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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 H_2SO_4 and $HClO_4$ 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):

$$PhC\equiv CH + H_2O \longrightarrow PhCOCH_3 \qquad (1)$$

$$PhC\equiv CH + 2RCOOH \longrightarrow PhCOCH_3 + (RCO)_2O \qquad (2)$$

The catalytic activities of HPA for the reactions (1) and (2) were examined and compared with those of typical conventional acid catalysts (H_2SO_4, $HClO_4$) 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 $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, and $H_4SiW_{12}O_{40}$. A small portion of the product was withdrawn periodically and analyzed by g.l.c. The products were identified by comparing their IR spectra with those of the authentic samples.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 H_2SO_4 and $HClO_4$ (Table 1). The hydration activities of the catalysts used were in the following order: $H_3PMo_{12}O_{40} > H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} \gg HClO_4 > H_2SO_4$. In case of H_2SO_4 catalyst, the reaction rate was almost proportional to the catalyst concentration, and the addition of a neutral salt (Na_2SO_4) lowered the rate. On the other hand, the rate obtained with HPA catalyst ($H_3PW_{12}O_{40}$) showed approximately second-order dependence on the catalyst concentration. The addition of a neutral salt of HPA ($Na_4SiW_{12}O_{40}$) increased the rate, but the salt was inactive by itself for the hydration. The activation energies observed with $H_3PW_{12}O_{40}$ and H_2SO_4 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)
$H_3PW_{12}O_{40}$	(0.61)	-		2.90
	(1.20)	-		5.94
	(1.73)	-		10.6
	(1.20)	$HgHPW_{12}O_{40}$	(0.018)	25.3
$H_3PMo_{12}O_{40}$	(1.18)	-		6.51
$H_4SiW_{12}O_{40}$	(0.90)	-		2.94
	(0.90)	$Na_4SiW_{12}O_{40}$	(2.51)	5.19
	(0.90)	$Na_4SiW_{12}O_{40}$	(5.03)	5.89
H_2SO_4	(3.65)	-		0.173
	(5.13)	-		0.191
	(5.16)	Na_2SO_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, H_2O 550 mmol, EtOH 14 ml.

the HPA-$HgHPW_{12}O_{40}$ catalyst system was more active than the H_2SO_4-$HgSO_4$ system at similar concentrations of each acid and Hg salt.

Furthermore, $H_3PW_{12}O_{40}$ 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:

$$\mathrm{PhC{\equiv}CH} + \mathrm{RCOOH} \longrightarrow \left(\mathrm{PhC(OCOR){=}CH_2}\right) \xrightarrow{\mathrm{RCOOH}} \left(\mathrm{PhC(OCOR)_2CH_3}\right) \longrightarrow \mathrm{PhCOCH_3} + \mathrm{(RCO)_2O}$$

In the presence of $H_3PW_{12}O_{40}$, PA reacted with acetic acid to be almost completely converted into acetophenone within 40 min. H_2SO_4, 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_3COOH	$H_3PW_{12}O_{40}$	(0.037)	40 min	100
	H_2SO_4	(0.056)	2 h	8.2
	None		2 h	0
C_2H_5COOH	$H_3PW_{12}O_{40}$	(0.033)	2 h	48.3
	H_2SO_4	(0.058)	2 h	1.2

a) PA:4.6 mmol. CH_3COOH:87 mmol. C_2H_5COOH:68 mmol.

References

1) Y. Onoue, Y. Mizutani, S. Akiyama, and Y. Izumi, CHEMTECH, July, p432(1978).
2) K. Urabe, K. Fujita, and Y. Izumi, Shokubai, 22, 223(1980).
3) Y. Izumi and K. Hayashi, Chem. Lett., 1980, 787.
4) K. Nomiya, T. Ueno, and M. Miwa, Bull. Chem. Soc. Jpn., 53, 827(1980).
5) K. Nomiya, Y. Sugaya, S.Sasa, and M. Miwa, ibid., 53, 2089(1980).

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