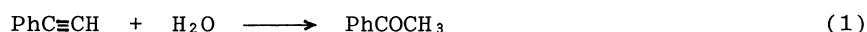


ELECTROPHILIC ADDITION REACTIONS TO PHENYLACETYLENE
CATALYZED BY HETEROPOLY ACID

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Heteropoly acid efficiently catalyzed the addition reactions of water and carboxylic acid to phenylacetylene to form acetophenone at 60°C in the liquid phase. The higher catalytic activity of heteropoly acid compared with H₂SO₄ and HClO₄ is due to the cooperative action of heteropoly anion.

Heteropoly acid (HPA) has recently been reported as an effective acid catalyst for the liquid-phase reactions such as hydration of olefin,^{1,2)} alcoholysis of epoxide,³⁾ and Friedel-Crafts reactions.^{4,5)} However, there were no detailed investigations relating to the catalysis of HPA for the electrophilic addition to acetylenic compounds. We now report the efficient catalysis of HPA for the addition reactions of water and carboxylic acid to phenylacetylene (PA):



The catalytic activities of HPA for the reactions (1) and (2) were examined and compared with those of typical conventional acid catalysts (H₂SO₄, HClO₄) in the homogeneous liquid phase at 60°C. In the hydration of PA, ethanol was used as a solvent in order to keep the reaction medium homogeneous. The HPA catalysts employed were H₃PW₁₂O₄₀, H₃PMo₁₂O₄₀, and H₄SiW₁₂O₄₀. A small portion of the product was withdrawn periodically and analyzed by g.l.c. The products were identified by comparing their IR spectra with those of the authentic samples. The catalytic activities for the hydration of PA were compared by the rate constants per unit catalyst concentration which were calculated from the time-conversion curves at low PA conversion.

All of the HPA catalysts were much more active for the hydration than H₂SO₄ and HClO₄ (Table 1). The hydration activities of the catalysts used were in the following order: H₃PMo₁₂O₄₀ > H₃PW₁₂O₄₀ > H₄SiW₁₂O₄₀ >> HClO₄ > H₂SO₄. In case of H₂SO₄ catalyst, the reaction rate was almost proportional to the catalyst concentration, and the addition of a neutral salt (Na₂SO₄) lowered the rate. On the other hand, the rate obtained with HPA catalyst (H₃PW₁₂O₄₀) showed approximately second-order dependence on the catalyst concentration. The addition of a neutral salt of HPA (Na₄SiW₁₂O₄₀) increased the rate, but the salt was inactive by itself for the hydration. The activation energies observed with H₃PW₁₂O₄₀ and H₂SO₄ catalysts were 24.2 and 27.5 kcal/mol, respectively, in the range of 55° to 70°C. These results suggest that the reaction is catalyzed by proton in essence but, in contrast with sulfate ion, heteropoly anion plays an important role in accelerating the reaction rate. Heteropoly anion probably interacts with a protonated PA molecule forming a stable complex or ion pair. As to the effect of Hg(II) salt,

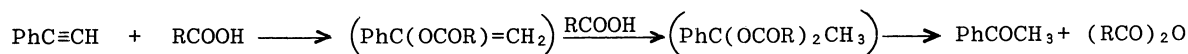
Table 1. Comparison of Catalytic Activities for Hydration of Phenylacetylene^{a)}

Catalyst ($\times 10^{-1}M$)	Salt ($\times 10^{-2}M$)	k ($\times 10^{-2}l/cat.mol.h$)
H ₃ PW ₁₂ O ₄₀ (0.61)	-	2.90
(1.20)	-	5.94
(1.73)	-	10.6
(1.20)	HgHPW ₁₂ O ₄₀ (0.018)	25.3
H ₃ PMo ₁₂ O ₄₀ (1.18)	-	6.51
H ₄ SiW ₁₂ O ₄₀ (0.90)	-	2.94
(0.90)	Na ₄ SiW ₁₂ O ₄₀ (2.51)	5.19
(0.90)	Na ₄ SiW ₁₂ O ₄₀ (5.03)	5.89
H ₂ SO ₄ (3.65)	-	0.173
(5.13)	-	0.191
(5.16)	Na ₂ SO ₄ (12.2)	0.122
(3.57)	HgSO ₄ (0.018)	2.11
HClO ₄ (3.54)	-	0.271

a) 60°C. PA 9.2 mmol, H₂O 550 mmol, EtOH 14 ml.

the HPA-HgHPW₁₂O₄₀ catalyst system was more active than the H₂SO₄-HgSO₄ system at similar concentrations of each acid and Hg salt.

Furthermore, H₃PW₁₂O₄₀ was applied to the addition reaction of carboxylic acid to PA. In the presence of acid catalysts, PA reacted with carboxylic acids to give acetophenone, and simultaneously carboxylic acids were converted into the corresponding acid anhydrides. This reaction is not a simple hydration but the one which proceeds via addition of carboxylic acid to PA, because the reaction rate decreased when even a small amount of water was added to the reaction medium. One of the possible reaction mechanisms is as follows:



In the presence of H₃PW₁₂O₄₀, PA reacted with acetic acid to be almost completely converted into acetophenone within 40 min. H₂SO₄, however, was much less active than the HPA at a similar proton concentration (Table 2).

Table 2. Addition of Carboxylic Acids to Phenylacetylene at 60°C^{a)}

	Catalyst (M)	Time	Conversion of PA (%)
CH ₃ COOH	H ₃ PW ₁₂ O ₄₀ (0.037)	40 min	100
	H ₂ SO ₄ (0.056)	2 h	8.2
	None	2 h	0
C ₂ H ₅ COOH	H ₃ PW ₁₂ O ₄₀ (0.033)	2 h	48.3
	H ₂ SO ₄ (0.058)	2 h	1.2

a) PA:4.6 mmol. CH₃COOH:87 mmol. C₂H₅COOH:68 mmol.

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