Effect of Concentration, Acid, Temperature, and Metal on Competitive Reaction Pathways for Decarbonylation and Decarboxylation of Formic Acid in Hot Water

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Hydrothermal reaction of formic acid has been studied by varying the following conditions: temperature (275 to 350 °C), concentration of formic acid (0.1 to 1 M), addition of HCl, and presence of metal alloy powders. In hot water, formic acid decomposes to CO and CO_2. The product ratio of CO to CO_2 strongly depends on the conditions. At higher concentrations and lower temperatures, the yield of CO gets larger. In most of the conditions studied here, the main product is not CO_2 but CO in contrast to previous works. Acid enhances the CO production and metal powders catalyze the decarboxylation pathway.

Recently, hot water including supercritical water receives much attention as a novel and clean medium for noncatalytic chemical reactions of environmental and industrial importance.[1–3] Formic acid plays a key role in controlling the cross-disproportionation reaction as an aldehyde in hot water,[2,3] and it is important to elucidate the pathways of its decomposition. There are two possible decomposition pathways for formic acid in hot water; one is the decarbonylation and the other is the decarboxylation as shown below,[4]

$$HCOOH \longrightarrow H_2O + CO \text{ (decarbonylation)}, \qquad (1)$$

$$HCOOH \longrightarrow H_2 + CO_2 \text{ (decarboxylation)}. \qquad (2)$$

Savage and co-workers studied the decomposition of formic acid in a flow reactor made of Hastelloy C-276 at 0.02 M in the temperature range of 320–500 °C and showed that the main product was CO_2.[5] Other authors also reported at higher concentrations (0.13 M[6] and 1 M[7]) that the main decomposition pathway is the decarboxylation. We reported, however, that as in the case of the neat gas,[8] the main product is CO for aqueous solutions of formic acid at 250 °C.[4] Bröll and co-workers reported that the competition depends on the temperature.[9] At temperatures lower than 320 °C, the main product is not CO_2 but CO. In this work, we show that several factors such as concentration of formic acid, addition of HCl, temperature, and vessel surface control the product ratio of CO to CO_2. Especially, we first elucidate the importance of the concentrations of the reactant and acid (HCl).

^{13}C-enriched formic acid (>99%) was obtained from ISOTEC. We used a JEOL NMR spectrometer (JNM-ECA400) equipped with a JASTEC superconductor magnet (9.4 T). The sample solution was put in a quartz tube (1.5-mm i.d. and 3.0-mm o.d.) and sealed after the substitution of air by argon. The sample tube was heated in a furnace and quenched by air. The system is on the vapor–liquid equilibrium curve of water under the conditions studied here. After the reaction, 7 tubes were put in a Pyrex NMR tube (10.0-mm o.d.). ^1H and ^{13}C spectra were measured for both the liquid and gas phases to determine the concentrations of the reactant and products. The ^{13}C free induction delay signals were accumulated 7500 to 250 times for the gaseous products from the reactant at 0.1 and 1 M, respectively.

Such metal alloy powders as SUS 316L (20 μm), Hastelloy C-276 (20 μm), and Inconel 625 (250 μm) were supplied from SANYO SPECIAL STEEL; the diameter is shown in the parentheses. Metal powders of 50 mg were added to the solutions of formic acid in heavy water (2.0 M, 100 mg). By means of NMR, it is difficult to determine the products because of the interference between radio wave and the metal powder. Instead, Raman spectroscopy was used to determine the products in the presence of the metal powders. The Raman spectrometer we used is obtained from Renisaw (RM1000B).

The concentration dependence of the gaseous products, CO and CO_2, was examined by ^{13}C NMR. Figure 1 shows the ^{13}C spectra for the gas phase at various initial concentrations of formic acid treated at 300 °C for 10 min. As seen in Figure 1a, CO_2 at 128 ppm is the main product and CO at 186 ppm is the minor product at a low concentration of 0.1 M. The mole fraction of CO_2 is determined to be 95% by integrating the CO_2 and CO peaks for both the gas and liquid phases; the solubility of CO at room temperature is negligibly small in ambient water while CO_2 is not. To our surprise, CO becomes dominant at high concentrations of 0.5 and 1.0 M; the mole fraction of CO_2 is 14 and 10% at 0.5 and 1.0 M, respectively. With increasing concentration, the ratio of CO to CO_2 gets larger. It is found[10] that this concentration dependence arises from the difference in the reaction order between the CO and CO_2 pathways, as shown below. When CO is dominant at higher concentrations, in fact, the ^1H

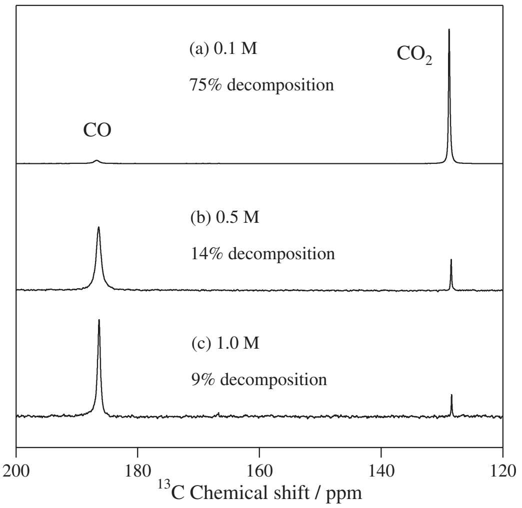

Figure 1. ^{13}C spectra for the gas phase of aqueous solutions of formic acid after treated at 300 °C for 10 min. Fraction of formic acid decomposition is shown in %. Intensity (y axis) is arbitrary.

spectrum for the gas phase indicates a drastic decrease of H_2, corresponding to the relative weight of Eq. 1 to Eq. 2.

Formic acid, which is the simplest carboxylic acid, is neither a strong nor weak acid in ambient water and ionized to a considerable extent. Hence the decarbonylation can be autocatalyzed by the liberated proton. When HCl is added, the CO formation rate is found to be larger. It is thus clear that the decarbonylation is accelerated by proton. Formic acid is not a strong acid and the proton concentration in aqueous solutions of formic acid is proportional to the square root of the concentration of formic acid in the condition studied here (acidity constant is 1.64×10^{-4} M at 30 °C and much smaller than the concentration of formic acid). We have first elucidated that the reaction order of the decarbonylation is 1.5 according to an independent experiment on the concentration dependence at 250 °C.[10]

In order to clarify the temperature dependence, the sample solutions were treated at 275, 300, 325, and 350 °C for 10 min. As shown in Figure 2, the CO_2 mole fraction is 6, 10, 13, and 18% at 275, 300, 325, and 350 °C, respectively. With the rise in the temperature, the CO_2 fraction gets larger with CO kept main. A difference in the activation energy between the decarbonylation and decarboxylation can be one of the reasons for the temperature dependence of the CO_2 fraction. In contrast to the results by Bröll et al.,[9] however, the main product is not CO_2 but CO even at 350 °C. This discrepancy is probably due to the metal (Inconel 625) tube surface catalysis.[7] Furthermore, the mole ratio (CO/CO_2) dependence on the reaction condition can be quantitatively understood only by the calculation of solvation free energies for all the products, CO, CO_2, H_2, and H_2O.[11]

In order to confirm the catalytic activity of the vessel surface to the decomposition of formic acid, the metal powder effect was examined. Figure 3 shows the Raman spectra for the gas phase of 2 M solutions of formic acid in heavy water with and without the metal alloy powders. Without the metal powder, the product is only CO as seen in Figure 3a; CO_2 peaks are not observed. With the metal powders, on the other hand, CO_2, D_2, and HD emerge as shown in Figures 3b–d. This result means that the metal surface of the vessels can catalyze the decarboxylation of formic acid under hydrothermal condition. This is one of the reasons why CO_2 was observed as a main product in the previous works.[5–7] The decomposition rates in the literature mentioned above are much faster than those studied here using the nonmetallic reaction vessel.

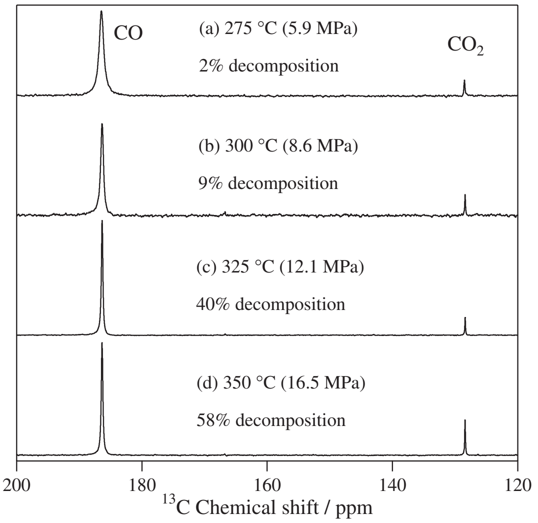

Figure 2. ^{13}C spectra for the gas phase of aqueous solutions of formic acid (1.0 M) treated at various temperatures for 10 min. Fraction of formic acid decomposition is shown in %. Intensity (y axis) is arbitrary. Since the system is on the vapor–liquid equilibrium curve of water, the equilibrium pressure is given above in the parentheses.

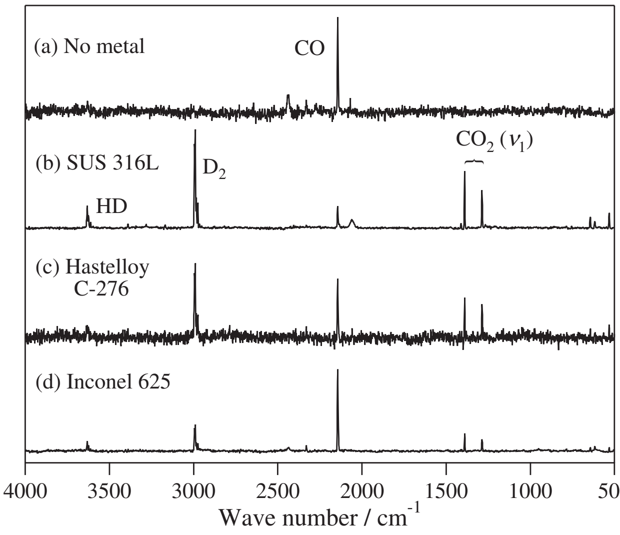

Figure 3. Raman spectra for aqueous solutions of formic acid (2.0 M, heavy water) after treated at 250 °C for 1 h with (a) no metal powder (10), (b) SUS 316L (30), (c) Hastelloy C-276 (5), and (d) Inconel 625 (300); integration times in seconds are shown in the parentheses.

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References

1 M. Nakahara, T. Tennoh, C. Wakai, E. Fujita, and H. Enomoto, *Chem. Lett.*, **1997**, 163.
2 Y. Tsujino, C. Wakai, N. Matubayasi, and M. Nakahara, *Chem. Lett.*, **1999**, 287.
3 Y. Nagai, C. Wakai, N. Matubayasi, and M. Nakahara, *Chem. Lett.*, **32**, 310 (2003).
4 Y. Tsujino, C. Wakai, N. Matubayasi, and M. Nakahara, *High Pressure Sci. Technol.*, **9**, 66 (1999).
5 J. Yu and P. E. Savage, *Ind. Eng. Chem. Res.*, **37**, 2 (1998).
6 A. B. Bjerre and E. Sorensen, *Ind. Eng. Chem. Res.*, **31**, 1574 (1992).
7 P. G. Maiella and T. B. Brill, *J. Phys. Chem. A*, **102**, 5886 (1998).
8 P. G. Blake and C. Hinshelwood, *Proc. R. Soc. London, Ser. A*, **255**, 444 (1960).
9 D. Bröll, C. Kaul, A. Krämer, P. Krammer, T. Richter, M. Jung, H. Vogel, and P. Zehner, *Angew. Chem., Int. Ed.*, **38**, 2998 (1999); the concentration of formic acid was not shown.
10 C. Wakai, K. Yoshida, Y. Tsujino, N. Matubayasi, and M. Nakahara, in preparation.
11 N. Matubayasi and M. Nakahara, et al., in preparation.