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Unusually Large Tunneling Effect on Highly Efficient Generation of Hydrogen and Hydrogen Isotopes in pH-Selective Decomposition of Formic Acid Catalyzed by a Heterodinuclear Iridium−Ruthenium Complex in Water

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Hydrogen has attracted much attention as an alternative clean energy, because the reaction of hydrogen with oxygen produces the requested energy and only water as an environmentally friendly side product.[1,2] However, the storage and transfer of hydrogen are difficult with current technology, because hydrogen gas is explosive with a poor volumetric energy density.[3] In this context, the interconversion of H_2 with CO_2 to formic acid (HCOOH) (eq 1) in the presence of an appropriate catalyst has merited special attention.[4] Although there have been a number of reports on the formation of

$$H_2 + CO_2 \rightleftarrows HCOOH \tag{1}$$

H_2 by the catalytic decomposition of formic acid,[5,6] improvement in the catalytic activity is highly desired.

On the other hand, an H/D exchange between HCOOH and D_2O would lead to production of D_2 and HD, which have been utilized as research tools in the various fields of science.[7−10] Abnormally large deuterium kinetic isotope effects (KIEs) were recently reported in protonolysis/deuterolysis of metal−alkyl complexes.[11] Such hydrogen tunneling has frequently been observed for C−H bond activation by transition metal complexes.[12,13] However, there has been no report on hydrogen tunneling for the catalytic production of hydrogen.

We report herein a large tunneling effect on the highly efficient production of hydrogen for the first time in the pH-selective decomposition of formic acid (HCOOH, DCOOH, or DCOOD), which is catalyzed by a heterodinuclear iridium−ruthenium complex $[Ir^{III}(Cp^*)(H_2O)(bpm)Ru^{II}(bpy)_2](SO_4)_2$ {$\mathbf{1}(SO_4)_2$, Cp* = η^5-pentamethylcyclopentadienyl, bpm = 2,2′-bipyrimidine, bpy = 2,2′-bipyridine} in H_2O and D_2O.

The catalyst $\mathbf{1}(SO_4)_2$ was synthesized quantitatively by a reaction of $[Ru^{II}(bpy)_2(bpm)](SO_4)$ with $[Ir^{III}(Cp^*)(H_2O)_3](SO_4)$ in H_2O at 298 K (see Experimental Section and S1 in the Supporting Information (SI)).

Hydrogen was produced efficiently when $\mathbf{1}(SO_4)_2$ was added to a deaerated aqueous solution of HCOOH.[14] CO_2 was formed together with H_2, but no CO was detected by GC. This suggests that HCOOH decomposes selectively to H_2 and CO_2 without formation of CO and H_2O. The rate of hydrogen production increases linearly with increasing $[\mathbf{1}(SO_4)_2]$ (S2). The turnover frequency (TOF) gradually increases with increasing [HCOOH/HCOONa] (total concentration of formate in the mixed solution of HCOOH with HCOONa) to approach a limiting value at pH 3.8 (S3). Such a saturation dependence of TOF on $[HCOO^-]$ indicates that hydrogen is produced via the formate complex $[Ir^{III}(Cp^*)(O(CO)H)(bpm)Ru^{II}(bpy)_2]^{3+}$ (**2**). The pH dependence of the limiting value of TOF is shown in Figure 1 (black circles), where the maximum TOF value (426 h^{-1})[15] is obtained at pH 3.8 which agrees with the pK_a value of HCOOH.[16] To the best of our knowledge, the value is the highest in the catalytic decomposition of formic acid in H_2O at ambient temperature. The decrease in TOF at pH > 3.8 indicates that the rate-determining step is the reaction of the hydride complex $[Ir^{III}(Cp^*)(H)(bpm)Ru^{II}(bpy)_2]^{3+}$ (**3**), produced by β-hydrogen elimination from **2**, with H_3O^+.

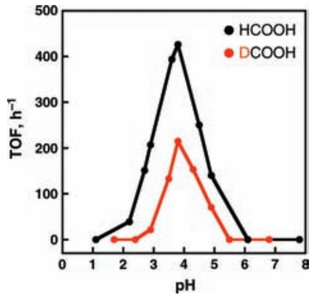

Figure 1. pH Dependence of the H_2 and HD evolution rates (TOFs) in the decomposition of HCOOH/HCOONa (0.83 M) (black circles) and DCOOH/DCOONa (0.83 M) (red circles) catalyzed by $\mathbf{1}(SO_4)_2$ (0.5 mM) in deaerated H_2O at 298 K.

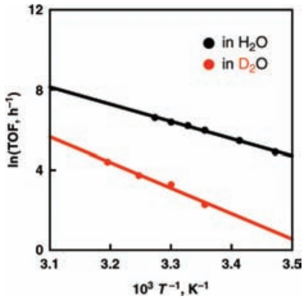

Figure 2. Arrhenius plots of TOF for the decomposition of HCOOH/HCOONa (3.1 M) catalyzed by $\mathbf{1}(SO_4)_2$ (0.3 mM) in deaerated H_2O (black circles) or D_2O (red circles) at pH 3.8 or pD 3.8, respectively.

When HCOOH/HCOONa was replaced by DCOOH/DCOONa in H_2O, deuterium kinetic isotope effects (KIE = 2.0 at pH 3.8 and 4.9) were observed as shown in Figure 1 (red circles). The KIE value increases with decreasing pH, KIE = 9.7 at pH 2.9 (S4). This indicates that a rate-determining step may be changed from the reaction of **3** with H_3O^+ at higher pH (e.g., pH 4.9) to the β-hydrogen elimination step to afford **3** accompanied by CO_2 evolution at lower pH (e.g., pH 2.9).

The temperature dependence of the TOF value was examined, and the Arrhenius plot in Figure 2 (black circles) afforded the activation energy of 17 kcal mol^{-1}. This value is much smaller than the activation energy of the decomposition of HCOOH without catalyst (78 kcal mol^{-1}).[17]

When the decomposition of HCOOH/HCOONa was performed with $\mathbf{1}(SO_4)_2$ in D_2O, HD was mainly formed together with D_2 at

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Scheme 1

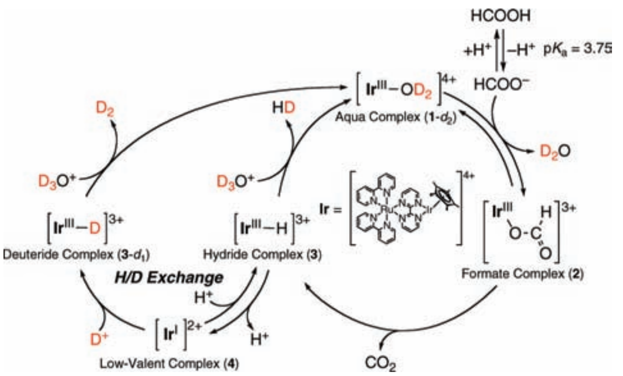

Table 1. Rates of Hydrogen Evolution (*v*), KIEs, and Isotope Distribution for Evolved Hydrogen Gas in Decomposition of Formic Acid Catalyzed by **1**$(SO_4)_2$ in H_2O or D_2O[a]

					fraction, mol %[c]		
entry	substrate	solvent	v, μmol min^{-1}	KIE[b]	H_2	HD	D_2
1	HCOOH	H_2O	4.8	–	100	0	0
2	HCOOD	D_2O	0.12	40	3[d]	57	40
3	DCOOH	H_2O	3.2	1.5	29	71	0
4	DCOOD	D_2O	0.12	40	0	5[e]	95

[a] Reaction conditions: **1**$(SO_4)_2$ (0.3 mM) and formic acid (HCOOH/HCOONa, HCOOD/HCOONa, DCOOH/DCOONa, or DCOOD/DCOONa) (3.1 M) in deaerated H_2O or D_2O at 298 K at pH or pD 3.8. [b] KIE = v (entry 1)/v (entry n) (n = 2, 3, and 4). [c] Analyzed by GC. [d] Commercially available HCOOD contains HCOOH in ca. 2%. [e] Commercially available DCOOD contains HCOOH, HCOOD, and/or DCOOH in ca. 2%.

various pD (S5). The ratio of generated D_2 and HD was constant during the catalytic reaction (S6). The formation of D_2 results from H/D exchange of **3** with D_3O^+. The proposed mechanism of the catalytic formation of HD and D_2 in the decomposition of HCOOH with **1**-d_2 is summarized in Scheme 1. The H/D exchange of the Ir–D complex (**3**-d_1) with H_3O^+ occurs via the dissociation of the Ir–D complex with H_2O to produce the Ir^I complex $[Ir^I(Cp^*)(bpm)Ru^{II}(bpy)_2]^{2+}$ (**4**) and H_2DO^+. At high pH, **3** is indeed converted to **4** (S7). The hydride complex **3** and Ir^I complex **4** are well characterized by the ^1H NMR spectra (see Experimental Section in SI and S8). The pK_a value of **3** was determined to be 3.9 by the pH titration (S9).

The presence or absence of tunneling can be determined from the temperature dependence of the KIE.[11,12,18] Values for the Arrhenius parameters $A_H/A_D \ll 1$ and $E_a(D) - E_a(H) > 1.2$ kcal mol^{-1} together with a large KIE value at 298 K (KIE > 9) are generally taken to unambiguously demonstrate the involvement of tunneling.[11–13,18] The Arrhenius plots for TOF in D_2O (red circles) vs H_2O (black circles) in Figure 2 afford $A(H_2O)/A(D_2O) = 3.1 \times 10^{-5}$, $E_a(D) - E_a(H) = 8.2$ kcal mol^{-1}, and an unusually large KIE value at 298 K (KIE = 40), which clearly indicate a tunneling pathway.

The production of hydrogen from the reaction of **3** with H_3O^+ involves the H–O bond cleavage in H_3O^+, accompanied by the formation of H–H bond with the hydride of **3**.

When the decomposition of HCOOH/HCOONa was performed with **1**$(SO_4)_2$ in D_2O at pD 3.8 at 298 K, the rate of hydrogen production (HD and D_2) was virtually the same as the rate of D_2 formation in the decomposition of DCOOD/DCOONa catalyzed by **1**$(SO_4)_2$ in D_2O (Table 1, entries 2 and 4). On the other hand, a KIE value in the decomposition of DCOOH/DCOONa catalyzed by **1**$(SO_4)_2$ in H_2O is significantly smaller than the KIE values in the decomposition of HCOOD/HCOONa and DCOOD/DCOONa in D_2O (Table 1, entries 2–4). These indicate that the rate-determining step in the overall hydrogen evolution reaction is not the β-hydrogen elimination step but the reaction of **3** with H_3O^+ to evolve H_2 at pH 3.8.

In summary, a heterodinuclear iridium–ruthenium complex **1** acts as the most effective catalyst for selective production of hydrogen from formic acid in an aqueous solution among catalysts reported so far. The unusually large tunneling effect was observed for the first time for the catalytic hydrogen production in H_2O vs D_2O. The selective formation of HD was also achieved by adjusting pH, providing a convenient way to produce HD, which would otherwise be quite difficult or expensive to obtain.

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Supporting Information Available: Experimental procedures, figures, and tables (S1–S9). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Lewis, N. S.; Nocera, D. G. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15729.
(2) Bockris, J. O'M. *Int. J. Hydrogen Energy* **2008**, *33*, 2129.
(3) (a) Rowsell, J. L. C.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4670. (b) Schlapbach, L.; Züttel, A. *Nature* **2001**, *414*, 353.
(4) (a) Fukuzumi, S. *Eur. J. Inorg. Chem.* **2008**, 1351. (b) Enthaler, S. *ChemSusChem* **2008**, *1*, 801. (c) Joó, F. *ChemSusChem* **2008**, *1*, 805.
(5) (a) Fellay, C.; Dyson, P. J.; Laurenczy, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 3966. (b) Loges, B.; Boddien, A.; Junge, H.; Beller, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 3962. (c) Boddien, A.; Loges, B.; Junge, H.; Beller, M. *ChemSusChem* **2008**, *1*, 751. (d) Fellay, C.; Yan, N.; Dyson, P. J.; Laurenczy, G. *Chem.—Eur. J.* **2009**, *15*, 3752. (e) Wiener, H.; Sasson, Y. *J. Mol. Catal.* **1986**, *35*, 277. (f) Gao, Y.; Kuncheria, J. K.; Jenkins, H. A.; Puddephatt, R. J.; Yap, G. P. A. *J. Chem. Soc., Dalton Trans.* **2000**, 3212.
(6) Fukuzumi, S.; Kobayashi, T.; Suenobu, T. *ChemSusChem* **2008**, *1*, 827.
(7) Loery, T.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper & Row: New York, 1987.
(8) (a) Ogo, S.; Kabe, R.; Uehara, K.; Kure, B.; Nishimura, T.; Menon, S. C.; Harada, R.; Fukuzumi, S.; Higuchi, Y.; Ohhara, T.; Tamada, T.; Kuroki, R. *Science* **2007**, *316*, 585. (b) Kure, B.; Matsumoto, T.; Ichikawa, K.; Fukuzumi, S.; Higuchi, Y.; Yagi, T.; Ogo, S. *Dalton Trans.* **2008**, 4747.
(9) *Inorganic Isotopic Synthesis*: Herber, R. H., Ed.; Benjamin: New York, 1962.
(10) (a) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155. (b) Kubas, G. J. *Chem. Rev.* **2007**, *107*, 4152. (c) Yarnell, A. T. *Chem. Eng. News* **2009**, *87*, 36.
(11) Bercaw, J. E.; Chen, G. S.; Labinger, J. A.; Lin, B.-L. *J. Am. Chem. Soc.* **2008**, *130*, 17654.
(12) Pan, Z.; Horner, J. H.; Newcomb, M. *J. Am. Chem. Soc.* **2008**, *130*, 7776.
(13) Kohen, A.; Klinman, J. P. *Acc. Chem. Res.* **1998**, *31*, 397.
(14) The presence of oxygen retarded hydrogen production, because the catalyst is used for the reduction of oxygen until oxygen is consumed.
(15) The value was derived from TON (= 142) for 20 min. A mononuclear iridium complex $[Ir(Cp^*)(bpm)(H_2O)]^{2+}$ exhibits negligibly lower TOF value (0.19 h^{-1}) than **1** in the decomposition of HCOOH/HCOONa under otherwise the same experimental conditions at pH 3.8.
(16) *Handbook of Chemistry and Physics*, 84th ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 2004.
(17) Ruelle, P.; Kesselring, U. W.; Nam-Tran, H. *J. Am. Chem. Soc.* **1986**, *108*, 371.
(18) Kwart, H. *Acc. Chem. Res.* **1982**, *15*, 401.

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