The Acid-catalyzed S_N1-like Acylation of *l*-Menthol

Fuminori AKIYAMA and Niichiro TOKURA

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka

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In a preceding paper[1] we reported that the propionylation of *l*-menthol in acetonitrile or liquid sulfur dioxide was a first-order-like reaction at a high initial concentration of *l*-menthol, even though the reaction was studied with equivalent amounts of *l*-menthol and propionyl chloride. This evidence will be studied in more detail in the present paper.

The second-order plot and the first-order plot in acetonitrile are visualized in Fig. 1 and Fig. 2. The slopes, k_1, of the apparent first-order plot were obtained at various concentrations of *l*-menthol, propionyl chloride, and *l*-menthyl propionate; they are shown in Table 1. The effect of the hydrogen chloride on the slope of the apparent first-order plot was also studied (*cf.* Fig. 3).

Table 1 and Fig. 3 indicate that the apparent first-order reaction is dependent on the concentrations of *l*-menthol and hydrogen chloride, but not on the concentrations of propionyl chloride and *l*-menthyl propionate:

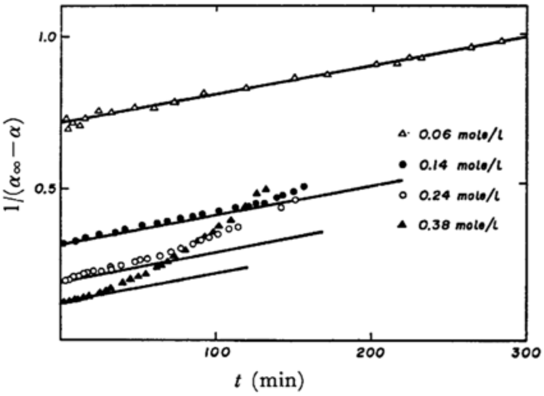

Fig. 1. Second-order plots in acetonitrile at 25°C.

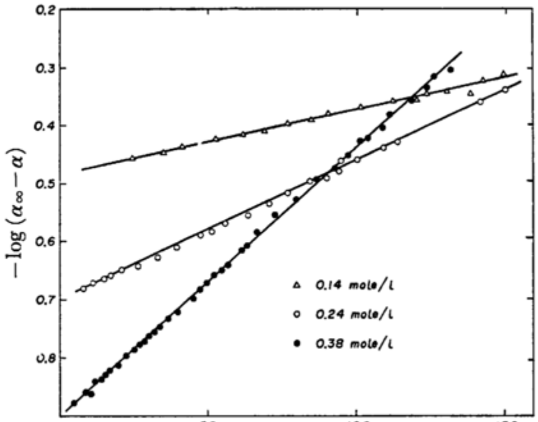

Fig. 2. First-order plots in acetonitrile at 25°C.

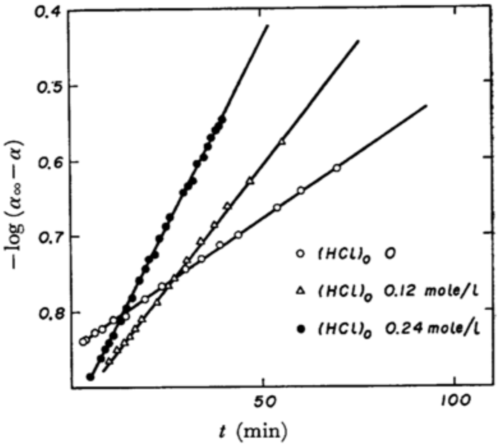

Fig. 3. Effect of hydrochloric acid on k_1 at 25°C. $(C_{10}H_{19}OH)_0$ 0.36 mol/*l*

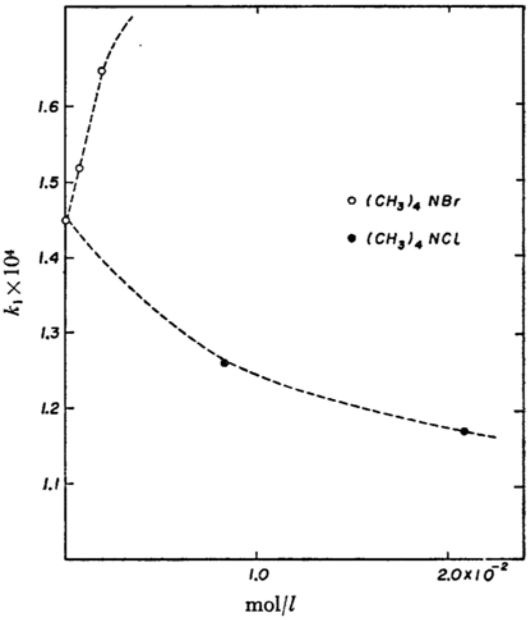

Fig. 4. Effect of $(CH_3)_4NBr$ and $(CH_3)_4NCl$ $(C_{10}H_{19}OH)_0$ 0.36 mol/*l*.

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[1] F. Akiyama and N. Tokura, This Bullettin, **39**, 131 (1966).

Table 1. The effect of the initial concentrations of *l*-menthol, propionyl chloride and *l*-menthyl propionate on the first-order reaction rate in acetonitrile at 25°C

($C_{10}H_{19}OH$) mol/*l*	(CH_3CH_2COCl) mol/*l*	($CH_3CH_2COOC_{10}H_{19}$) mol/*l*	k_1, sec^{-1}
0.14	0.14	0	3.85×10^{-5}
0.24	0.24	0	9.19×10^{-5}
0.24	0.24	0.25	8.75×10^{-5}
0.24	0.24	0.35	8.87×10^{-5}
0.36	0.24	0	1.43×10^{-4}
0.38	0.38	0	1.63×10^{-4}
0.38	0.19	0	1.53×10^{-4}
0.48	0.24	0	2.28×10^{-4}
0.67	0.38	0	3.11×10^{-4}

$$k_1 = k_1^\circ(C_{10}H_{19}OH) + k_1^\circ(HCl) \qquad (1)$$

Therefore, the apparent first-order propionylation may not be an intrinsic first-order reaction. The effect of tetramethylammonium bromide and tetramethylammonium chloride on the apparent first-order propionylation was also studied; it is shown in Fig. 4.

This figure shows the acceleration of the reaction by tetramethylammonium bromide and the retardation of the reaction by tetramethylammonium chloride. Therefore, the apparent first-order propionylation may be assumed to contain a S_N1-like reaction. Perhaps the second term of Eq. (1), the propionylation catalyzed by hydrogen chloride, is the S_N1-like acylation:

$$CH_3CH_2COCl \xrightarrow{HCl} CH_3CH_2CO^+ + Cl^-\cdots HCl \qquad (2)$$

The catalytic effect of hydrogen chloride is assumed to be that of a general acid catalysis. Other general acids, propionic acid and acetic acid, accelerate the apparent first-order reaction, as is shown in Fig. 5.

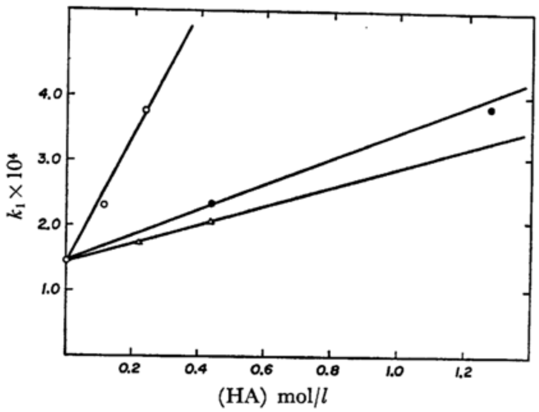

Fig. 5. The catalytic effect of hydrochloric acid, acetic acid and propionic acid. $(C_{10}H_{19}OH)_0$ 0.36 mol/*l*

○ hydrochloric acid+propionic acid
● acetic acid
△ propionic acid

Hydrogen chloride may have a retardation effect by means of the free chloride ion which is generated by the dissociation of hydrogen chloride, as well as an acceleration effect. Furthermore, hydrogen chloride may escape from the reaction solution partially. Therefore, an exact quantitative explanation of the effect of hydrogen chloride is difficult in the case of such a high concentration of hydrogen chloride.

However, the present authors can explain the propionylation of *l*-menthol at a high initial concentration of *l*-menthol as follows. In the initial stage of the reaction, a S_N2-type propionylation of *l*-menthol takes place. With the progress of the reaction, hydrogen chloride is generated and a S_N1 like propionylation, catalyzed by hydrogen chloride, takes place. As the decrease in the reaction rate with the consumption of *l*-menthol is compensated for by the acceleration of the reaction with the generation of hydrogen chloride, the propionylation is apparently a first-order reaction. At a low initial concentration of *l*-menthol, the propionylation of *l*-menthol is a second-order reaction, as is shown in Fig. 1. Perhaps the S_N1-like acylation does not take place without a general acid catalyst.

In a less polar solvent, benzene or chloroform no S_N1-like propionylation catalyzed by hydrogen chloride takes place, as has been shown in the preceding paper.[1] Because of the lack of the stabilization of the acylium ion in acyl halide in compared with that of the carbonium ion from the tertiary alkyl halide, the S_N1-like mechanism of acylation may require the aid of the acid catalyst in the polar solvent.

Experimental

Materials. Commercial extra-pure-grade *l*-menthol was used without further purification. Acetonitrile was dried with phosphorus pentoxide and distilled. The acetonitrile was distilled over potassium carbonate. Commercial propionyl chloride was distilled.

The Kinetic Procedure. The polarimetric procedure used for kinetic followings was described previously. A graphic representation of the apparatus was also found therein[1,2] The details of the kinetic procedure was also explained in a preceding paper.[1] Hydrogen chloride was generated by the following reaction:

$$CH_3COCl + H_2O \rightarrow CH_3COOH + HCl$$

After the addition of a definite amount of water, the effect of hydrogen chloride was studied.

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[2] N. Tokura and F. Akiyama, This Bulletin, **37**, 1723 (1964).