The Catalytic Effect of Alcohol and Mercaptan on the Michael Reaction of Acrylates

Kohei Sanui and Naoya Ogata

Chemistry Department, Sophia University, Chiyoda-ku, Tokyo

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It was previously shown[1,2] that acrylates such as ethyl acrylate add with amino alcohols to form β-amino acid derivatives quantitatively; room-temperature polycondensation in the presence of basic catalysts follows to form polyamide ether through rearrangement.

$$CH_2{=}CHCOOR + NH_2CH_2CH_2OH \longrightarrow HOCH_2CH_2NHCH_2CH_2COOR \xrightarrow{\text{Base}} \text{-[-}NHCH_2CH_2OCH_2CH_2CO\text{-]-}$$

Ethanolamine, which has a lower basicity than aliphatic amines, reacts more than 10 times as fast as aliphatic amines, and a great accerelating effect of the hydroxyl group on the reactivity of the amino group of ethanolamine was observed. In order to elucidate this accerelating effect, several amino alcohols were synthesized and the rates of their addition to ethyl acrylate were determined in tetrahydrofuran (–THF–) solutions by using gas chromatographic analysis. The results in Table 1 show that the rate constants are almost independent of the chain length between amino and hydroxyl groups; it may be presumed that the accerelating effect of amino alcohols is due not to the intramolecular, but to the intermolecular interactions.

Table 1. Rate constant of the reaction of amino alcohols with ethyl acrylate in THE at 20°C

Amino alcohol	k_1, l/mol, min
Ethanolamine	2.4×10^{-2}
γ-Propanolamine	2.0×10^{-2}
δ-Pentanolamine	1.5×10^{-2}
ε-Hexanolamine	2.0×10^{-2}
n-Butylamine	2.1×10^{-3}

Therefore, the rate of the addition of *n*-butylamine to ethyl acrylate was determined in the presence of the same amounts of such active hydrogen compounds as alcohol or mercaptan.

$$CH_2{=}CHCOOR + n\text{-}BuNH_2 \xrightarrow{k_1} n\text{-}BuNHCH_2CH_2COOR$$

Table 2 shows that alcohol, water and mercaptan accerelate the reaction of ethyl acrylate; the accerelating effect of mercaptan is particularly large, the rate being 350 times as fast as in the absence of mercaptan. It was found by gas chromatographic analysis of the reaction products that the amount of *n*-butylamine keeps constant all through the reaction, showing that amine accerelates the addition of the mercaptan to ethyl acrylate. The effect of the concentration of amine is shown in Table 3.

Table 2. Catalytic effect of active hydrogen compounds on the addition reaction of *n*-butylamine with acrylate (in THF, 1 mol/l, 20°C)

Catalyst	k_1, l/mol, min
None	2.1×10^{-3}
n-Butyl alcohol	9.1×10^{-3}
s-Butyl alcohol	7.1×10^{-3}
t-Butyl alcohol	6.5×10^{-3}
Ethanol	8.0×10^{-3}
Water	1.5×10^{-2}
n-Butyl mercaptan	7.7×10^{-1}

Table 3. The effect of amine concentration on the addition reaction of *n*-butyl mercaptan with ethyl acrylate (in THF, 1 mol/l, 20°C)

Concn. of *n*-butyl amine mol/l	k_1, l/mol, min
0	0
0.25	0.051
0.50	0.14
1.00	0.53
2.00	2.93

Even a small amount of *n*-butylamine accerelates the addition reaction very rapidly, showing that the mercapto group is more neucleophilic than amine. Therefore, it is concluded that amino thiol reacts with acrylate at the mercapto group.

The infrared spectrum of *n*-butylamine and ethyl acrylate did not show any significant shifts of the characteristic bands of each in the presence of mercaptan, alcohol or water; also no shift of the O–H or S–H bands was observed. Therefore, it is still not clear whether or not the great catalytic activity of water and alcohol is due to the complex formation with acrylate, resulting in the polarity change in the vinyl group of acrylate. Further, detailed studies are now in progress.

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[1] N. Ogata and T. Asahara, This Bulletin, **39**, 1486 (1966).

[2] N. Ogata and T. Asahara, *J. Polymer Sci.*, Part B, **4**, 273 (1966).