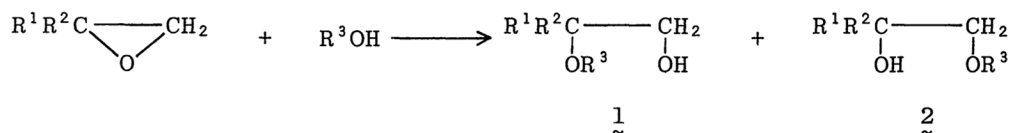# EFFICIENT CATALYSIS OF HETEROPOLY ACID
FOR ALCOHOLYSIS OF EPOXIDE

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Heteropoly acid (HPA) was found to catalyze the alcoholysis of epoxide more efficiently than the conventional acid catalysts such as sulfuric acid, perchloric acid and p-toluenesulfonic acid, at $45°C$ in the homogeneous liquid phase. The reason for the high catalytic activity of HPA is also discussed.

Besides showing selective catalysis in the vapor-phase oxidation reactions,[1] heteropoly acid (HPA) and its salts have recently been reported to be effective catalysts for the liquid-phase reactions such as oxidation of olefin,[2] hydration of olefin[3] and polymerization of benzyl alcohols.[4] We have been interested in the acid catalysis of HPA in the homogeneous liquid systems and already pointed out the role of heteropoly anion in the catalytic action of HPA for the hydration of propylene in an aqueous solution.[3] We now report the efficient catalysis of HPA for the addition of alcohol to epoxide giving the corresponding hydroxy ethers in the liquid phase under relatively mild reaction conditions.

$$R^1R^2C\underset{O}{\diagdown\diagup}CH_2 + R^3OH \longrightarrow \underset{\underset{1}{OR^3\quad OH}}{R^1R^2C-CH_2} + \underset{\underset{2}{OH\quad OR^3}}{R^1R^2C-CH_2}$$

a: $R^1=CH_2Cl$, $R^2=H$, $R^3=$allyl   e: $R^1=R^2=Me$, $R^3=t$-Bu

b: $R^1=Et$, $R^2=H$, $R^3=n$-Pr   f: $R^1=Ph$, $R^2=H$, $R^3=n$-Pr

c: $R^1=Et$, $R^2=H$, $R^3=t$-Bu   g: $R^1=Ph$, $R^2=H$, $R^3=t$-Bu

d: $R^1=R^2=Me$, $R^3=n$-Pr

All runs were carried out in the homogeneous liquid phase at $45°C$. In order to repress the polymerization of epoxides, an excess of the reactant alcohol (20ml) was used for each epoxide (2ml). The HPA catalysts employed were 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$), 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$) and 12-tungstosilicic acid ($H_4SiW_{12}O_{40}$). The reaction products were analyzed by means of g.l.c. The hydroxy ethers, 1 and 2, were identified by their IR and ^{1}H-NMR spectra as well as by comparing their retention times in g.l.c. with those of the isomers, 2, that could be almost exclusively obtained by use of alkali catalysts.

In the presence of HPA catalysts, epichlorohydrin (ECH) reacted with allyl

alcohol at 45°C being almost completely converted with high selectivity (95-97%)
into 1-allyloxy-3-chloro-2-propanol (2a), a precursor of allyl glycidyl ether.
No polymeric by-product was formed. Water had little effect on the ECH conversion
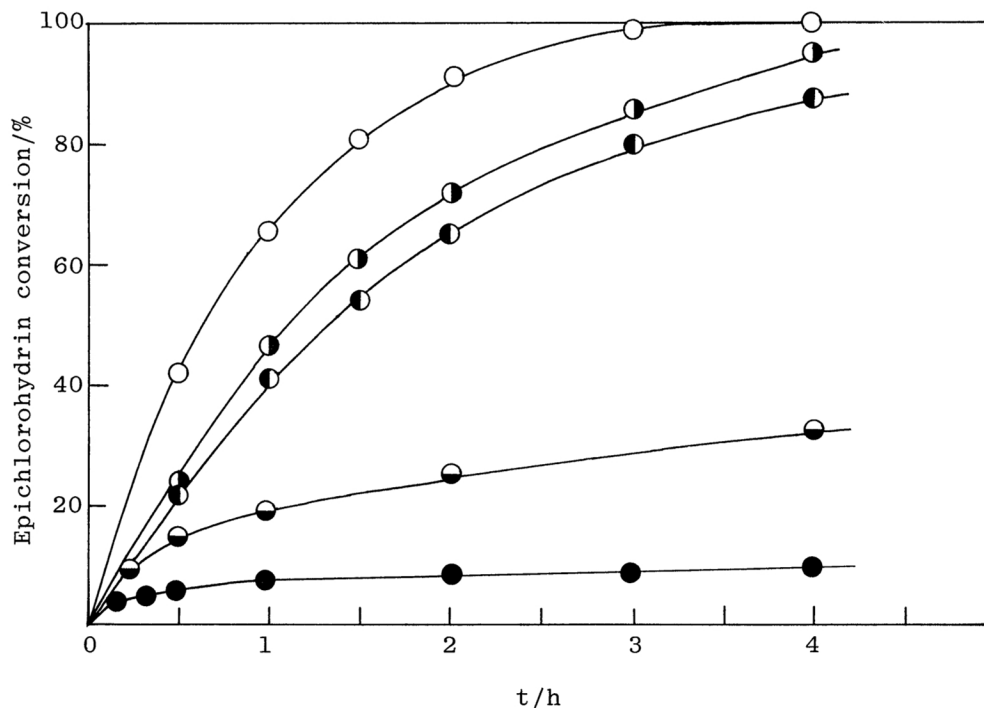and the selectivity of 2a so long as its concentration did not exceed 6×10^{-2}M.

Fig. 1.   Reaction of epichlorohydrin with allyl alcohol at 45°C.
Allyl alcohol/ECH mole ratio=11.5, ◯: $H_3PW_{12}O_{40}$(0.00157M), ◖: $H_3PMo_{12}O_{40}$
(0.00166M), ◖: $H_4SiW_{12}O_{40}$(0.00124M), ◓: $HClO_4$(0.0152M), ●: H_2SO_4(0.0528M).

On the other hand, H_2SO_4 and $HClO_4$ were much less active than HPA. Even in
the solutions of considerably high concentration of H_2SO_4 and $HClO_4$, the reaction
rates were very slow and, furthermore, decreased rapidly with the elapse of time
(Fig. 1). Much higher concentration of H_2SO_4, together with reflux condition, is,
therefore, required for converting ECH completely into 2a as indicated in the
conventional synthetic method.[5]

In case of HPA catalyst, the reaction rate was proportional to the concentra-
tions of ECH and HPA, respectively. This suggests that the reaction proceeds via
S_N1 mechanism.

The table shows the catalytic activities of $H_3PW_{12}O_{40}$ and p-toluenesulfonic
acid (TsOH) for the additions of 1-propanol (PrOH) and tert-butyl alcohol (t-BuOH)
to 1,2-epoxybutane, isobutene oxide and styrene oxide. At a similar catalyst
concentration, the HPA converted each epoxide into the corresponding hydroxy ethers
much faster than TsOH. Thus the HPA was found to be generally applicable as an
efficient and selective catalyst to the alcoholysis of epoxide. Particularly, it
is suitable for obtaining hydroxy ether isomers, 1, that would be difficult to be
formed by base catalysts.

The rapid decrease in the reaction rate observed with H_2SO_4 catalyst (Fig. 1)

Table   Alcoholysis of Epoxide Catalyzed by $H_3PW_{12}O_{40}$ and TsOH at 45°C

Epoxide	Alcohol	Mole ratio[a]	Reaction time, h	Catalyst $(x10^{-3}M)$	Epoxide conversion, %	Hydroxy ethers yield,[b] %	selectivity,[c] %
1,2-Epoxybutane	PrOH	11.6	5	HPA (1.99)	100	94.5	64 (2b)
				TsOH(1.95)	0.3	100	58 (2b)
	t-BuOH	9.2	5	HPA (6.04)	60	88.0	66 (2c)
				TsOH(6.14)	0.0	-	-
Isobutene oxide	PrOH	11.9	2.5	HPA (30.6)	100	98.6	84 (1d)
				TsOH(31.0)	78	100	99 (1d)
	t-BuOH	9.41	3	HPA (30.2)	70	96.0	99 (2e)
				TsOH(36.1)	3	100	90 (2e)
Styrene oxide	PrOH	15.2	2	HPA (4.82)	100	100	93 (1f)
				TsOH(5.30)	7.0	100	92 (1f)
	t-BuOH	12.1	4	HPA (61.2)	77	97.8	87 (1g)
				TsOH(62.5)	8.8	100	85 (1g)

a) Alcohol/epoxide.
b) Calculated from the g.l.c. peak areas of hydroxy ethers and unidentified
    polymeric by-products.
c) Composition of the main hydroxy ether isomer.

implies that the acid might react with allyl alcohol, ECH or the product hydroxy ether (2a) to form an alkyl sulfate, resulting in the loss of its acidity. So we qualitatively examined the change in the specific conductance of the reaction system as a measure of acidity change (Figs. 2 and 3).

The conductance sharply decreased with the reaction time (curve a) in case of H_2SO_4 catalyst (Fig. 2). This decrease corresponded well to the rapid decrease of the reaction rate observed at the same time (curve b). The introduction of an additional amount of 2a to this system gave little influence on the conductance. The conductance began to reduce noticeably when ECH was added to the allyl alcohol $-H_2SO_4$ system (curve c). The decrease in the catalytic activity of H_2SO_4 is, therefore, likely due to the reduction of acidity as a result of equilibrated formation of an ester, probably glycol monosulfate, from H_2SO_4 and ECH.

In case of $HClO_4$ catalyst, the degree of decrease in the conductance was not so large as that observed with H_2SO_4 (Fig. 3, curve a). On the other hand, HPA catalyst showed little effect on the conductance of the reaction system (Fig. 3, curve b), which suggests that HPA hardly reduces its acidity during the reaction and maintains its high catalytic activity. However, compared with the corresponding value of $HClO_4$ catalyst, the catalytic activity of HPA per unit catalyst concentration is considered still too high to explain only by the change of the conductance or the acidity of the reaction system. We presume that the hetero-

poly anion plays an important role in the high efficiency of HPA catalyst in this way that the anion forms a stable ion-pair intermediate with a carbocation or an oxonium ion produced from epoxide and proton.
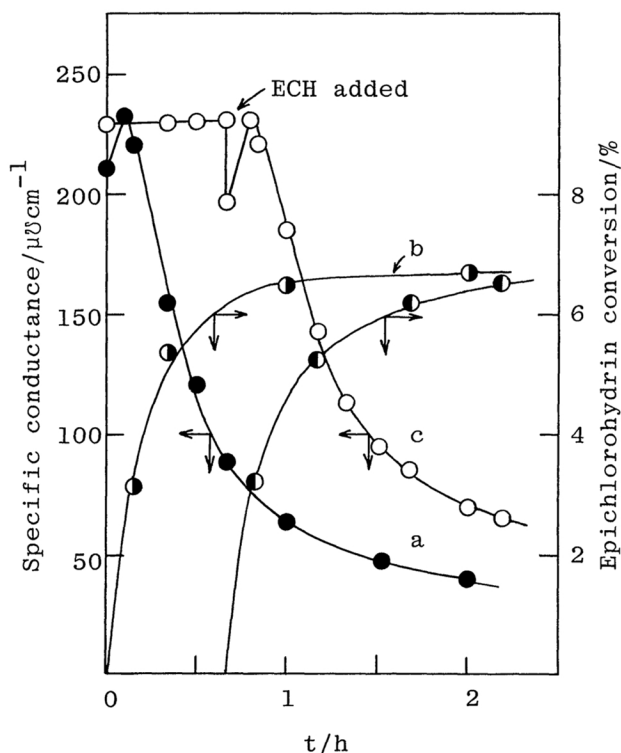

Fig. 2. Specific conductance at 25.5°C in H_2SO_4 (0.0127M) system. ECH (51.2mmol.) was added to allyl alcohol (588mmol.) from the start (●, ◐) and after 40 min (○, ◑).
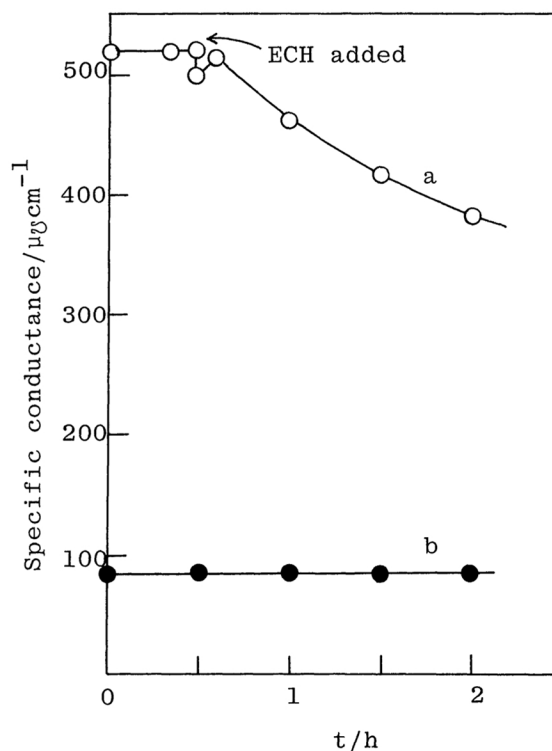
Fig. 3. Specific conductance at 25.5°C in $HClO_4$ (0.0138M, ─○─) and $H_3PW_{12}O_{40}$ (0.0014M, ─●─) systems. ECH (51.2mmol.) was added to allyl alcohol (588mmol.) from the start (●) and after 30 min (○).

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