Studies on the Kinetics of Addition Reactions of Carbon Monoxide with Organic Compounds in Hydroiodic Acid under High Pressure (Part 1)*

—The Addition Reaction of Carbon Monoxide with Ethyl Iodide—

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Summary: The addition reaction of carbon monoxide with ethyl iodide in aqueous hydroiodic acid was investigated under high pressure in the range of 30 to 90 kg/cm². The yield of propionic acid was fairly high and the rate of formation was the first order reaction with respect to carbon monoxide and ethyl iodide. The overall activation energy has been found to be 13.0 kcal/mole, which contains the molar enthalpy change of equilibrium reaction (2), i.e., the heat of dissociation of C₂H₅I and the activation energy of reaction (3), i.e., the reaction between the ethyl cation and carbon monoxide.

1 Introduction

Addition reactions of carbon monoxide with olefins in various acid media, such as concentrated sulfuric acid^{1)~6)}, phosphoric acid⁷⁾, anhydrous hydrogen fluoride^{3), 6)}, monohydroxyfluorboric acid and its mixture with phosphoric or sulfuric acid⁸⁾ and aqueous boron trifluoride^{9)~10)}, have been well known, and those olefins higher than C₄ react quite readily with carbon monoxide^{11)~13)}. On the other hand, those olefins lower than C₃ react with carbon monoxide under more severe conditions¹⁴⁾. Recently, Kanbara et al. obtained propionic acid in good yields through the reaction of ethyl fluoride in aqueous hydrogen fluoride¹⁵⁾.

In these reactions, it is expected that the activity of acidic catalysts might have a linear relationship with the acid strength. Usually, the acidity function (H₀) is used as a measure of acid strengths. When H₀ has a large negative value, its acid strength is large. The approximate pK_a values of HF, HCl, HBr and HI are 3, -7, -9 and -10, respectively¹⁶⁾. Therefore, HI has the largest negative H₀ value, which means HI is the strongest acid among them.

Considering the relationship between the acidity function and acid concentration, it may be concluded that even a strong acid, such as conc. HCl or HBr, is insufficient to act as a catalyst under atmospheric pressure. Thus, we have used

hydrogen iodide as a catalyst which is expected to be the strongest acid medium and investigated kinetically the addition reaction of carbon monoxide with ethyl iodide.

2 Experimental

Ethyl iodide (E.P. grade), hydroiodic acid (G.R. grade, 57 wt% aqueous solution of HI), silver carbonate (C.P. grade) and sodium hydroxide (E.P. grade) were all purchased from Nakarai Chemicals, Ltd., and were used without further purification.

Carbon monoxide was kindly supplied by the Institute for Chemical Research, Kyoto University, which was prepared from formic acid and hot concentrated sulfuric acid having a purity of more than 97% by a gas chromatography.

The reaction was carried out in a glass vessel inserted into a stainless steel autoclave (capacity: 100 ml) equipped with a magnetic stirrer. Weighed amounts of hydroiodic acid and ethyl iodide were charged into the autoclave. After the temperature of the autoclave had become constant at the desired level, carbon monoxide was introduced and the stirring started. Carbon monoxide was supplied continuously to maintain the total pressure of the autoclave constant during the reaction. At the end of reaction time the autoclave was quickly cooled with ice water. The aqueous solution was neutralized with Ag₂CO₃ to remove the hydrogen iodide and filtered, then the filtrate which contained the Ag-salt of organic acid was converted into free acid by passing it

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through a column of exchange resin (Amberlite 120B) and titrated with aqueous 0.1 N-NaOH. Prior to quantitative analysis, some mixtures of propionic acid and hydroiodic acid were prepared. These mixtures were analysed by the same procedure as mentioned above to obtain the factor of propionic acid yield.

3 Results

3.1 Preliminary Experiments

Before the study of kinetic treatment, preliminary experiments were carried out. The aqueous solution, after passing through the column of exchange resin, was analysed with a gas chromatography (Hitachi K53) equipped with a flame ionization detector. A column (2 m $\times$ 3 mm) with 20% polyethylene glycol or SE-30 on 60/80 mesh Chromosorb W-NAW was used. And nitrogen was used as the carrier gas. Propionic acid was the only acid produced. The yield of propionic acid was determined by NaOH titration.

Figure 1 shows the relationship between the stirring speed and the rate of propionic acid formation. Above 1,000 rpm the stirring speed did not affect the reaction rate under the condi-

Fig. 1 Effect of Stirring Speed on Yield of Propionic Acid

Fig. 2 Effect of Mole Ratio of HI to C_2H_5I on Yield of Propionic Acid

tions given in the figure suggesting that stirring speed of 1,000 rpm was sufficient to make the liquid phase reaction the rate-determining under the conditions used.

Figure 2 shows the relationship between the mole ratio of HI to C_2H_5I and the yield of acid. From this result, one can see that the yield of propionic acid increases with mole ratio and it becomes constant above the mole ratio 40. The broken line in **Fig. 2** gives the results obtained by the reaction in which carbon monoxide was charged first and then the temperature was raised. The results thus obtained are higher than those obtained by usual methods. This means that the reaction occurs during the period of rising temperature.

Figure 3 shows the effects of temperature on the reaction. The maximum yield was obtained at near 180°C. Above 180°C, the reaction involved some side reactions such as polymerization. And after the run, some dark brown oily material was obtained.

From the results described above, the following conditions were adopted for the kinetic measurements: reaction temperature lower than 180°C, HI/ C_2H_5I mole ratio 45, stirring speed 1,000 rpm.

3.2 Kinetic Measurements

Effects of temperature on the yield examined at 100, 120 and 140°C are shown in **Fig. 4**. From the results one can see that the yield of propionic acid increased with increasing temperature. In the Figure, the ordinate is given by the apparent yield of propionic acid which includes the additional yield resulting from the reaction during the cooling period. Namely, the apparent yield at zero time in the Figure must be attributed to the

Fig. 3 Effect of Temperature on Yield of Propionic Acid at Reaction Time of 60 and 120 min

Fig. 4 Effect of Temperature on Apparent Yield of Propionic Acid

Fig. 5 Effect of Temperature on Corrected Yield of Propionic Acid

reaction taking place during the cooling period.

In order to get the real yield, the following correction was made: As a first approximation, the yield of propionic acid obtained during the period of cooling was assumed to be proportional to the amount of reactant which remained unreacted, giving a proportionality constant equal to $Y_0/(1-Y_0)$ at zero time.

Therefore the following correction equation was used in each run.

$$Y_c = Y_a - \frac{Y_0}{1-Y_0} (1-Y_a) \quad (1)$$

where Y_c is the corrected mole fraction of propionic acid, Y_a the apparent mole fraction and Y_0 the mole fraction at zero time.

In Fig. 5 we show the results thus corrected. Hereafter, we shall use these corrected results.

Figure 6 shows the effects of pressure on the yield of acid at 180°C. Obviously the yield was increased with increasing pressure.

Fig. 6 Effect of Pressure on Corrected Yield of Propionic Acid

4 Discussion

According to the reaction mechanism proposed by Kanbara et al.¹⁵⁾, the following modified reaction scheme is assumed:

Namely, ethyl iodide in aqueous HI dissociates partly to produce an ionic intermediate cation (may be a carbonium cation), and an equilibrium reaction exists. The ionic intermediate formed will combine with the dissolved carbon monoxide to produce propionyl iodide, followed by the fast hydrolyzation reaction to form propionic acid.

Taking into account that HI is present in large excess over C_2H_5I , reaction (2) is assumed to be a pseudo first order reaction; reaction (4) is very fast and the rate of formation of propionic acid is equal to that of propionyl iodide.

Assuming the rate determining process to be Eq. (3) and a steady state condition for the intermediate cation, the following rate equation is derived:

$$\begin{aligned} \frac{d[C_2H_5COOH]}{dt} &= \frac{d[C_2H_5COI]}{dt} \\ &= k_2 H_{CO} P_{CO} [C_2H_5 + I - H_3O + I^-] \\ &= \frac{k_1 k_2 H_{CO} P_{CO}}{k_{-1} + k_2 H_{CO} P_{CO}} ([C_2H_5I]_0 - [C_2H_5COOH]) \end{aligned} \quad (5)$$

Integrating this equation:

Fig. 7 Plot of $\ln\{[C_2H_5I]_0/([C_2H_5I]_0 - [C_2H_5COOH])\}$ vs. Reaction Time

Fig. 8 Plot of $10/\ln\{[C_2H_5I]_0/([C_2H_5I]_0 - [C_2H_5COOH])\}$ vs. $1/P_{CO}$

$$\ln \frac{[C_2H_5I]_0}{[C_2H_5I]_0 - [C_2H_5COOH]} = \frac{k_1 k_2 H_{CO} P_{CO}}{k_{-1} + k_2 H_{CO} P_{CO}} t \quad (6)$$

where H_{CO} is Henry's constant for CO in the solution and P_{CO} the pressure of CO over the reaction medium.

In the derivation of the above equation, it is assumed that CO is present in large excess over C_2H_5I and its concentration is constant during the reaction.

Figure 7 shows the plot of $\ln\{[C_2H_5I]_0/([C_2H_5I]_0 - [C_2H_5COOH])\}$ against reaction time in good linear relationship consistent with Eq. (6). Thus the slope of this straight line gives the apparent rate constant, namely $k_{overall} = k_1 k_2 H_{CO}$.

Fig. 9 Plot of $k_{overall}$ vs. P_{CO}

Fig. 10 Arrhenius Plot of Overall Rate Constant

$P_{CO}/(k_{-1} + k_2 H_{CO} P_{CO})$ being still a function of carbon monoxide pressure.

An alternative expression of Eq. (6) is given by Eq. (7):

$$\frac{t}{\ln\{[C_2H_5I]_0/([C_2H_5I]_0 - [C_2H_5COOH])\}} = \frac{k_{-1}}{k_1 k_2 H_{CO} P_{CO}} + \frac{1}{k_1} \quad (7)$$

giving a linear relationship between the term on the right-hand side and $1/P_{CO}$ at constant time. In **Fig. 8** we show the result of the plot of the term on the right-hand side of Eq. (7) against $1/P_{CO}$ at the reaction time of ten minutes. The result is a good straight line whose slope and intercept give the value of 500 for $k_{-1}/k_2 H_{CO}$. This means that $k_2 H_{CO}$ is negligibly small compared with k_{-1} .

Figure 9 shows the relation between $k_{overall}$

and P_{CO} , and a good linear straight line is also obtained, where P_{CO} results from the difference between the vapor pressure of aqueous solution and the total pressure. Thus one can conclude that $k_{overall}$ is equal to k_1k_2/k_{-1} .

Figure 10 is an Arrhenius plot of the overall rate constant resulting in a straight line. The slope gives the overall activation energy of 13.0 kcal/mol, which contains the molar enthalpy change of reaction(2) and the activation energy of reaction (3).

From the above discussions one can conclude as follows:

Propionic acid can be produced in good yields in the HI catalyzed carbonylation reaction when ethyl iodide is used as the raw material.

The rate equation derived from the proposed mechanism involving the liquid phase reaction of dissolved carbon monoxide with ethyl cation as the rate determining, which is the first order reaction with respect to CO pressure and C_2H_5I , has been shown to elucidate the observed facts satisfactorily.

The overall activation energy was found to be 13.0 kcal/mol, which contains the molar enthalpy change of reaction(2), i.e., the heat of dissociation of C_2H_5I and the activation energy of reaction (3), namely, the reaction between ethyl cation

and carbon monoxide to form propionyl iodide.

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