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Controlling the Equilibrium of Formic Acid with Hydrogen and Carbon Dioxide Using Ionic Liquid

Yoshiro Yasaka, Chihiro Wakai, Nobuyuki Matubayasi, and Masaru Nakahara*

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

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The equilibrium for the reversible decomposition of formic acid into carbon dioxide and hydrogen is studied in the ionic liquid (IL) 1,3-dipropyl-2-methylimidazolium formate. The equilibrium is strongly favored to the formic acid side because of the strong solvation of formic acid in the IL through the strong Coulombic solute−solvent interactions. The comparison of the equilibrium constants in the IL and water has shown that the pressures required to transform hydrogen and carbon dioxide into formic acid can be reduced by a factor of ~100 by using the IL instead of water. The hydrogen transformation in such mild conditions can be a chemical basis for the hydrogen storage and transportation using formic acid.

1. Introduction

One of the key roles played by solution physical chemistry is to find a new method and principles for controlling reaction pathways under suitable conditions. Such a challenge is made here by focusing on solvent effect on the simple and useful reaction related to reversible storage of hydrogen. The reversible hydride-transferred reaction of formic acid (FA)

$$\mathrm{HCOOH} \rightleftarrows \mathrm{CO_2} + \mathrm{H_2} \qquad (1)$$

has been studied in relation to the water gas shift reaction[1] via FA intermediate,[2–4] as well as a synthetic route to use carbon dioxide as a carbon source of organic compounds.[5–16]

The free energy change accompanying reaction 1 is a very large negative in the gas phase ($\Delta G = -43.4$ kJ/mol, standard state = 1 bar[17]) so that the reaction is almost irreversible. In ambient and hot water, on the other hand, the equilibrium can be controlled by tuning the solvation of the reactants and products.[2–4] The computational free energy analysis[4] predicted that as the temperature is lowered to the ambient in water, the reactant and product sides may be comparable in stability due to the hydration effect characterized macroscopically by the high dielectric constant. In thermally expanded subcritical water, the $CO_2 + H_2$ side is more stable as a consequence of the decreased hydration. Thus the proton-donating and accepting FA is more stabilized microscopically through the hydrogen bonding strengthened at lower temperatures. Here we show that the stability preference can be reversed in order to make milder the reaction conditions of temperature and pressure when the reactant FA is stabilized with the extremely strong solvation by full charges of ionic liquid (IL) instead of the weaker one by partial charges of neutral molecules of water. ILs are organic liquid electrolytes with a low melting point near room temperature and attract much attention as green solvent with a very low vapor pressure,[18] strong solvation power,[19,20] and multiple solvation interactions useful for a variety of applications.[21] In this paper we show how to control the reversible FA reaction related to rather inert hydrogen using IL.

Attempts to synthesize FA through the backward process of reaction 1 have been made in weakly solvating environments for the past 3 decades. Inoue et al. reported first FA synthesis in benzene catalyzed by a Pd complex.[5] Noyori et al. used supercritical CO_2 as the solvent and reactant in the presence of amines as a base and Rh complexes as catalysts.[6,7] These syntheses would require considerable pressures unless stoichiometric amounts of bases are used, because the equilibrium of eq 1 strongly favors the gaseous product side in nonpolar molecular solvents. McCollom et al. observed FA formation in the form of sodium salt in subcritical water in the presence of sodium hydroxide; metal complexes were not necessary for accelerating the reaction rate in this high-temperature reaction, but a base was used to shift the equilibrium to the product side.[8] The resort to bases can be avoided when some solvents with more powerful solvation than benzene, supercritical carbon dioxide, or hot water are used. In fact, Fukuzumi et al. reported formation of FA in ambient water in acidic conditions,[9,10] although relatively high pressures were still required. The synthetic difficulties have been circumvented here by focusing on the unique solvation of IL from the viewpoint of physical chemistry.

The reversible reaction represented by eq 1 is interesting and useful also for application. The hydride-transferred decomposition of FA (eq 1) is one of the elementary processes of the water gas shift reaction via FA intermediate

$$\mathrm{CO} + \mathrm{H_2O} \rightleftarrows \mathrm{HCOOH} \rightleftarrows \mathrm{CO_2} + \mathrm{H_2} \qquad (2)$$

which have played a historical role in hydrogen preparation from water in industries.[1–3] The formation and decomposition of FA through each of the two reversible paths can be controlled by the solvent, thermodynamic conditions, and/or catalysts, and this is important for industrial application. By using IL and Ru catalyst, we can selectively operate the hydride-shift pathway, which is related to the chemical storage of hydrogen as FA.

Hydrogen, which is abundant on Earth and in the universe, is a source of water and an ultimately clean fuel for the next generation without carbon dioxide emission. Hydrogen is renewable as it can be regenerated by employing more or less costly chemical processes, such as electrolysis or photolysis of

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* To whom correspondence should be addressed, nakahara@scl.kyoto-u.ac.jp.

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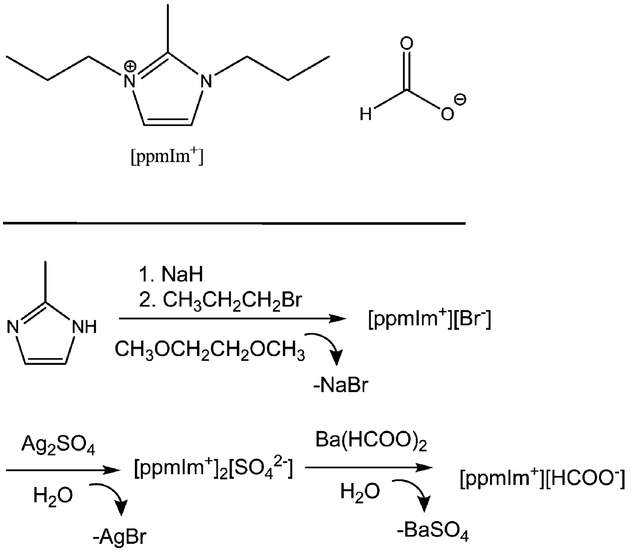
SCHEME 1: Structure and Preparation of the IL 1,3-Dipropyl-2-methylimidazolium Formate ([ppmIm$^+$][HCOO$^-$])



water[22] and biomass reforming,[23] and is further obtained as byproduct in iron and soda industries. However, the low liquefaction temperature of hydrogen has been a burden to hydrogen technology; compare the liquefaction temperatures of hydrogen with those of popular fuels: −253 °C for hydrogen, −161 °C for methane (natural gas), −25 °C for dimethyl ether, 1 °C for butane, and 30−200 °C for gasoline. Hydrogen is often compressed by using heavy containers, but the high pressure is not suitable for handling a highly flammable gas. Therefore, other clean fuels, such as methanol and dimethyl ether, are now considered more realistic alternatives to fossil fuels as advocated by Olah et al.[24]

Here we show that hydrogen can be chemically stored in the form of FA very efficiently by using IL. The formation of FA can be achieved at pressures not far away from atmospheric. The "transformed hydrogen", FA, can be a candidate to overcome the above-mentioned drawbacks inherent in the hydrogen energy technology. FA liquefies at such a convenient temperature as 101 °C and thus it serves as a hydrogen stock in the liquid state.

2. Experimental Section

2.1. Materials. The ionic liquid (IL), 1,3-dipropyl-2-methylimidazolium formate ([ppmIm$^+$][HCOO$^-$]) was synthesized according to Scheme 1 and Supporting Information. Materials employed for the synthesis were supplied by Aldrich (2-methylimidazole), Nacalai (2-bromopropane, sodium hydride, 2-propanol, barium hydroxide octahydrate, acetonitrile), and Wako (1,2-dimethoxyethane, silver sulfate, formic acid, acetone, methanol) and used without further purification. Intermediate products synthesized as [ppmIm$^+$][Br$^-$] and [ppmIm$^+$]$_2$[SO$_4^{2-}$] were purified as much as possible by recrystallization using acetone and acetonitrile, respectively, since the final product [ppmIm$^+$][HCOO$^-$] could not be recrystallized due to the low melting point and instability in solvents with carbonyl group like acetone. ^{13}C-enriched formic acid (99 atom %, 95% solution in water) was obtained from ISOTEC and used after drying by boron oxide. A ruthenium complex, RuCl$_2$(PPh$_3$)$_4$ (PPh$_3$ = triphenylphosphine) was obtained from Aldrich.

The substitution of the hydrogen at position 2 of the imidazole ring by a methyl group was necessary to improve the thermal stability of the IL against the reaction studied here. Also it was found that the methyl group is undesirable as the alkyl on the nitrogen atom of the imidazole ring, since it was more easily detached than longer alkyl groups at high temperatures. Therefore we used the *n*-propyl group for both of the nitrogen sites.

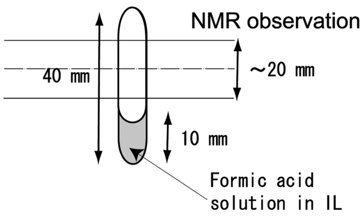


Figure 1. Sample configuration for the in situ NMR measurements for the gas phase.

2.2. NMR Measurements. The formic acid (FA) decomposition reaction was monitored in the following procedure. The reaction solution was prepared by mixing FA and 0.5−1 wt % ruthenium catalyst (RuCl$_2$(PPh$_3$)$_4$) in the IL. The complex was very slowly (~12 h) dissolved in the IL at room temperature, generating a pale yellow solution.[25] The solution was sealed in a quartz tube (2.5 mm inner diameter and 4 cm long, 25% filled in space by the solution) and heated at each constant temperature using a standard 5 mm NMR probe loaded on JEOL ECA500w (wide bore). The ^{1}H and ^{13}C NMR spectra were taken in situ for the gas phase to quantify H_2 and CO_2 evolved without breaking the quartz reactor as can be seen in Figure 1.

Typical ^{1}H and ^{13}C NMR spectra in the gas phase are shown in Figure 2. As shown, H_2 (panel a) and CO_2 (panel b) are the only products detected. The time evolution of the H_2 and CO_2 concentrations (pressure) in the gas phase is shown in Figure 2c. Although the amounts of H_2 and CO_2 produced appear to be unequal, it is due to the difference of the gas solubility in the IL; in the gas phase more H_2 is present than CO_2, and vice versa in the liquid phase. After ~5 days of reaction time, H_2 and CO_2 no longer increased, and thus the reaction equilibrium was perfectly attained. Since the reaction was carried out in a sealed reactor and the measurements were done in a noninvasive way by NMR, the concentrations of the chemical species in the liquid phase, although not directly observed, could be estimated based on the mass conservation law and Henry's law as described below.

2.3. Equilibrium Analysis. The equilibrium constant K_{IL} for the decarboxylation of FA is defined as

$$K_{\mathrm{IL}} = \frac{c_{\mathrm{H_2}}^{(\mathrm{liq})} c_{\mathrm{CO_2}}^{(\mathrm{liq})}}{c_{\mathrm{HCOOH}}^{(\mathrm{liq})}} \tag{3}$$

where c is the equilibrium molar concentration (mol/L) of the species specified as the subscript in the phase specified as the superscript. It is shown below how to determine the liquid-phase concentrations from the gas-phase NMR observation. Since the reaction proceeded in a sealed reactor, the mass balances for carbon and hydrogen were maintained as

$$C_0 = c_{\mathrm{HCOOH}}^{(\mathrm{liq})} + c_{\mathrm{CO_2}}^{(\mathrm{liq})} + \frac{1-\rho}{\rho} c_{\mathrm{CO_2}}^{(\mathrm{gas})} = c_{\mathrm{HCOOH}}^{(\mathrm{liq})} + c_{\mathrm{H_2}}^{(\mathrm{liq})} + \frac{1-\rho}{\rho} c_{\mathrm{H_2}}^{(\mathrm{gas})} \tag{4}$$

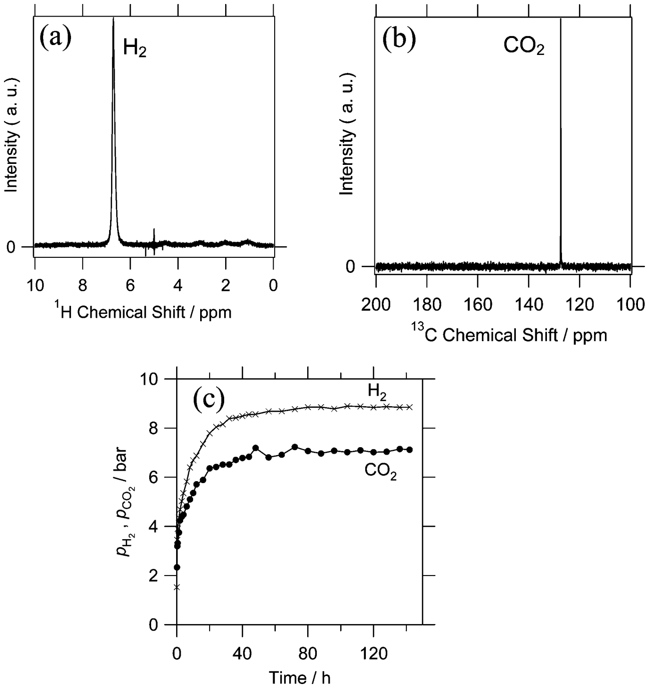


Figure 2. NMR spectra and the time evolution. (a) and (b) ^{1}H and ^{13}C NMR spectra obtained for the gas phase, respectively. No carbon monoxide was detected around 185 ppm in ^{13}C NMR spectrum. (c) Time evolution of the H_2 and CO_2 pressures as observed by in situ NMR at 60 °C. The reaction solution was the $H^{13}COOH$ solution in [ppmIm$^+$][$H^{12}COO^-$] (mole ratio 0.64:1) with 0.75 wt % Ru catalyst. The CO_2 ($= {}^{12}CO_2 + {}^{13}CO_2$) concentration plotted here was obtained by dividing the observed $^{13}CO_2$ gas-phase concentrations by 0.47 (the overall ^{13}C enrichment of formic acid determined for the initial reaction mixture).

where C_0 is the initial concentration of FA and ρ is the filling factor (the volume ratio of the liquid phase to the total reactor, equal to 0.25).[26] The value of ρ was measured before the reaction at room temperature, and its change in the course of the reaction was neglected. The concentrations in the liquid phase ($c^{(\mathrm{liq})}$) and the gas phase ($c^{(\mathrm{gas})}$) are related by the Ostwald constant γ. It is defined for hydrogen as

$$\gamma_{H_2} = c_{H_2}^{(\mathrm{gas})}/c_{H_2}^{(\mathrm{liq})} \tag{5}$$

The value of γ_{H_2} in the IL ([ppmIm$^+$][HCOO]$^-$) was determined in this work, and the results are shown in the Appendix. By combining eqs 4 and 5, we obtain

$$c_{H_2}^{(\mathrm{liq})} = c_{H_2}^{(\mathrm{gas})}/\gamma_{H_2} \tag{5$'$}$$

$$c_{HCOOH}^{(\mathrm{liq})} = C_0 - \left(\frac{1-\rho}{\rho}c_{H_2}^{(\mathrm{gas})} + c_{H_2}^{(\mathrm{liq})}\right) \tag{6}$$

$$c_{CO_2}^{(\mathrm{liq})} = C_0 - c_{HCOOH}^{(\mathrm{liq})} - \frac{1-\rho}{\rho}c_{CO_2}^{(\mathrm{gas})} \tag{7}$$

which can be evaluated directly from C_0, $c_{H_2}{}^{(\mathrm{gas})}$, and $c_{CO_2}{}^{(\mathrm{gas})}$.

3. Results and Discussion

The observed partial pressures of H_2 (p_{H_2}) and CO_2 (p_{CO_2}) at equilibrium are shown in Table 1 in the temperature range of 40−105 °C together with the concentration of formic acid (FA) in the liquid phase before the reaction and after the equilibriation. The equilibrium pressures are in the range of 3−23 bar (0.3−2.3 MPa) and not far from atmospheric. The temperature effect is positive, and the equilibrium pressures increase by a factor of ~2 as the temperature is increased by 40 °C. The results indicate in turn that we can synthesize FA at such mild pressures of H_2 and CO_2 because reaction 1 is reversible. At room temperature, even atmospheric pressure can induce formation of FA in the IL. Thus the reaction conditions in the IL are made dramatically milder than the hydrothermal one. As shown below, the IL is the most efficient solvent for shifting the equilibrium of reaction 1 to the FA side.

TABLE 1: Equilibrium Conditions for the Formic Acid Formation and Decomposition*

T (°C)	C_0 (mol/L)	p_{H_2} (bar)	p_{CO_2} (bar)	$c_{HCOOH}{}^{(\mathrm{liq})}$ (mol/L)
40	2.43	4.2	3.5	1.9
60	2.24	8.9	7.1	1.3
80	2.48	11	7.4	1.4
105	3.79	23	22	1.4

* The partial pressures of H_2 (p_{H_2}) and CO_2 (p_{CO_2}) in equilibrium with the formic acid solution in the IL as measured by in situ NMR measurements. The concentrations of formic acid before the reaction and at the equilibrium are denoted by C_0 and $c_{HCOOH}{}^{(\mathrm{liq})}$, respectively. p_{CO_2} tends to be smaller than p_{H_2} because CO_2 dissolves better in the IL than H_2.

The solvent effect on the FA synthesis can be understood by comparing the equilibrium constant K in eq 3 in various chemical environments. The equilibrium constant is related to the free-energy change of the reaction ΔG as

$$\Delta G = -RT \ln K \tag{8}$$

where the reference state of the concentration is taken as 1 mol/L. We can shift the thermodynamic equilibrium constant in a much wider range by changing the solvent than by changing temperature only. The small K or large positive ΔG is an indication of the good solvent for FA synthesis (backward process of reaction 1). Such good solvents stabilize the product (HCOOH) and destabilize the reactants ($H_2 + CO_2$) to favor the FA synthesis. When the solvent is an IL, the chemical species involved in the reaction are solvated by the ions and subject to various types of solute−solvent interactions.[21] In particular, formic acid is so small and polar that its solvation by formate ions in the IL is dominated by the Coulombic and/or hydrogen-bonding interactions. For such apolar solutes as hydrogen and carbon dioxide, on the other hand, the interactions are driven mainly by weaker dispersive ones.

The values of K_{IL} (the equilibrium constant in the IL) are plotted in Figure 3a. They are compared with those obtained in the hydrogen-bonding molecular solvent water (K_{water})[4] and in the gas phase (K_0) without solvent.[17] The chemical potential of the polar solute FA is considered to decrease (stabilized) in the sequence

$$\text{vacuum} > \text{water} > \text{IL}$$

as the solvation power increases in the sequence

$$\text{vacuum} < \text{water} < \text{IL}$$

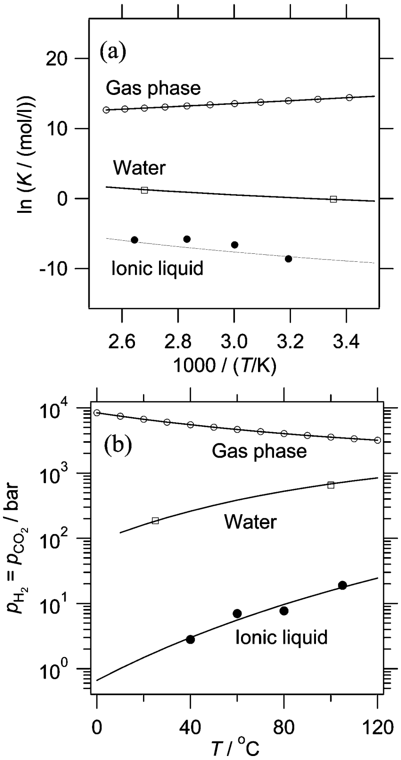


Figure 3. Equilibrium analysis of the formic acid formation and decomposition. (a) The equilibrium constant is compared in the gas phase (open circle, data from ref 17), water (open square, ref 4), and the IL (filled circle, this work) in the temperature range of 0−120 °C. The standard state is taken by 1 mol/L in each case. (b) The H_2 (p_{H_2}) and CO_2 (p_{CO_2}) gas pressures in equilibrium with 1 mol/L of formic acid are compared for water and the IL. Also shown are the p_{H_2} and p_{CO_2} in equilibrium with 1 bar (30−40 mmol/L) of formic acid.

As a consequence, it is expected that the equilibrium shifts to the FA side and the equilibrium constant in eq 3 becomes smaller in this sequence. As seen in Figure 3a, the equilibrium constant is in the order

$$K_0 > K_{\mathrm{water}} > K_{\mathrm{IL}}$$

The smallest equilibrium constant in the IL implies that the backward process of reaction 1 (FA formation) can be achieved most efficiently.

The H_2 (p_{H_2}) and CO_2 gas pressures (p_{CO_2}) required for synthesizing 1 mol/L of FA through the backward process of reaction 1 in the IL and water are compared in Figure 3b.[27] Also shown are the pressures of H_2 and CO_2 required for synthesizing 1 bar (30−40 mmol/L) of gaseous FA by the gas-phase reaction. We can see the marked difference in the pressure conditions required for FA synthesis. By using the IL we can reduce the gas pressure by a factor of 10^2 in comparison to water. The factor is 10^3 when compared to the gas-phase reaction. The decrease of the reaction temperature in the IL allows us to decrease the pressure. As can be seen in Figure 3b, FA can be synthesized under ambient temperature and pressure (p_{H_2},p_{CO_2} ∼ 1 bar) by using IL.

Interestingly, FA can serve as the chemical tank more efficiently in the IL than in hot water.[2] To store hydrogen, we pressurize H_2 with CO_2 around or above the equilibrium pressure and allow them to be absorbed in the IL.[28] When hydrogen is in need, H_2 can be released back from FA by simply removing the applied pressure. The output hydrogen pressure (p_{H_2}) can be controlled by tuning the temperature as shown in Figure 3b. It is to be noted that this cyclic process is carbon neutral despite the emission of CO_2 in the second process. The hydrogen storage efficiency (energy density per weight or volume) can be drastically improved when FA formed in the IL phase is distilled and separated in the pure form. The distillation from the IL is very convenient because the vapor pressure of the IL is negligibly low. One more important merit of using IL instead of hot water is that the CO + H_2O pathway can be effectively hindered by the overwhelmingly disfavored stabilization of the CO_2 + H_2 side of eq 2; no CO peak in Figure 2b.

Although FA synthesis from H_2 and CO_2 has been attempted in many molecular solvents, such as benzene,[5] toluene,[11] tetrahydrofuran,[12,13] acetone,[14] alcohols,[15] water,[8−10,16] and supercritical CO_2,[6,7] bases have often been used to enhance hydrogen transformation, because the reaction equilibrium is otherwise in favor of the starting materials (H_2 and CO_2) in these solvents. The added base can shift the equilibrium to the FA side in the following way. When basic aqueous media are used, for example, carbon dioxide is converted into the corresponding hydrogen carbonate salt by 1 equiv of base and then reacts with hydrogen to form the formate salt. Since FA is by far stronger as an acid than carbon dioxide, the formation of the formate salt in basic conditions becomes much easier than the formation of FA in acidic conditions as seen in the free energy diagram in Figure 4a. The equilibrium control by base, however, suffers from a drawback; the formate salt thus synthesized must be treated with 1 equiv of acid to recover FA in the acidic form. Overall, 1 equiv of base and acid is to be consumed. This is not advantageous from the environmental point of view when industrial application is considered. The IL studied here can shift the FA formation equilibrium as effectively as a base but, more importantly, without chemical wastes and energy loss as seen in Figure 4b. This is characteristic of the equilibrium control by solvation.

As a summary, we have examined the equilibrium of FA with hydrogen and carbon dioxide in ILs. By comparison of the equilibrium constants obtained in ILs with those in water and vacuum (gas phase), it has been revealed that the Coulombic solvation power of the IL plays a key role in shifting the reaction equilibrium to the FA side. As a medium for the simple and important reaction, the IL investigated here is quite different from polar molecular solvents, whereas their similarity and difference are conducted by solvatochromic studies using fluorescent molecules much larger than formic acid. The formation of FA from hydrogen and carbon dioxide can be a basis of chemical storage of hydrogen, and in this work we have shown that FA formation can be achieved most efficiently in ILs. The use of mild operating temperatures and pressures without resorting to bases in FA synthesis in ILs is an advantage for industrial applications. One may consider that FA formation presented here is a very slow thermal reaction when compared to the sophisticated laser-induced chemical dynamics on picosecond or femtosecond time scales, but nevertheless it is sufficiently faster than the fossil fuel formation in nature occurring on the geological time scale.

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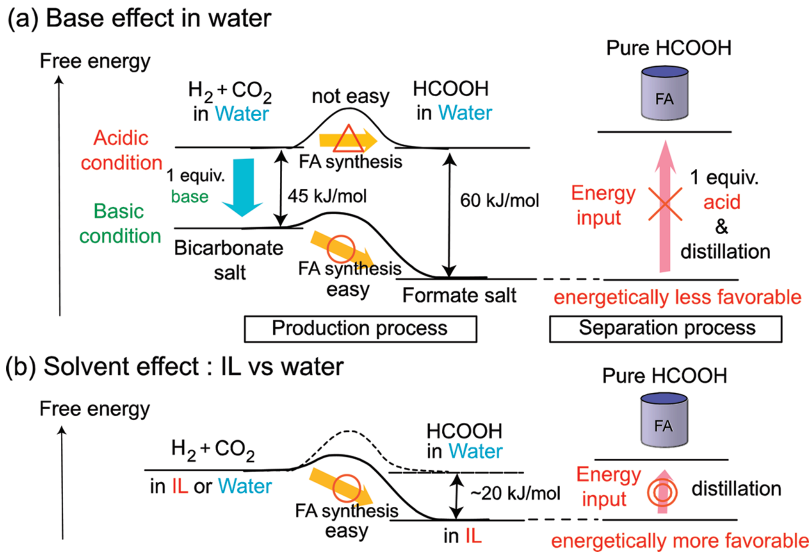

Figure 4. Free energy diagram for the formic acid (FA) production and separation in water and the IL. (a) In acidic conditions in water, the FA formation is not energetically favored (orange bold arrow with the triangle that means a marginally useful level). The effect of the addition of a base in water is the larger solvation stabilization (black arrows) of the product side (HCOOH) than the reactant side ($H_2 + CO_2$). Therefore, in basic conditions the production process is energetically favored (orange bold arrow with the circle that means a useful level), but the resultant formate salt must be treated with a strong acid (e.g., sulfuric acid) to recover HCOOH in the separation process. Note the large energy input required (red bold arrow with the cross that means no useful level) in the separation process. (b) The solvent effect of the IL is the stabilization of HCOOH. Therefore, in the IL, the production process is energetically favored (orange bold arrow with the circle), and the energy input required in the separation process is small (red bold arrow with the double circles that means the most useful level). Compare with the case (a) and note the energy-saving and waste-free nature in the overall process.

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Appendix

Ostwald Constant of H_2. The Ostwald constant γ of hydrogen is defined as

$$\gamma_{H_2} = c_{H_2}^{(gas)}/c_{H_2}^{(liq)} \quad (5)$$

The value of γ_{H_2} in the IL ([ppmIm$^+$][HCOO$^-$]) was determined as follows. Lithium aluminum deuteride ($LiAlD_4$, Cambridge Isotope Laboratories) and the IL (containing 2 mol/L of FA but not Ru catalyst) were sealed in a 20 cm long quartz tube as in Figure 5a. When the portion of the quartz tube holding $LiAlD_4$ was heated at 240 °C for 2 h, $LiAlD_4$ decomposed into D_2 (with 20% DH as impurities) and residual solids as in Figure 5b. The quartz tube was equilibrated at 22 (in an air-conditioned room) or 97 °C (in an electric furnace) for a sufficiently long time and then the D_2 concentration in the gas and liquid phase was measured by ^{2}H NMR. Here we used a deuterated compound because the ^{1}H NMR signal of H_2 tends to be interfered by the protons of the imidazolium cation. As shown in Figure 5c, it took 1 month for the D_2 to dissolve in the IL at 22 °C, but only a few days at 97 °C. The obtained γ_{H_2} values at 22 and 97 °C were 55 and 37, respectively, as measured at ~2 MPa of D_2. These values were interpolated or extrapolated to any temperature assuming an Arrhenius-type temperature dependence.

The gas dissolution constants obtained here were comparable to those found in literature. Kumelan et al. measured H_2 solubility in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim$^+$][PF_6^-]) and 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([hmim$^+$][TFSI$^-$]).[29,30] Their results can be interpreted in terms of the Ostwald constant γ_{H_2} of 39.3 and 25.3 at 22 °C and 21.9 and 15.1 at 97 °C for the former and latter ILs, respectively. Finotello et al. studied the H_2

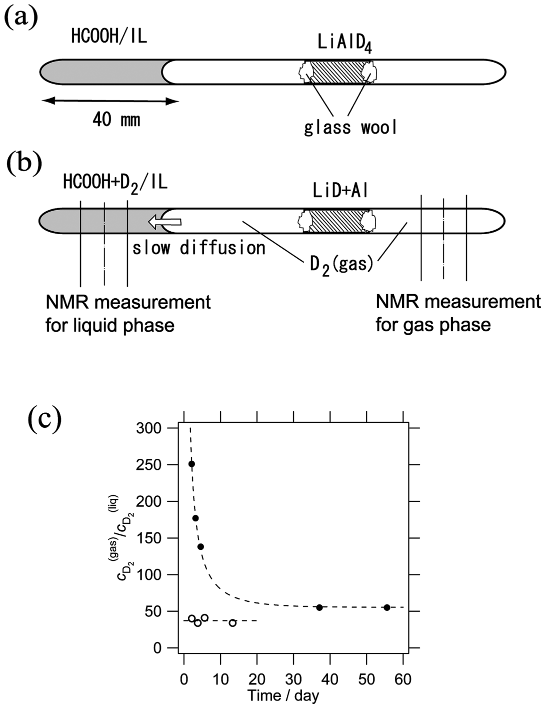

Figure 5. Measuring the Ostwald constant of D_2. (a) Sample configuration for the measurement. (b) $LiAlD_4$ in the quartz tube decomposed to evolve D_2 gas when the right side of the tube was heated at 240 °C for 2 h. (c) Time evolution of the $c_{D_2}^{(gas)}/c_{D_2}^{(liq)}$(molar concentration ratio) at 22 (filled circles) and 97 °C (open circles) as a function of time. Here the time origin was taken by the time when $LiAlD_4$ was heated and decomposed into D_2.

solubility in several ILs and showed that ILs with larger molar volumes result in smaller Ostwald constants.[31] It is therefore reasonable that the Ostwald constant for [ppmIm$^+$][HCOO$^-$] (molar volume of 0.21 L/mol in the pure state at room temperature) obtained here is significantly larger than that for [hmim$^+$][TFSI$^-$] (0.33 L/mol) but is closer to that for [bmim$^+$]-[PF$_6^-$] (0.21 L/mol).

Supporting Information Available: Description of preparation of ILs. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) Care should be taken in preserving the reaction solutions in a sealed bottle, because the inner gas pressure gradually rises due to the evolution of H_2 and CO_2 even at room temperature.

(26) In the mass conservation equation (eq 4), we do not distinguish such presumable derivatives of CO_2 in the IL as H_2CO_3 (formed via hydration with impurity water in the IL) and HCO_3^- (formed via acid dissociation) because the liquid phase was not observed in the in situ NMR experiments. Thus the $c_{CO_2}{}^{(liq)}$ calculated by eq 7 collectively means $c_{CO_2}{}^{(liq)} + c_{H_2CO_3}{}^{(liq)} + c_{H_2CO_3^-}{}^{(liq)}$. Additional ^{13}C NMR measurements of the IL phase after the decomposition reaction of FA in the IL (10 days at 60 °C) showed two broad peaks designated as CO_2 (126 ppm) and H_2CO_3/HCO_3^- (159 ppm) with an intensity ratio of 3:1; note that H_2CO_3 and HCO_3^- is indistinguishable in NMR due to the fast proton transfer. This observation gives that $c_{CO_2}{}^{(liq)}: (c_{H_2CO_3}{}^{(liq)} + c_{H_2CO_3^-}{}^{(liq)}) = 3:1$ and that $c_{CO_2}{}^{(liq)}$ calculated by eq 7 may differ from the real value of $c_{CO_2}{}^{(liq)}$by a factor of ~3/4. Nevertheless, the following discussions on the solvent effect on the equilibrium constant are unaffected by such a relatively small error.

(27) Here our discussion is confined without losing any generality to the simple case in which $p_{H_2} = p_{CO_2}$ under the assumption that the gas solubility obeys Henry's law.

(28) When the FA solution in the IL is directly used as a hydrogen storage tank, its energy density is not very high and below ~10 g of H_2/L (10 g of H_2/kg). Since FA is freely soluble in the IL, the hydrogen energy density of the FA/IL system can be increased as much as possible up to the energy density of pure FA (53 g of H_2/L). However, the solvation power of the IL to promote FA formation from H_2 and CO_2 decreases as the IL is diluted by FA formed. Thus FA formation becomes thermodynamically more difficult. Note that the equilibrium constant determined here is only applicable under such conditions that the mole ratio of FA to the IL is fairly smaller than ~1 (~5 mol/L of FA).

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