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LETTERS

NMR Spectroscopic Evidence for an Intermediate of Formic Acid in the Water−Gas−Shift Reaction

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The water−gas−shift (WGS) reaction ($CO + H_2O \rightleftarrows CO_2 + H_2$) is investigated in connection to formic acid. Using NMR spectroscopy, the reversible decomposition pathways of formic acid to both sides of the WGS reaction are studied in hot water at 240−260 °C. This reversibility strongly suggests that formic acid exists as an intermediate in the WGS reaction, and it is indeed demonstrated that carbon monoxide is treated in hot water to produce formic acid. The present result enables us to generate and store hydrogen in the liquid form of formic acid and to transform formic acid to hydrogen in water by tuning the thermodynamic conditions.

Hydrogen is a distinguished fuel for the next generation. It is renewable and burned to water without emission of carbon dioxide, a greenhouse gas, in contrast to nonrenewable coal and oil. Liquid hydrogen, however, needs an extremely low temperature (−253 °C), much lower than liquified natural gas (−160 °C). Hydrogen, involving two 1s electrons, has so weak intermolecular interactions or affinities with itself and others (solvents, hosts, or alloys) that a large amount of energy is consumed for its compaction to the liquid state. For the advance of the hydrogen fuel technology, it is necessary to find a useful chemical reaction to solve physical and chemical problems: how to generate it with a sufficiently low cost in energy and how to make it compact for safe storage and transportation.

In the present work, we show that formic acid (HCOOH), the simplest carbon-one (C1) carboxylic acid, is such a key compound; HCOOH is in its liquid state between 8.4 and 100.8 °C and freely soluble in water (nonflammable and safe!). The idea for the transformation and recovery of hydrogen has been induced by our recent study on the effect of concentration, acidity, temperature, and metal on the reaction pathways for decarbonylation and decarboxylation of formic acid in hot water at 275−350 °C.[1] These reactions are expressed as

$$HCOOH \rightarrow CO + H_2O \qquad \text{(decarbonylation or dehydration)} \quad (1)$$

$$HCOOH \rightarrow CO_2 + H_2 \qquad \text{(decarboxylation or dehydrogenation)} \quad (2)$$

Before the two reactions are found to be competitive,[1,2] the decomposition pathway (2) was considered to be main.[3,4] The dominance of the single pathway can be understood by considering the catalytic effect of metal surface of reaction vessels and higher temperatures. Note that formic acid is subject to the decarbonylation like other aldehydes.[5,6]

When hot water is employed as the reaction medium, reversibility is often attained.[7,8] It is then reasonable to assume that both the decarbonylation and decarboxylation reactions are reversible in hot water and can be expressed as

$$CO + H_2O \rightleftarrows HCOOH \rightleftarrows CO_2 + H_2 \qquad (3)$$

This strongly suggests the presence of formic acid as an

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intermediate in the water−gas−shift (WGS) reaction in hot water under certain conditions. Indeed, our previous reaction results for aldehydes are well explained by supposing the presence of the intermediate formic acid in the WGS reaction.[5,6,9,10] In the present work, we have shown the reversibility of the competing decomposition pathways of formic acid and succeeded in detecting formic acid as an intermediate of the WGS reaction between water and carbon monoxide at 250 °C by applying NMR spectroscopy. The first attempt to detect formic acid as the intermediate of the WGS reaction was done by Rice et al.[11] using a flow system made of metal in supercritical water at 410−520 °C and 2−60 MPa after the prediction based on the electronic state calculation by Melius et al.[12] Here we show that they could not detect the intermediate because their experimental temperatures were much higher than the present ones. The high temperature is expected to dramatically shift the WGS reaction to the side of CO_2 and H_2.[1] The metal surface should also have accelerated the reaction from HCOOH to CO_2 and H_2 and made it impossible to detect HCOOH as an intermediate at the initial stage of the reaction.[1] The computation of the electronic energy for a cluster of formic acid and waters by Melius et al.[12] was improved by Savage et al.[13] and Ohmine et al.[14] The competitive decomposition pathways, eqs 1 and 2, were considered to be controlled by the cis−trans isomerization of formic acid.

The thermodynamic treatment of the equilibrium provides the essential answer to which is preferable, high or low temperature, to stabilize formic acid enough to be detectable in hot water. The stability of formic acid is controlled by the free energy of formation at the isolated state and the solvation free energy. According to the standard formation free energy for the species in the gas phase, both the reactions 1 and 2 have negative free energy changes in the absence of solvent, and the free energy change for reaction 2 is a few tens of kJ/mol more negative than that for the reaction 1. The solvation free energy was obtained by the method of energy representation[15] along the liquid branch of the coexistence curve of hot water up to 300 °C.[16] It was found that although the CO_2 side is electronically more stable than the CO side, the solvation suppresses the decarboxylation at low temperatures. Actually, the solvation effect is on the order of ∼30 kJ/mol and is stronger by ∼10 kJ/mol at 200 °C than at 300 °C. Furthermore, due to the cancellation of the HCOOH and H_2O solvations, the solvent effect on reaction 1 is not strongly dependent on the thermodynamic state examined. To emphasize the CO path and achieve a reasonable rate of kinetics, therefore, we set the temperature at ∼250 °C for the detection of formic acid.

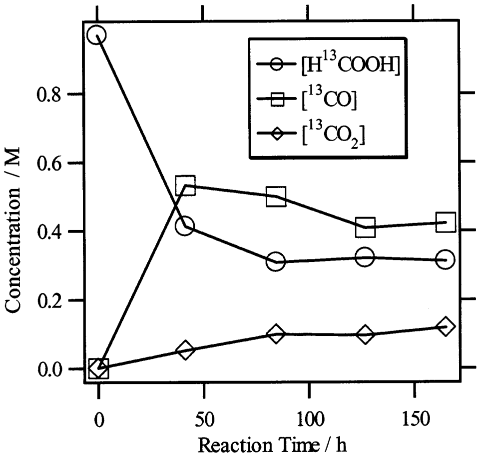

Figure 1. Transition to the decomposition equilibria of formic acid with carbon monoxide and dioxide in hot water at 250 °C.

We took the temperature range of 240−260 °C and established a long-time profile of the reversible decompositions of formic acid in hot water. An aqueous solution of ^{13}C-enriched HCOOH at 1 M (mol/L) was introduced and sealed in quartz tubes (reaction vessels) of 1.5 mm (i.d.) and 3.0 mm (o.d.). Water was purified using a Milli-Q Labo (Millipore) filter system. $H^{13}COOH$ (>99% enriched) was obtained from ISOTEC. The sample solution for the reaction at 240, 250, and 260 °C occupies 76, 78, and 80% of the internal volume of the vessels, respectively, at room temperature; the volume ratio thus defined is denoted here as the filling factor. At the reaction temperatures, the filling factors of all these samples reach 97% due to the liquid expansion, and the equilibrium pressure of CO becomes ∼20 MPa. The filling factor is made large enough so that the CO gas generated can dissolve into hot water with a high pressure of CO and promote the backward reaction of eq 1. The reaction took place in a furnace within an error of 1 °C and was quenched by air. The quenched vessel involved the liquid and gas phases, and both phases were measured to follow the mass balance. Note that CO has a much smaller solubility (∼1 mM in ambient water) than CO_2. To improve the sensitivity, a set of seven tubes placed in an NMR tube of 10 mm (i.d.) was used for the NMR measurements, in particular, for ^{13}C. When the gas phase was measured, the vessel was turned upside down. In this case, the liquid-phase stayed at the top and its interfering signal was absent with a far enough meniscus from the rf coil. The partition in the liquid phase, expressed as the mole amount in the liquid phase to the total, is ∼10 and ∼60% for ^{13}CO and $^{13}CO_2$, respectively, in the quenching measurements at room temperature.

Figure 1 illustrates the time evolution of the decomposition products at 250 °C. It turns out that the main decarbonylation and the minor decarboxylation pathways reach equilibria after about ∼40 and ∼80 h, respectively; the equilibration time can be markedly shortened by the addition of acids or metals, as reported previously.[1] Carbon (C1) is observed to distribute among CO, HCOOH, and CO_2 at equilibrium probabilities of 0.55, 0.34, and 0.11, respectively, at 250 °C; the corresponding C1 probabilities are 0.53, 0.41, and 0.06 at 240 °C after 177 h, and 0.24, 0.15, and 0.61 at 260 °C after 177 h. The equilibrium concentration of formic acid is 0.15−0.41 M at the temperatures and CO pressures studied. The WGS equilibrium in eq 3 is shifted to the left at the lower temperatures of 240 and 250 °C, and to the right at the higher temperature of 260 °C.

The presence of the intermediate formic acid can be more directly demonstrated. We start from hot water and ^{13}C-enriched carbon monoxide prepared in a quartz tube of 2.5 (i.d.) and 4.0 mm (o.d.). To obtain ^{13}CO, we used the decomposition pathway of ^{13}C-enriched formic acid, eq 1. The following method is a most convenient one to compress ^{13}CO into a quartz tube with water. Two long (25 cm) and bent quartz tubes were used to prepare the aqueous ^{13}CO solution. $H^{13}COOH$ (1 M, reactant) and HCl (2 M, catalyst) were put into one of the tubes and neat H_2O into the other. Both tubes were connected after the substitution of the air inside by argon. The bent tube structure is required to prevent the solutions from mixing together during the reaction of the CO production in a furnace at 200 °C for 30 min. After cooling by air, the H_2O side was cooled by liquid N_2 in order to condense ^{13}CO into the H_2O side before disconnecting it from the other. Thus we could seal only ^{13}CO and H_2O into the quartz tube used. The filling factor in the present case is 50 and 60% at room and the reaction temper-

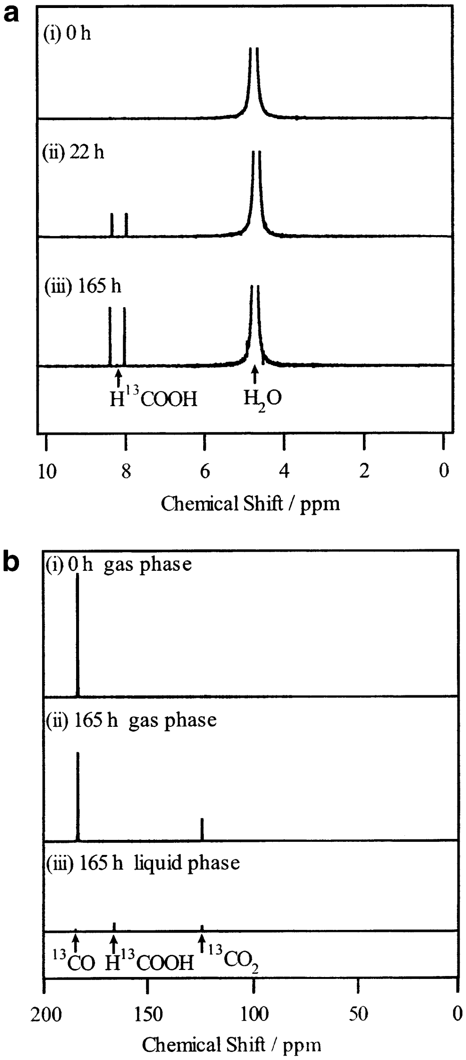

Figure 2. ^{1}H (a) and ^{13}C (b) spectra of formic acid generated from the noncatalytic water−gas−shift reaction at 250 °C. (a) The ^{1}H spectrum for the aqueous solution of ^{13}CO was taken after the reaction at 250 °C was quenched; for the liquid phase at 0 (i), 22 (ii), and 165 h (iii). (b) ^{13}C spectrum: for the gas phase at 0 (i) and 165 h (ii), and for the liquid phase at 165 h (iii). In the ^{1}H spectra for the gas phase, H_2 was detected. We did not use those spectra for quantitative analysis, however, because H_2 may leak slowly through hot quartz.

atures, respectively, owing to the difficulty in this method to make the filling factor as large as that of the decomposition case.

In Figure 2a, we show the liquid-phase ^{1}H spectrum of formic acid generated from the noncatalytic WGS reaction at 250 °C. We used a JEOL NMR spectrometer (ECA600, 13.6 T). Formic acid (H^{13}COOH) does appear; note that it did not exist at all in the aqueous solution of carbon monoxide (^{13}CO) in the beginning. The new signal assigned to formic acid is a doublet due to the ^{13}C−H coupling. This ensures that formic acid arises exclusively from ^{13}CO first incorporated and not from any impurity. We reconfirmed the formation of formic acid by taking ^{13}C NMR spectra both in the gas and liquid phases, as shown in Figure 2b.

For the equilibrium analysis, it is important to examine the time evolution of the reactant and products. Figure 3 illustrates the quenched concentrations of H^{13}COOH, ^{13}CO, and ^{13}CO$_2$ as functions of time. For a quantitative product analysis against time, the ^{1}H FID signals were accumulated 32 times for the liquid products quenched at room temperature, and the ^{13}C FID signals were accumulated 250 to 1000 times for the liquid and gas products, respectively, in the ^{1}H-gated decoupling measurement with a long enough delay time. In the gaseous phase, neat deuterated benzene was used as an external reference. The partition in the liquid phase is $\sim$3% and $\sim$40% for CO and CO_2, respectively, at room temperature. The partitions of CO and CO_2 are smaller than in the decomposition case because of the lower pressure in the gas phase. The reaction time may be divided into three stages: 0−20, 20−100, and 100−165 h. In the initial stage, almost all of the consumed ^{13}CO is converted into H^{13}COOH. In the second stage, 20−100 h, an additional decrease of ^{13}CO occurs due to the transformation to ^{13}CO$_2$, with H^{13}COOH kept almost constant. The increasing curve of the ^{13}CO$_2$ concentration is convex downward. In the third stage, after 100 h, H^{13}COOH is in equilibrium with ^{13}CO and ^{13}CO$_2$. In the early reaction stage, H^{13}COOH is in equilibrium mainly with ^{13}CO at a high enough ^{13}CO pressure. Thus, the direct conversion of ^{13}CO into H^{13}COOH as an intermediate is demonstrated in the WGS reaction mixture. Furthermore, we note that the rate of the generation of H^{13}COOH becomes faster as the concentration of the acid product increases.[1]

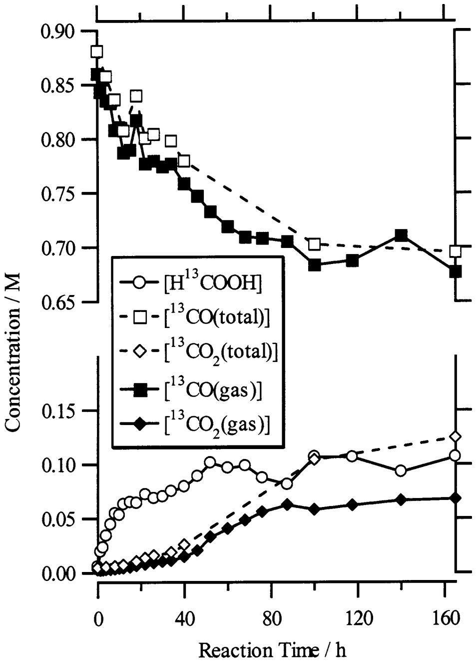

Figure 3. Time dependence of the product yields in the noncatalytic water−gas−shift reaction at 250 °C.

The reversibility of eq 3 demonstrated above leads us to predict that HCOOH can be generated also from CO_2 and H_2 in hot water, with or without catalysts. The conversion of CO_2 and H_2 to HCOOH was performed by Noyori et al.[17] in supercritical CO_2 with a metal catalyst and an organic base. The formation is enhanced by the excess amount of the reactant carbon dioxide and the added base that can stabilize the product through neutralization; even at room temperature, the catalyst makes the rate high enough by lowering the reaction barrier.

As shown here, we have succeeded in verifying the reversibility of the decompositions of formic acid, eqs 1 and 2, and the presence of formic acid as an intermediate in the WGS reaction (eq 3) by applying high-resolution NMR spectroscopy to both the gas and the liquid phases. Combining these findings, we will be able to utilize formic acid for the transportation and storage of hydrogen and to circumvent the obstacles in the industrial application of hydrogen fuel. The success arises from the promotion of the yield of formic acid in two ways. One is lowering the reaction temperature in hot water and the other is increasing the pressure of carbon monoxide. In the overall process of the hydrogen production, water serves as an oxidant two times, in the water−gas and the water−gas−shift reactions for C and CO, respectively. The C1 results presented here provide a chemical basis for the hydrogen gas fuel technology using formic acid.

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