic components from the obtained catalyst phase (1 g) with benzene (5 cm^3) was repeated.

sodium salt, $Na_3PMo_{12}O_{40}$. Thus, the rate of 2,4,6-triethyl-1,3,5-trioxane formation was first-order with respect to the concentration of proton. Furthermore, the rate of propanal cyclotrimerization was greatly affected by the number of water molecules; the reaction rate constant decreased with increase in the amount of added water over about 33 eq. of heteropoly anion, whereas it was unchanged at low water content less than crystal water, 32.5 eq. (Fig. 6). Recycle-run activities dropped drastically after the fifteenth run (Fig. 1), and this is caused by the accumulation of water in the catalyst phase.

The reaction rate obtained without stirring was nearly equal to that with stirring. Furthermore, the same reaction rate was also observed on consecutively separating the bottom phase of catalyst. This indicates that the heteropoly acids dissolved in the reacant aldehyde catalyse the cyclotrimerization, and that the catalyst phase separated in the bottom phase is not concerned in the cyclotrimerization reaction.

Fig. 7 shows the changes in both volume of catalyst phase and concentration of catalyst in product phase during the course of propanal cyclotrimerization catalysed by 1 g of $H_3PMo_{12}O_{40}$ for 10 g of propanal at room temperature. The volume of bottom catalyst phase increased with conversion of propanal, while the concentration of $H_3PMo_{12}O_{40}$ decreased in the upper solution phase.

Characterization of Catalyst Phase.—The composition of organic compounds in the bottom catalyst phase was estimated by extracting organic compounds with benzene, since heteropoly acids are insoluble in non-polar solvents (Table 4). The first and second extraction included both propanal and 2,4,6-triethyl-1,3,5-trioxane, whereas the third and further extractions included only propanal. Thus, the heteropoly acid interacted with propanal rather than 2,4,6-triethyl-1,3,5-trioxane. The molar ratio of propanal to 2,4,6-triethyl-1,3,5-trioxane was 2.46 : 1 at the end of extraction, and this value was close to the ratio of 2.38 : 1 which was evaluated from the integration of the characteristic NMR chemical shifts of methylene proton. Although a ratio of 10 : 11 for propanal and 2,4,6-triethyl-1,3,5-trioxane had been previously reported,[18] such a ratio might have occurred through the overestimation of the amount of 2,4,6-triethyl-1,3,5-trioxane observed in the catalyst phase neutralized with base. Calculated from the ratio of 2.46 : 1 for propanal and 2,4,6-triethyl-1,3,5-trioxane, the composition of the catalyst phase was a molar ratio of *ca.* 1 : 32.5 : 20.2 : 8.22 for $H_3PMo_{12}O_{40}$, H_2O, propanal, and 2,4,6-triethyl-1,3,5-trioxane at a conversion of 88.9%. Since the composition in the catalyst phase corresponds to a propanal conversion level of 55%, the proportion of propanal in the catalyst phase is much larger than in the product phase.

Infrared spectra of the catalyst phase are illustrated in Fig. 8 for the reaction of propanal with $H_3PMo_{12}O_{40}$. In a spectrum of the recovered catalyst phase, four characteristic absorption peaks of Keggin-type heteropoly acid, ν(P–O), ν(Mo=O$_t$), ν(Mo–O$_c$–Mo), and ν(Mo–O$_e$–Mo), were observed at 1049, 949, 871 and 789 cm^{-1}, respectively [Fig. 8(d)]. The Keggin structure of heteropoly acid was maintained in the catalyst phase. Organic compounds were also detected in the catalyst phase: aldehyde at 1700 cm^{-1}, ν(C=O); cyclic ether at 1170 cm^{-1}, ν(C–O–C). The liquid catalyst phase was solidified on heating at 80 °C, and the resulting solid showed a spectrum similar to that of $H_3PMo_{12}O_{40}$ itself [Fig. 8(a)]. Since the organic compounds included in the catalyst phase could be removed either by such a simple evacuation or by extraction with benzene, it is clear that the interaction between heteropoly acid and organic compounds was very weak.

The change in IR spectra of heteropoly acid standing on sodium chloride crystal plate was monitored on adding a small amount of propanal [Fig. 8(b), (c)]. When a drop of propanal was added to $H_3PMo_{12}O_{40}$, the heteropoly acid was changed into a greenish viscous solid from a yellow powder [Fig. 8(b)]. In the IR spectrum of this viscous solid, the absorption due to

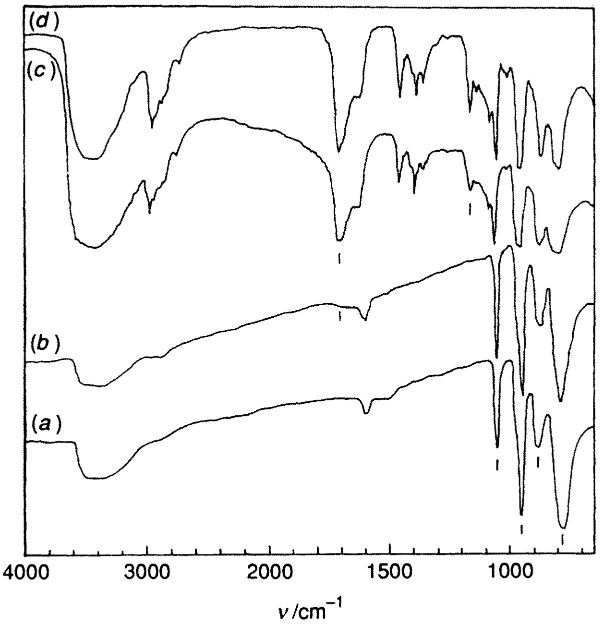


Fig. 8 IR spectra of the separated bottom catalyst phase: (*a*) $H_3PMo_{12}O_{40}$ itself; (*b*) viscous green solid, a drop of propanal was added to the solid in (*a*); (*c*) green liquid, a drop of propanal was added to the solid in (*b*); (*d*) a separated catalyst phase, 10 g of propanal catalysed by 1 g of $H_3PMo_{12}O_{40}$ at room temperature for 2 h

the ether bond of 2,4,6-triethyl-1,3,5-trioxane at 1170 cm^{-1} is absent, whereas absorption for carbonyl group of propanal is present at 1700 cm^{-1}. The carbonyl group of propanal is speculated to coordinate to either heteropoly acid or crystal water. Another drop of propanal led to a change in phase from solid to green solution, and an absorption due to the ether bond of 2,4,6-triethyl-1,3,5-trioxane appeared at 1170 cm^{-1} [Fig. 8(*c*)]. Moreover, further addition of propanal resulted in phase separation into green and colourless liquids. The spectrum in Fig. 8(*c*) is substantially identical to that of the separated catalyst phase shown in Fig. 8(*d*). Consequently, consistent with the results of the extraction experiments (Table 4), propanal is coordinated to the heteropoly acid in the catalyst phase solution.

The phase separation phenomenon during the propanal cyclotrimerization has been speculated to occur as follows: At first the reaction proceeds in the homogeneous phase, and at that time the polarity of the reaction mixture gradually decreases with increase in content of the less polar product 2,4,6-triethyl-1,3,5-trioxane. Heteropoly acid complexes coordinated to propanal become insoluble in the product-rich solution, and they then separate out and accumlate in a bottom phase.

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