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Chain Carbonylation of Methoxymethyl Chloride by Using AgSbF6 Catalyst under High Pressure of CO

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Abstract: The chain carbonylation of methoxymethyl chloride (**1**) by the use of $AgSbF_6$ catalyst smoothly proceeded under high pressure of carbon monoxide to give methyl methoxyacetate after treatment with methanol. The reaction was highly dependent on the CO pressure and the reaction temperature, indicating the presence of equilibrium processes. From the temperature dependence of the equilibrium constant, the enthalpy change of the reaction was calculated to be -25.4 kJ mol^{-1}.

INTRODUCTION

The reaction of unstable carbocation or highly polarized ionic complex with carbon monoxide is one of the important carbon-carbon bond formation reactions. Several methods have been developed for converting olefins, alcohols, and alkyl halides to carboxylic acid or its derivatives by using acid catalyzed carbonylation by way of formation of the cationic or highly polarized species as a key intermediate.[1] However, as exemplified by Koch reaction, many of these reactions give complicated mixture of products due to side reactions such as isomerization, olefin formation, disproportionation, or oligomerization.[1] On the other hand, Nojima *et al.* reported the carbonylation of various alkyl halides in the presence of ethanol in the $SbCl_5$-liquid SO_2 system at -70 °C under atmospheric pressure of carbon monoxide to give carboxylic esters.[2,3] The formation of acyl-cation type complex prevented other side reactions, and hence the carbonylation selectively occurred.

Previously, we reported the carbonylation of methoxymethyl chloride (**1**) using BF_3 at 10 ~ 40 °C under 150 kg cm^{-2} of carbon monoxide (equation 1).[4] The reaction is supposed to proceed through rapid ionization of chloride **1** to a resonance-stabilized cationic intermediate **4**. The stable methoxymethyl cation **4** has not only been directly observed and characterized in superacid solution at -60 °C by NMR spectroscopy[5], but actually isolated as the stable, crystalline fluoroantimonate salt[6] by Olah and his coworkers.

$$\underset{\mathbf{1}}{CH_3OCH_2Cl} + CO \xrightarrow{BF_3} \underset{\mathbf{2}}{[CH_3OCH_2CO^+\ BF_3Cl^-]} \xrightarrow{CH_3OH} \underset{\mathbf{3}}{CH_3OCH_2COOCH_3} \qquad (1)$$

$$\underset{\mathbf{4}}{\left[\, CH_3O - CH_2^+ \longleftrightarrow CH_3O^+{=}CH_2 \,\right] BF_3Cl^-}$$

However, from the viewpoint of an organic synthetic method, the carbonylation using BF_3 did not necessarily seem to be a quite effective method, since a stoichiometric amount of BF_3 was required, and the reaction was terminated at a certain stage due to the presence of an equilibrium process.[4] The Lewis acid BF_3 could not work as a catalyst because of a strong interaction between BF_3 and the carbonylation product, i.e.

methoxyacetyl chloride (**5**). Then it is of particular interest to examine the effect of Lewis acid which has lower acidity than BF_3.[7] We have found that the carbonylation of methoxymethyl chloride (**1**) can proceed by the use of a catalytic amount of $AgSbF_6$ (equation 2). This chain carbonylation apparently involves the formation of cationic intermediates. The yield of the carbonylation product depends on the CO pressure and the reaction temperature, suggesting that this reaction also involves some equilibrium step(s), as will be described below.

$$\underset{\mathbf{1}}{CH_3OCH_2Cl} \xrightarrow[\text{sulfolane}]{\text{CO} \atop AgSbF_6\ \text{(catalyst)}} \underset{\mathbf{5}}{CH_3OCH_2COCl} \xrightarrow{CH_3OH} \underset{\mathbf{3}}{CH_3OCH_2COOCH_3} \qquad (2)$$

RESULTS AND DISCUSSION

Reaction

A mixture of a catalyst and methoxymethyl chloride (**1**) in sulfolane was reacted in a stirring-type stainless-steel autoclave under 50 ~ 200 kg cm^{-2} of CO at -20 ~ 25 °C. The depression of CO pressure essentially stopped after the reaction time of about 10 min. Methanol was injected into the autoclave by the use of a plunger pump. GLC analysis of the reaction mixture showed two products. One was identified as methyl methoxyacetate which was derived from the carbonylation product, i.e. methoxyacetyl chloride (**5**). The other was identified as dimethoxymethane which is the methanolysis product of unchanged chloride **1**.

First, the effect of various Lewis acid catalysts was examined upon carbonylation of chloride **1**. Either of $AgSbF_6$, $AgPF_6$, and $SbCl_3$ was not completely soluble in sulfolane. However, when chloride **1** was added to a suspension of $AgSbF_6$ or $AgPF_6$ in sulfolane, the catalyst completely dissolved and new white precipitates were immediately formed. In contrast, $SbCl_5$ dissolved in the solution of chloride **1** in sulfolane without formation of any precipitate. As shown in Table 1, $AgSbF_6$ (5 mol%) was found to be the best catalyst for the carbonylation of chloride **1**. When the reaction was carried out with the stirring rate of 500 and 1300 rpm, the carbonylation product was obtained in 40.7 and 40.8 % yield, respectively. Thus, the stirring rate of 500 rpm seemed sufficient. $AgPF_6$ was almost as effective as $AgSbF_6$, but apparently $SbCl_3$ was ineffective.

Table 1. Effect of the Catalyst on Carbonylation of Methoxymethyl Chloride (**1**) [a]

catalyst	mmol	methyl methoxyacetate (%) [b]	TON [c]
$AgSbF_6$	1.0	40.8	8.2
$AgSbF_6$	0.5	32.9	13.2
$AgSbF_6$	1.0	40.7 [d]	8.1
$AgSbF_6$ [e]	1.0	24.1	4.8
$AgSbF_6$	2.0	31.2	3.1
$AgPF_6$	1.0	37.2	7.5
$SbCl_5$	1.0	34.5	6.9
$SbCl_3$	1.0	0	0

[a] The reaction was carried out with chloride **1** (20.0 mmol) in sulfolane (2.5 mL) at 0 °C under 100 kg cm^{-2} of CO for 4 h with stirring rate of 1300 ~ 1400 rpm. [b] The yield was determined by GLC and is based on **1**. [c] Molar ratio of produced ester to the catalyst. [d] Stirring rate was 500 rpm. [e] The reaction was carried out without solvent.

Figure 1 shows a plot of the yield of methyl methoxyacetate (**3**) versus reaction time before adding of methanol under 100 kg cm^{-2} of CO at 0 °C by the use of $AgSbF_6$ (5 mol%) as a catalyst. The product yield did not substantially increase after the reaction time of 2 h, and the reaction appeared to reach an equilibrium state. The initial rate of reaction was too fast to determine by the conventional method; the yield of ester **3** was already 30.5 % at the reaction time of 15 min.

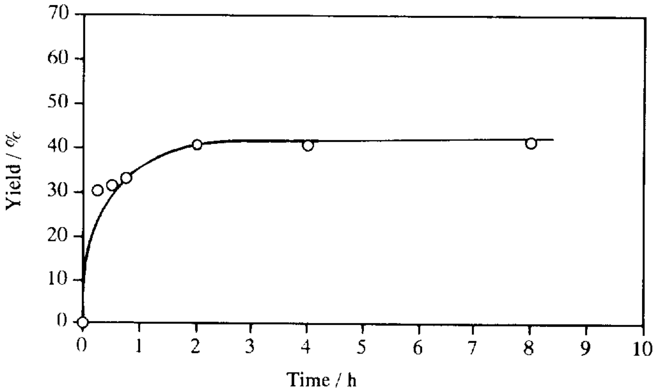


Fig. 1. Plot of the yield of ester **3** vs. reaction time at 0 °C under 100 kgcm^{-2} of CO.

In order to confirm the presence of equilibrium state, the effects of the CO pressure and the reaction temperature upon the ester yield were examined. The results are summarized in Table 2. The higher pressure of CO and the lower reaction temperature resulted in an increase in the yield of ester **3**. Because the reaction mixture froze at -25 °C, the reaction was performed only at the temperature higher than -20 °C.

Table 2. Carbonylation of Methoxymethyl Chloride (**1**) Catalyzed by $AgSbF_6$ (5 mol%)

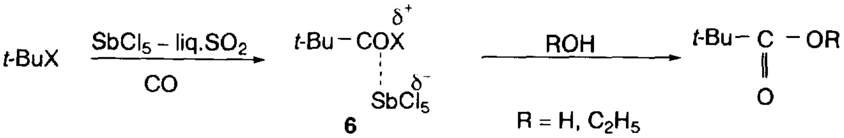
Temp. (°C)	CO (kg cm^{-2})	Time (h)	methyl methoxyacetate (%)[a]	dimethoxymethane (%)[a]
-20	50	8	49.1	—[b]
-20	100	8	62.3	—[b]
-20	150	8	72.1	25.1
-10	50	8	38.9	56.1
-10	100	8	52.3	—[b]
-10	150	8	62.6	37.1
0	50	8	25.4	—[b]
0	100	8	41.8	57.6
0	150	8	48.6	—[b]
0	200	8	56.0	—[b]
25	50	21	15.3	—[b]
25	100	4	22.2	—[b]
25	150	21	30.0	65.7

[a] The yield was determined by GLC. [b] Not determined.

Reaction mechanism

Previously, Nojima *et al.*[3] reported that carbonylation of *t*-butyl chloride proceeds to give the corresponding carboxylic acid or its ester by the use of equimolar or excess amount of $SbCl_5$ under atmospheric pressure of CO, and they proposed the formation of polar coordinate complex **6** rather than the ion pair as an intermediate.[3,8,9] On the other hand, we have postulated intermediate formation of ionic species **4** in our previous work of carbonylation of methoxymethyl chloride in the presence of a stoichiometric amount of BF_3. In the present work, we suppose that the first formation of salt (**7**) of stable methoxymethyl cation is playing an important role in a catalytic cycle.

Scheme 1



We propose the following mechanism involving unambiguous formation of cation **7** for the $AgSbF_6$ catalyzed carbonylation of chloride **1**. The reaction is clearly initiated by the rapid and irreversible formation of cation **7** together with the precipitates of AgCl (equation 3). Cation **7** then reacts reversibly with carbon monoxide to produce acyl cation **8** (equation 4),[10] which would produce acyl chloride **5** and regenerate **7** by chloride-ion abstraction from the starting chloride **1**, again in a reversible reaction (equation 5). Thus, once the reaction is initiated by formation of cation **7**, the overall reaction could be formally represented as equation 6.

$$\underset{\mathbf{1}}{CH_3OCH_2Cl} + AgSbF_6 \longrightarrow \underset{\mathbf{7}}{CH_3OCH_2^+\,SbF_6^-} + AgCl\downarrow \qquad (3)$$

$$\underset{\mathbf{7}}{CH_3OCH_2^+\,SbF_6^-} + CO \rightleftharpoons \underset{\mathbf{8}}{CH_3OCH_2CO^+\,SbF_6^-} \qquad (4)$$

$$\underset{\mathbf{8}}{CH_3OCH_2CO^+\,SbF_6^-} + \underset{\mathbf{1}}{CH_3OCH_2Cl} \rightleftharpoons \underset{\mathbf{5}}{CH_3OCH_2COCl} + \underset{\mathbf{7}}{CH_3OCH_2^+\,SbF_6^-} \qquad (5)$$

$$\underset{\mathbf{1}}{CH_3OCH_2Cl} + CO \overset{K}{\rightleftharpoons} \underset{\mathbf{5}}{CH_3OCH_2COCl} \qquad (6)$$

The equilibrium constant (K) of this reaction is expressed as

$$K = \frac{x_e}{a_0 - x_e}\,\frac{1}{[CO]_l} = \frac{x_e}{a_0 - x_e}\,\frac{1}{H_{CO}\,P_{CO}} \qquad (7)$$

where a_0, x_e, H_{CO}, and P_{CO} denote the initial concentration of chloride **1**, the equilibrium concentration of methoxyacetyl chloride, Henry constant of the CO gas, and the pressure of CO, respectively. Alternatively, taking into consideration of solubility of CO into the liquid phase, the equilibrium constant (K') is simplified into equation 8.

$$K' = K H_{CO} = \frac{x_e}{a_0 - x_e} \frac{1}{P_{CO}} \tag{8}$$

The feasibility of such relationship was demonstrated by linear correlation between $x_e/(a_0-x_e)$ and P_{CO} as shown in Figure 2. From the slope of each line, the following values were obtained as the equilibrium constant, K' : 1.69×10^{-2} $kg^{-1}cm^2$ at -20 °C, 1.10×10^{-2} $kg^{-1}cm^2$ at -10 °C, 6.30×10^{-3} $kg^{-1}cm^2$ at 0 °C, and 2.78×10^{-3} $kg^{-1}cm^2$ at 25 °C. From the temperature dependence of the equilibrium constant given in Figure 3, the overall enthalpy change in the equation 7 is calculated to be -25.4 kJ mol^{-1}.

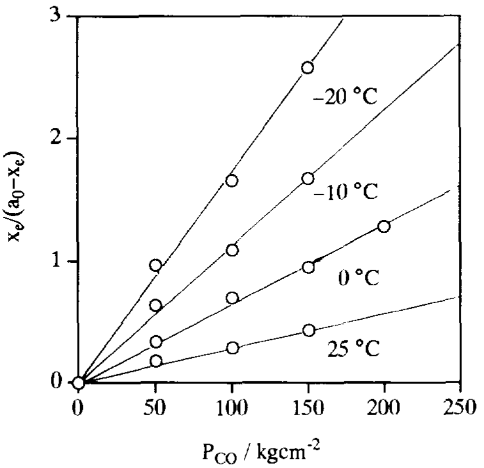


Fig. 2. Plot of $x_e/(a_0-x_e)$ vs. P_{CO}.

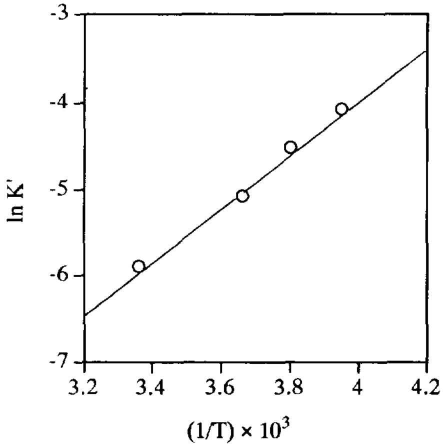


Fig. 3. Plot of ln K' vs 1/T.

The silver-ion catalyzed carbonylation was also attempted under similar conditions for the halides such as *t*-butyl chloride, chloroacetone, and also for benzyl chloride and bromide. Except for the case of *t*-butyl chloride, which afforded very low yield (3%) of methyl pivalate after 4 h at 0 °C under 100 kg cm^{-2} of CO, no carbonylation product was detected by GLC analysis, and the starting halides were recovered almost quantitatively. These results clearly indicate that the explicit formation of stable carbocation is essential for the catalytic chain carbonylation reaction.

EXPERIMENTAL

GLC analyses (2 m × 5 mm columns packed with 10 % Apieson grease L on Uniport HP 60/80 mesh or 20 % Polyethylene glycol 400 on Celite 545 60/80 mesh) were carried out on a Hitachi 163 instrument with flame-ionization detectors and N_2 as a carrier gas. *m*-Xylene and methyl acetate were used as the internal standard for determination of methyl methoxyacetate and dimethoxymethane, respectively. Sulfolane was distilled under reduce pressure; 98-100 °C / 1 Torr. Commercially available methoxymethyl chloride, silver hexafluoroantimonate ($AgSbF_6$), silver hexafluorophosphate ($AgPF_6$), antimony pentachloride ($SbCl_5$), and antimony trichloride ($SbCl_3$) were used as received without further purification. Carbon monoxide, the purity of which was above 98 % , was prepared from H_2SO_4 and HCO_2H by the standard method.

General Procedure

A mixture of methoxymethyl chloride (1.61 g, 20.0 mmol), silver hexafluoroantimonate (0.344 g, 1.0 mmol) and sulfolane (2.5 mL) was charged into a stirring-type stainless-steel autoclave (50 mL) equipped with an internal glass vessel. Air was flushed out with CO several times, and CO was charged up to the desired pressure. The autoclave was placed in a constant temperature bath and then stirred at 1300 ~ 1400 rpm for 8 h. Methanol (3.0 mL) was injected into the autoclave by means of a high pressure plunger pump and stirring continued for another 30 min. The autoclave was allowed to warm to room temperature and then the reaction mixture was poured into ether. An insoluble white precipitate (AgCl) was removed by filtration. The resulting solution was analyzed by GLC using *m*-xylene and methyl acetate as internal standards. GLC analysis showed two products. They were identified as methyl methoxyacetate and dimethoxymethane by comparison with authentic samples.

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