Hydrothermal C−C Bond Formation and Disproportionation of Acetaldehyde with Formic Acid

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Reaction pathways and kinetics of C2 (carbon-two) aldehyde, acetaldehyde (CH_3CHO), and formic acid HCOOH or HOCHO, are studied in neutral and acidic subcritical water at 200−250 °C. Acetaldehyde is found to exhibit (i) the acid-catalyzed C−C bond formation between acetaldehyde and formic acid, which generates lactic acid ($CH_3CH(OH)COOH$), (ii) the cross-disproportionation, where formic acid reduces acetaldehyde into ethanol, and (iii) the aldol condensation. The lactic acid formation is a green C−C bond formation, proceeding without any organic solvents or metal catalysts. The new C−C bond formation takes place between formic acid and aldehydes irrespective of the presence of α-hydrogens. The hydrothermal cross-disproportionation produces ethanol without base catalysts and proceeds even in acidic condition, in sharp contrast to the classical base-catalyzed Cannizzaro reaction. The rate constants of the reactions (i)−(iii) and the equilibrium constant of the lactic acid formation are determined in the temperature range of 200−250 °C and at HCl concentrations of 0.2−0.6 M (mol/dm^3). The reaction pathways are controlled so that the lactic acid or ethanol yield may be maximized by tuning the reactant concentrations and the temperature. A high lactic acid yield of 68% is achieved when acetaldehyde and formic acid are mixed in hot water, respectively, at 0.01 and 2.0 M in the presence of 0.6 M HCl at 225 °C. The ethanol yield attained 75% by the disproportionation of acetaldehyde (0.3 M) and formic acid (2.0 M) at 225 °C in the absence of added HCl.

1. Introduction

The chemistry of aldehyde is rich in hydrothermal conditions.[1–15] It has been found that a central role is played by formic acid (HOCHO) in controlling the richness. Formic acid can induce such hydrothermal aldehyde reactions as an acid-catalyzed C−C bond formation and a noncatalytic cross-disproportionation.[3,6,7,9–13,15] The C−C bond formation for formaldehyde (HCHO), C1 aldehyde, is a chemical evolution from C1 to C2 compounds, which generates glycolic acid ($CH_2(OH)COOH$) in acidic hydrothermal conditions. The simplest amino acid, glycine, can then be obtained from glycolic acid by amination. As previously shown, the cross-disproportionation between formaldehyde and formic acid provides us with a green process for alcohol formation. Here we extend the study on the hydrothermal C−C bond formation and the cross-disproportionation to acetaldehyde (CH_3CHO), the simplest C2 aldehyde with α-hydrogens.

The C−C bond formation is of great importance for organic synthesis.[16] Ordinary C−C bond formations are carried out in severe conditions typically with metal catalysts in anhydrous solvents and therefore limited to certain donor−acceptor pairs. In recent years, there have been studies on such hydrothermal C−C bond formations as the noncatalytic Beckmann and pinacol rearrangements, the Claisen−Schmidt condensation, and the Diels−Alder reaction.[17–19] A kinetic study is carried out here on the acid-catalyzed hydrothermal C−C bond formation between acetaldehyde and formic acid that can generate lactic acid. Lactic acid is an important material as a food acidulant, a preservative, a monomer for various plastics, and so on.[20] At present, lactic acid is commercially produced through the cyanation of acetaldehyde in the presence of catalysts or the carbohydrate fermentation. The lactic acid formation in subcritical water can serve as an alternative to conventional methods. The new method shown here is a one-pot reaction without such a toxic reactant as hydrogen cyanide. Although various hydrothermal organic reactions are reported, in most cases only the reaction products are focused on.[1,2] Utility of the multipath reactions can be realized only when we establish a control or selection scheme for the pathway of interest. In this work, based on the kinetic analysis, we show how to achieve the pathway control of the hydrothermal acetaldehyde reaction for the lactic acid.

Now there has been considerable interest in alcohol as a source of energy, and it is desirable to develop versatile methods for alcohol formation. Ethanol is one of the most important chemicals as a renewable energy source, a solvent, and a key material in the manufacture of drugs, plastics, lacquers, and cosmetics.[20] Generally, ethanol is produced through the fermentation of sugar crops and corn and such metal-catalyzed processes as the hydration of ethane, hydrogenation of acetaldehyde by hydrogen, and reactions of synthesis gas. By the hydrothermal cross-disproportionation of acetaldehyde with formic acid, we can produce ethanol without any catalysts. Here, we show how the ethanol formation can be maximized among multiple reaction pathways of aldehyde in hydrothermal conditions.

The experimental procedure is in section 2. In section 3.1, we discuss the reaction scheme of the hydrothermal reactions of acetaldehyde and formic acid. In section 3.2, the equilibrium and kinetics of the lactic acid formation, the cross-disproportionation, and the aldol condensation are discussed. On the basis of the rate constants of these reactions and the equilibrium

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TABLE 1: Reaction Conditions

concn (M)[a]				
CH_3CHO	HCl	HCOOH	temp/°C	type of analysis[b]
0.30	0	0	225	Q
0.30	0	2.0	225	Q
0.30	0.3	2.0	225	Q
0.10	0.6	2.0	225	Q
0.01	0.2	2.0	225	Q
0.01	0.4	2.0	225	Q
0.05	0.6	2.0	200	K
0.05	0.6	2.0	210	K
0.05	0.6	2.0	225	K
0.05	0.6	2.0	250	K
0.05	0.4	2.0	225	K
0.05	0.3	2.0	225	K
0.05	0.2	2.0	225	K
0.01	0.6	2.0	200	K
0.01	0.6	2.0	225	K
0.01	0.6	2.0	250	K

[a] Listed reactant concentrations are those at room temperature. [b] The symbols Q and K denote the qualitative analysis with fixed reaction time of 2 h and the kinetic analysis with the time evolution of reactant and product concentration, respectively.

constant, we discuss how to control the reaction pathways for lactic acid and ethanol formations in section 4. Conclusions are in section 5.

2. Experimental Section

Acetaldehyde (99%) obtained from Merck Co. and ^{13}C-enriched acetaldehyde (99 atom %) and ^{13}C-enriched formic acid (99 atom %) obtained from ISOTEC were used as received. HCl (2 M (mol/dm^3)) and formic acid (99%) were obtained from Nacalai and used without further purification. ^{13}C-enriched sodium L-lactate (99 atom % and 20% in H_2O) was obtained from Euriso-top and used as received. As a solvent, water (H_2O) was purified using a Milli-Q Labo (Millipore) filter system.

The reaction conditions are listed in Table 1. Acetaldehyde, HCl, and formic acid were sealed in a quartz tube. In the qualitative analysis, for example, the size of the reactor tube for 0.3 M of acetaldehyde was 2.2 mm i.d. and 3.0 mm o.d., whereas for the reaction mixtures with 2.0 M formic acid, the tube size was 2.6 mm i.d. and 4.0 mm o.d. A quartz tube of 1.5 mm i.d. and 3.0 mm o.d. was used in the kinetic analysis. The gas phase of each sample was substituted with argon and the filling factor (volume ratio of the solution to the total sample tube) was mostly set to 70% unless otherwise stated. The reaction temperature was varied from 200 to 250 °C. In this temperature range, gas and liquid phases coexist and the water density is uniquely determined by the saturation curve. The filling factor is also changed from that at room temperature by the temperature elevation according to the water densities in the gas and liquid phases. The acid (HCl) concentration was varied from 0.2 to 0.6 M. The temperature and acid concentration are chosen so that acetaldehyde exhibits both C−C bond formation and disproportionation and that the reaction rates can be studied by minute-time scale analysis using NMR.[9,13] After a sample was heated for a desired reaction time in an electric furnace, it was cooled to room temperature within 1 min by air. The sample was put in a Pyrex NMR tube of 5.0 mm o.d. and the ^1H- and proton-decoupled ^{13}C NMR spectra were measured at 5−80 °C with 400 MHz NMR (ECA, JEOL).[21,22] For the proton-decoupled ^{13}C NMR measurement, the inverse-gated decoupling pulse sequence is applied, which enables us to determine the product concentrations from the proton-decoupled ^{13}C NMR spectra. In the reaction tube, the liquid and gas phases coexist and the both are measured to identify all the products as described elsewhere.[10]

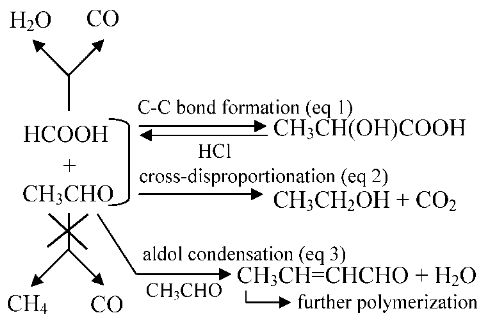

Figure 1. The pathways of the reaction of acetaldehyde in subcritical water at 200−250 °C.

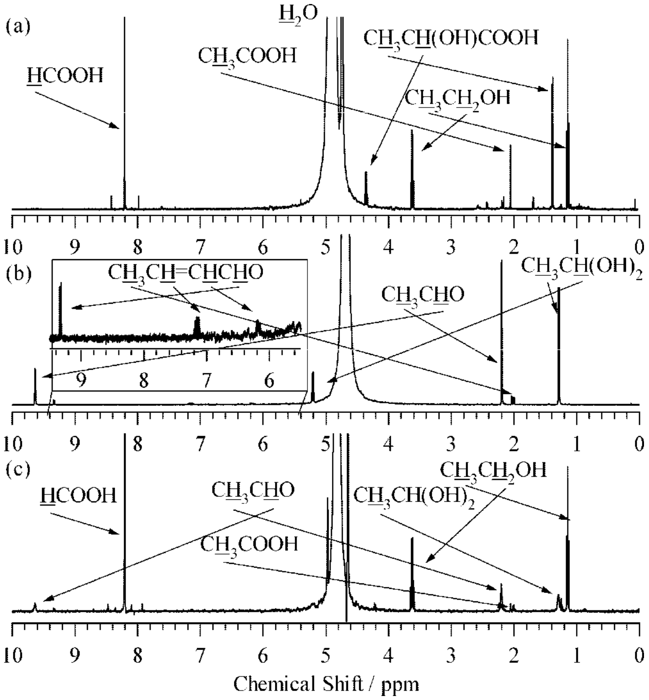

Figure 2. ^1H NMR spectra of the liquid phase for the reactions of (a) acetaldehyde (0.3 M) and formic acid (2.0 M) in the presence of HCl (0.3 M) after 2 h at 225 °C, (b) acetaldehyde (0.3 M) after 2 h at 225 °C, and (c) acetaldehyde (0.3 M) and formic acid (2.0 M) after 2 h at 225 °C. The signal of ethanediol in (c) is hidden by the peak of H_2O. The spectra in (a) and (c) are measured at 5 °C, and the spectrum in (b) is measured at 30 °C. The chemical shift of water differs among the three spectra because it is affected by the temperature and pH of the solution. Acetic acid observed in (a)−(c) is an impurity contained in reactant acetaldehyde.

In the kinetic analysis, the time evolution was observed for the reactants and products at time intervals of 1−15 min. A series of samples were used for the kinetics based on the NMR spectra. A number of samples were prepared for each reaction mixture, and every sample was assigned to a different reaction time as previously described.[13] This is because it takes about 1 min until the sample attains the desired reaction temperature. The reaction time was set to 2 min or longer, and the product concentration of the 2-min sample is subtracted from that of every other reacted sample in order to practically cancel out the error in the early reaction time.

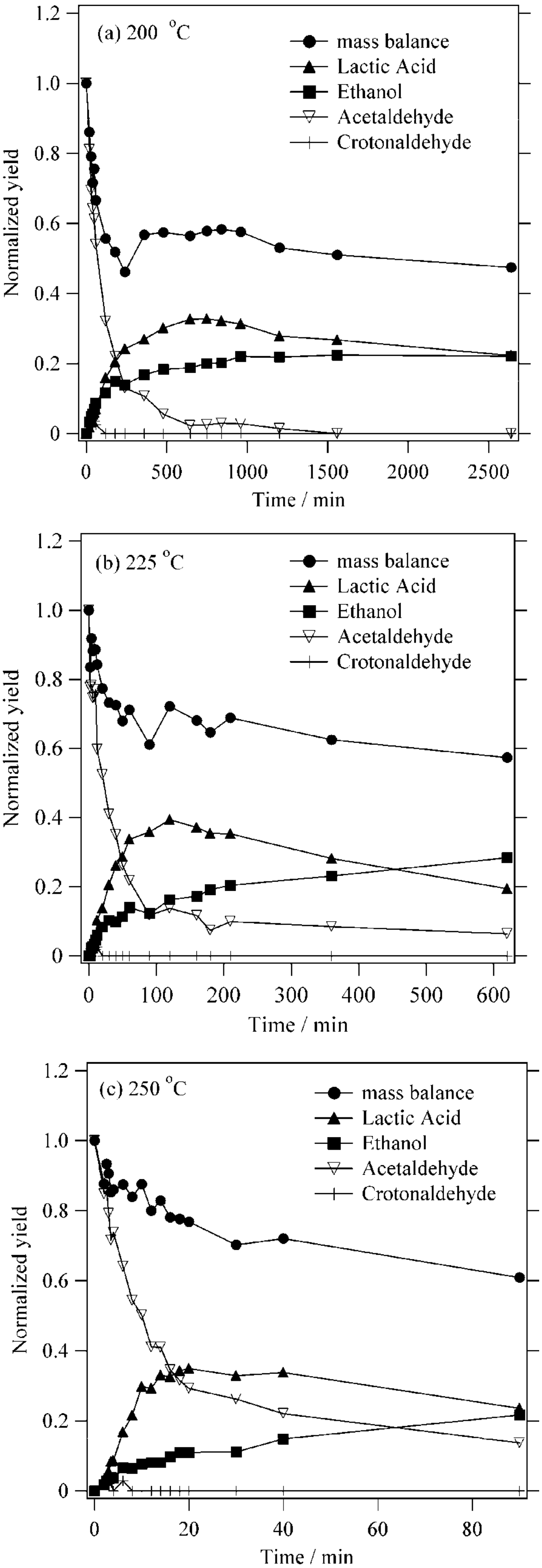

Figure 3. The time evolution of the reactants and products in the reaction of acetaldehyde (0.05 M) and formic acid (2.0 M) in the presence of HCl (0.6 M) at (a) 200 °C, (b) 225 °C, and (c) 250 °C. The sample filling factor η is 0.7 at room temperature. The normalized yield is the ratio of product concentration against the initial concentration of acetaldehyde. In the NMR measurement, a part of acetaldehyde is hydrated into ethanediol. In panels a−c, the sum of unhydrated acetaldehyde and ethanediol concentrations is expressed as the acetaldehyde concentration.

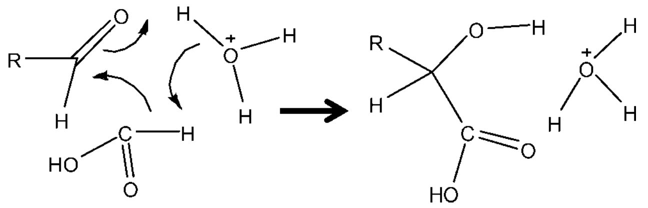

Figure 4. Proposed reaction mechanism of the C−C bond formation.

3. Results

We cannot establish a scheme for optimizing the hydrothermal production of lactic acid or ethanol from acetaldehyde without examining the product distribution, the reaction pathways, and the kinetics. To this end, we have applied ^{1}H and ^{13}C NMR spectroscopy to identify and quantify the reactants and products as functions of time.

3.1. Products and Reaction Pathways.

Here we clarify the pathways of the reaction between acetaldehyde and formic acid in hot water at 200−250 °C based on the time-dependent distribution of products. Figure 1 summarizes the reaction pathways disclosed here.

3.1.1. C−C Bond Formation.

We have studied the reaction of acetaldehyde (C2) with formic acid (C1) in the presence of HCl. Figure 2a shows the ^{1}H NMR spectrum of the liquid phase for the reaction between acetaldehyde (0.3 M) and formic acid (2.0 M) in the presence of HCl (0.3 M) at 225 °C and 2 h. The products identified are in the following decreasing order:

$$CH_3CH_2OH\ (13) > CH_3CH(OH)COOH\ (11) > CH_3CHO \text{ and } CH_3CH(OH)_2\ (4)$$

The numbers in the parentheses are yields in terms of carbon atoms originated from acetaldehyde; note that ethanediol ($CH_3CH(OH)_2$) is the hydrated form of acetaldehyde and that the mass balance is lost due to competing reactions that generate water-insoluble oil products[23] as mentioned in section 3.1.3. Lactic acid is formed through the following C−C bond formation:

$$CH_3CHO + HCOOH \xrightarrow{HCl} CH_3CH(OH)COOH \qquad (1)$$

It is noted that the acid-catalyzed hydrothermal C−C bond formation with formic acid is possible also for acetaldehyde with α-hydrogens. This is unexpected from the conventional knowledge because in the ambient reaction of aldehyde with α-hydrogens, the aldol condensation is dominant in acidic and basic conditions.[16,24,25] In the absence of HCl, no lactic acid is observed, as discussed below. As a matter of fact, the acidity of formic acid is not high enough to catalyze the C−C bond formation. A strong acid is thus indispensable for the C−C bond formation. The formation of hydroxyl carboxylic acid from the corresponding aldehyde is a novel hydrothermal C−C bond formation without using organic solvents nor metal catalysts. The kinetics is discussed in section 3.2.

3.1.2. Cross-Disproportionation.

Formic acid plays a key role as a reducing reagent in hydrothermal reactions.[3,6,7,9−13,15] In the case of the hydrothermal formaldehyde (C1) reaction, alcohol can form from both cross-disproportionation (oxidation and reduction between formaldehyde and formic acid) and self-disproportionation (oxidation and reduction between two molecules of formaldehyde). The cross-disproportionation was found to proceed faster than the self-disproportionation, indicating the stronger reducing ability of formic acid than that of formaldehyde.[9,13]

TABLE 2: Equilibrium Constant of the Lactic Acid Formation K_{CC} and Rate Constants of the Lactic Acid Formation k^{f}_{CC}, the Cross-Disproportionation k_{CD}, and the Aldol Condensation k_A

		rate constants		
temp/°C	equilibrium constant K_{CC}/M^{-1}	k^{f}_{CC}/(10^{-5} M^{-2} s^{-1})	k_{CD}/(10^{-5} M^{-1} s^{-1})	k_A/(10^{-3} M^{-2} s^{-1})
200	23 ± 1	4.0 ± 0.3	2.2 ± 0.1	5.0 ± 0.6
210	11 ± 3	11 ± 1	5.4 ± 0.2	6.0 ± 0.4
225	7 ± 1	25 ± 3	11 ± 1	8 ± 1
250	2.6 ± 0.7	(12 ± 1) × 10	41 ± 3	27 ± 5
		k^{f}_{CC}	k_{CD}	k_A
pre-exponential factor/M^{-2} s^{-1} (k^{f}_{CC} and k_A), M^{-1} s^{-1}(k_{CD})		7×10^{10}	2×10^{8}	3×10^{5}
activation energy/(kcal/mol)		32	28	16

It is of interest to see whether the difference in the reactivity between the two types of disproportionations is also observed for the case of the C2 aldehyde.

In the neutral hydrothermal reaction of acetaldehyde at 225 °C, no ethanol formed and crotonaldehyde ($\mathrm{CH_3CH{=}CHCHO}$) is the only product, as seen in Figure 2b. The self-disproportionation of acetaldehyde, therefore, does not proceed at 225 °C.[26] In the reaction of acetaldehyde and formic acid, as seen in Figure 2c, the following products are observed:

$$\mathrm{CH_3CH_2OH}\ (45) > \mathrm{CH_3CHO}\ \text{and}\ \mathrm{CH_3CH(OH)_2}\ (28) > \mathrm{CH_3CH{=}CHCHO}\ (5)$$

Ethanol is formed as a primary product through the following cross-disproportionation:[6,10]

$$\mathrm{CH_3CHO + HCOOH \rightarrow CH_3CH_2OH + CO_2} \tag{2}$$

Here formic acid reduces acetaldehyde into ethanol without any catalyst, in contrast to the classical Cannizzaro reaction that requires a large amount of base like NaOH.[16] In fact, we have achieved a high ethanol yield of 75% after 8 h in the reaction of 0.3 M of acetaldehyde and 2.0 M of formic acid at 225 °C. Thus we can obtain alcohol by the simple addition of formic acid to the corresponding aldehyde.[3,6,7,9–13,15]

3.1.3. Aldol Condensation. In the hydrothermal reaction of acetaldehyde, crotonaldehyde is generated as an unwanted product as seen in Figure 2b. The presence of crotonaldehyde indicates the aldol condensation followed by the dehydration of aldol ($\mathrm{CH_3CH(OH)CH_2CHO}$).[10,16] The formation can be initiated by the elimination of an acidic α-hydrogen expressed as

$$\mathrm{2CH_3CHO \rightarrow CH_3CH(OH)CH_2CHO \rightarrow CH_3CH{=}CHCHO + H_2O} \tag{3}$$

This is typical of aldehydes with α-hydrogens under acidic and basic conditions at room temperature according to the textbook knowledge.[16,24,25] The aldol-condensation product, crotonaldehyde, can polymerize to form water-insoluble oil.[10,11] The aldol condensation causes a loss in mass balance (∼30%) in the present analysis as mentioned above.[27,28] It is thus indispensable to suppress the aldol condensation for the selective formations of lactic acid and ethanol.

3.2. Equilibrium and Kinetics. To maximize the lactic acid and ethanol yields, the reactant and acid concentrations as well as the filling factor must be tuned so that the path weights of the lactic acid formation and the cross-disproportionation may be large enough. We first determine the equilibrium constant of the lactic acid formation and then the rate constants of the lactic acid formation, the cross-disproportionation, and the aldol condensation.

TABLE 3: Estimated Values of k^{f}_{CC}/k_{CD}, k^{f}_{CC}/k_A, and $K_{CC}[\mathrm{HCOOH}]_{eq}/(1 + K_{CC}[\mathrm{HCOOH}]_{eq})$ in the Temperature Range 150−300 °C

temp/°C	k^{f}_{CC}/k_{CD} (M^{-1})[a]	k^{f}_{CC}/k_A[a]	$K_{CC}[\mathrm{HCOOH}]_{eq}/$ $1 + K_{CC}[\mathrm{HCOOH}]_{eq}$[b]
150	3	1×10^{-3}	1.00
175	4	4×10^{-3}	0.98
200	5	9×10^{-3}	0.93
225	6	2×10^{-2}	0.74
250	7	5×10^{-2}	0.49
275	9	1×10^{-1}	0.22
300	10	2×10^{-1}	0.10

[a] The values of k^{f}_{CC}, k_{CD}, and k_A are estimated from the Arrhenius plot based on Table 2. [b] The values for the reaction in which the initial formic acid concentration is 2.0 M and the sample filling factor η is 0.7 at room temperature. η is 0.76, 0.79, 0.81, 0.84, 0.88, 0.92, and 0.99, respectively, at reaction temperatures of 150, 175, 200, 225, 250, 275, and 300 °C.

3.2.1. Lactic Acid Formation Equilibrium. It is important to see when the lactic acid formation reaches an equilibrium. Figures 3a−c show the time evolution of the reactants and products in the reaction of acetaldehyde (0.05 M) and formic acid (2.0 M) with HCl (0.6 M) at temperatures of 200, 225, and 250 °C, respectively. As shown, lactic acid initially increases and then begins to decrease while ethanol increases monotonically. The maximum lactic acid concentration is located at ∼650, ∼120, and ∼20 min, respectively, at 200, 225, and 250 °C. The presence of the maximum indicates that lactic acid formation (eq 1) reaches an equilibrium. Ethanol, on the other hand, monotonically increases; the equilibrium of the cross-disproportionation rests far on the product side as in the case of methanol formation from formaldehyde.[29] As an indication of the exclusive consumption of acetaldehyde by the two competing reactions, the sum of the concentrations of lactic acid and ethanol is almost constant after the time of the maximum concentration of lactic acid.[30,31] As seen in Figures 3a−c, the increase of the temperature can drastically shorten the reaction time at which lactic acid concentration reaches a maximum.

The equilibrium constant of the lactic acid formation K_{CC} is expressed as

$$K_{CC} = \frac{k^{f}_{CC}}{k^{b}_{CC}} = \frac{[\mathrm{CH_3CH(OH)COOH}]_{eq}}{[\mathrm{CH_3CHO}]_{eq}[\mathrm{HCOOH}]_{eq}} \tag{4}$$

where k^{f}_{CC} and k^{b}_{CC} are the forward and backward rate constants, respectively. The subscript eq denotes that the system under consideration is at equilibrium for the reaction of eq 1. The values of K_{CC} are obtained from the NMR-determined concentrations of the species involved and listed in Table 2. K_{CC} increases from 2.6 to 23 by the temperature decrease from 250 to 200 °C. The lactic acid formation is exothermic (the standard

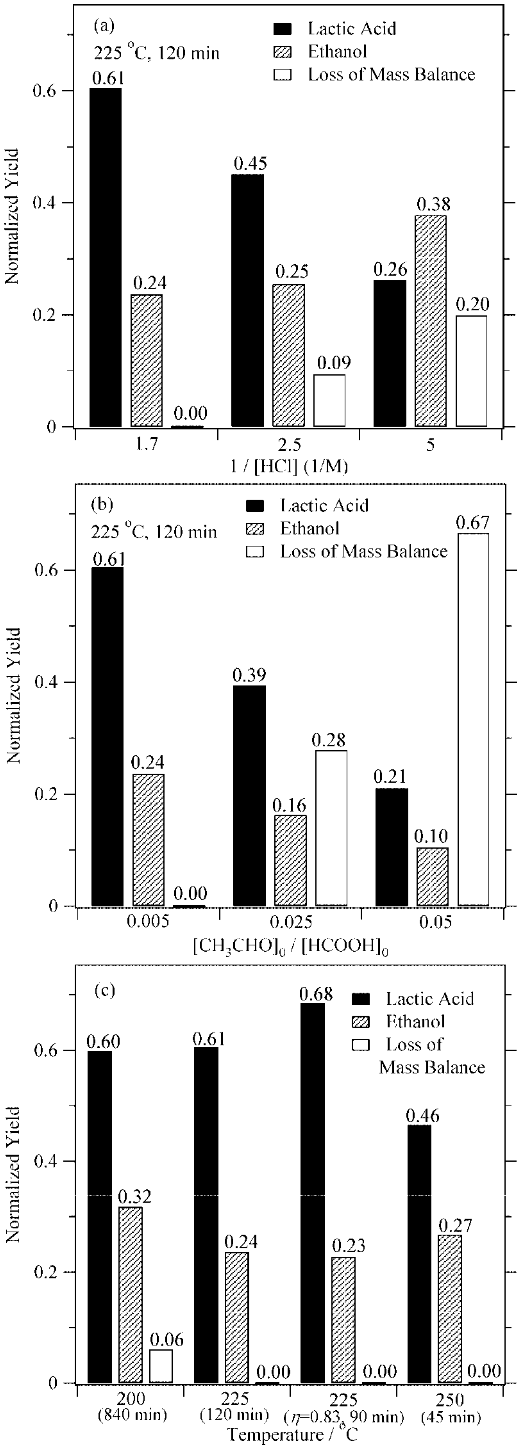

Figure 5. Lactic acid and ethanol yields and the loss of mass balance in the reaction of (a) acetaldehyde (0.01 M) and formic acid (2.0 M) with the variation of HCl concentration (0.2, 0.4, and 0.6 M) and (b) formic acid (2.0 M) in the presence of HCl (0.6 M) with the variation of acetaldehyde concentration (0.1, 0.05, and 0.01 M) at 225 °C. In panels a and b, the reaction time is fixed at 120 min and the sample filling factor is η is 0.7 at room temperature ($\eta = 0.84$ at 225 °C). (c) shows the yields in the reaction of acetaldehyde (0.01 M) and formic acid (2.0 M) with HCl (0.6 M) with the variation of temperature (200, 225, and 250 °C) when the lactic acid yield took maximum. Times in parentheses denote the reaction time of lactic acid maximization at each condition. The sample filling factor η is 0.7 at room temperature ($\eta =$ 0.81, 0.84, and 0.88, respectively, at 200, 225, and 250 °C) except for the third entry labeled $\eta = 0.83$, in which η at room temperature is 0.83 so that η becomes close to unity (0.99) at reaction temperature of 225 °C. At each entry, the sum of the mass balance and the lactic acid and ethanol yields are not 100% because there is unreacted acetaldehyde.

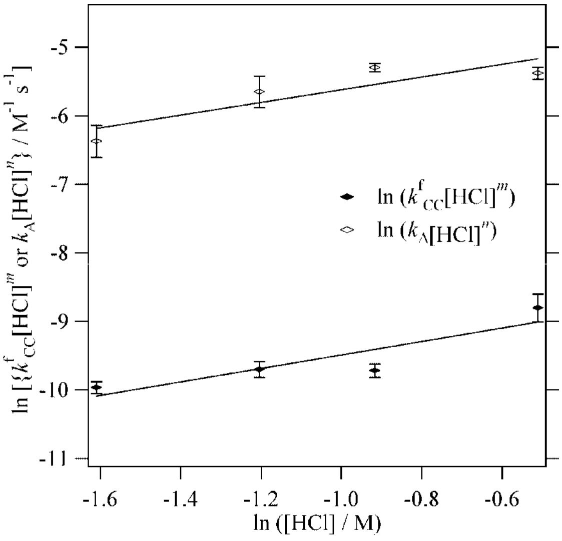

Figure 6. Logarithm of the product of the rate constant and HCl concentration (ln $k^f_{CC}[HCl]^m$ for the lactic acid formation and ln $k_A[HCl]^n$ for the aldol condensation) against the logarithm of HCl concentration at 225 °C.

enthalpy change, $\Delta H° \approx -20$ kcal/mol) and the equilibrium is favored to the product side by a temperature drop.

3.2.2. Rate Laws and Constants. When we attempt to control the multiple pathways exclusively for lactic acid or ethanol, we should determine the rate constants of the lactic acid formation k^f_{CC}, the cross-disproportionation k_{CD}, and the aldol condensation k_A. We can give the rate equations for the lactic acid formation (eq 1) and the cross-disproportionation (eq 2) as follows:

$$\frac{d[CH_3CH(OH)COOH]}{dt} = k^f_{CC}[HCl]^m[CH_3CHO][HCOOH] - k^b_{CC}[HCl]^m[CH_3CH(OH)COOH] \quad (5)$$

$$\frac{d[CH_3CH_2OH]}{dt} = k_{CD}[CH_3CHO][HCOOH] \quad (6)$$

where m denotes the reaction order with respect to the acid.[32] The square brackets denote the concentration. We can determine the rate constants for eqs 5 and 6 using the initial rate. To determine k^f_{CC} and k_{CD}, eqs 5 and 6 are integrated and fitted to the experimentally obtained time evolution of lactic acid and ethanol concentrations, respectively, in the early reaction stage; see Appendices A and B for details. The lactic acid formation is found to be a first-order reaction ($m = 1$) with respect to the acid.

To control the reaction pathways for the lactic acid or ethanol formation, it is important to suppress the competing aldol condensation as much as possible. The rate constant of the aldol condensation k_A is determined as follows. The progress of the aldol condensation cannot be monitored directly by the concentration of aldol or crotonaldehyde due to further polymerization.[10] Using the sum of the mass balance loss and the crotonaldehyde yield, the rate equation for the aldol condensation is expressed as

$$\frac{d([CH_3CHO]_{loss} + 2[CH_3CH{=}CHCHO])}{dt} = k_A[HCl]^n[CH_3CHO]^2 \quad (7)$$

Here, $[CH_3CHO]_{loss}$ is the mass balance loss in terms of the acetaldehyde concentration and n denotes the reaction order with respect to the acid. The concentration of crotonaldehyde is multiplied by 2 and converted into the concentration of consumed acetaldehyde in eq 7. To control the reaction pathways for the lactic acid formation or ethanol formation, we are interested in the rate of acetaldehyde consumption by the aldol condensation. See Appendix B for the determination of k_A. The aldol condensation is found to be a first-order reaction ($n = 1$) with respect to the acid.

Table 2 lists the values of k^f_{CC}, k_{CD}, and k_A determined at 200, 210, 225, and 250 °C. These results lead to their Arrhenius plots along the liquid branch of the saturation curve of water. The pre-exponential factors and activation energies are obtained as shown in the table. The reaction order of the acid concentration in the lactic acid formation is first as in the case of the glycolic acid formation from formaldehyde.[13] This suggests a similar reaction mechanism. One proton is considered to participate in the reaction. We have found that the carboxyl group of formic acid makes the carboxyl group of glycolic acid in the previous study with ^{13}C-enriched formaldehyde.[13] On the basis of these results we can propose the reaction mechanism of the C−C bond formation as shown in Figure 4, where a proton takes part in a six-membered ring and the carboxyl group of formic acid is bonded to aldehyde through the formation of a C−C bond. In this mechanism, the carbonyl carbon and oxygen of aldehyde are simultaneously subjected to nucleophilic and electrophilic attacks, respectively. A similar transition-state structure with a six-membered ring has been found in ab initio calculation for the self- and cross-disproportionations of formaldehyde.[33]

4. Discussion

In this section, we show how we can control the reaction pathways in the direction desirable for the lactic acid and the ethanol formations on the basis of the kinetic parameters so far determined.

4.1. Lactic Acid Formation. Lactic acid becomes the primary product when the lactic acid formation proceeds faster than the cross-disproportionation and the aldol condensation. This condition is satisfied by the following relations:

$$\frac{d[CH_3CH(OH)COOH]}{dt} > \frac{d[CH_3CH_2OH]}{dt} \tag{8}$$

$$\frac{d[CH_3CH(OH)COOH]}{dt} > \frac{d([CH_3CHO]_{loss} + 2[CH_3CH{=}CHCHO])}{dt} \tag{9}$$

Using the rate constants, we can rewrite (8) and (9) as

$$k^f_{CC}[CH_3CHO][HCOOH][HCl] - k^b_{CC}[CH_3CH(OH)COOH][HCl] > k_{CD}[CH_3CHO][HCOOH] \tag{10}$$

$$k^f_{CC}[CH_3CHO][HCOOH][HCl] - k^b_{CC}[CH_3CH(OH)COOH][HCl] > k_A[CH_3CHO]^2[HCl] \tag{11}$$

At the beginning of the reaction, there is no contribution from the backward reaction of the lactic acid formation ($-k^b_{CC}[CH_3CH(OH)COOH][HCl]$). Thus from (10) and (11), we obtain the following conditions necessary for the favored lactic acid formation:

$$\frac{1}{[HCl]} < \frac{k^f_{CC}}{k_{CD}} \tag{12}$$

$$\frac{[CH_3CHO]}{[HCOOH]} < \frac{k^f_{CC}}{k_A} \tag{13}$$

As can be seen from (12) and (13), we can increase the relative rate of the lactic acid formation to the cross-disproportionation and that to the aldol condensation, respectively, by increasing [HCl] and decreasing [CH$_3$CHO] at a given temperature and formic acid concentration. Because (12) and (13) are derived when the backward reaction is negligible, they are necessary conditions for the lactic acid selection. In Table 3, the values of k^f_{CC}/k_{CD} and k^f_{CC}/k_A are listed over a wide temperature range from 150 to 300 °C. By tuning the acid and initial reactant concentrations so that (12) and (13) are satisfied, we can make the initial rate of the lactic acid formation faster than those of the cross-disproportionation and the aldol condensation.

Because (12) and (13) are necessary conditions in an early stage for the maximization of the lactic acid yield, we add one more condition to be satisfied at a later reaction time. When the lactic acid formation reaches the equilibrium, the concentration ratio of lactic acid to acetaldehyde is expressed (cf. eq 4) as

$$\frac{[CH_3CH(OH)COOH]_{eq}}{[CH_3CHO]_0 - [CH_3CHO]_{CD+A,eq} - [CH_3CH(OH)COOH]_{eq}} = K_{CC}[HCOOH]_{eq} \tag{14}$$

where $[CH_3CHO]_0$ and $[HCOOH]_{eq}$ denote the initial concentration of acetaldehyde and the equilibrium concentration of formic acid, respectively. $[CH_3CHO]_{CD+A,eq}$ is the sum of aldehyde concentrations consumed by the cross-disproportionation and the aldol condensation. As seen from eq 14, the equilibrium concentrations, $[CH_3CH(OH)COOH]_{eq}$, $[HCOOH]_{eq}$, and $[CH_3CHO]_{CD+A,eq}$ may vary during the progress of the cross-disproportionation and the aldol condensation. The lactic acid yield is obtained from eq 14 as

$$\frac{[CH_3CH(OH)COOH]_{eq}}{[CH_3CHO]_0} = \frac{K_{CC}[HCOOH]_{eq}\left(1 - \frac{[CH_3CHO]_{CD+A,eq}}{[CH_3CHO]_0}\right)}{1 + K_{CC}[HCOOH]_{eq}} \tag{15}$$

Because $[CH_3CHO]_{CD+A,eq}/[CH_3CHO]_0$ is always positive, the following relation holds:

$$\frac{[CH_3CH(OH)COOH]_{eq}}{[CH_3CHO]_0} < \frac{K_{CC}[HCOOH]_{eq}}{1 + K_{CC}[HCOOH]_{eq}} \tag{16}$$

Relation 16 means that the lactic acid yield cannot overwhelm $K_{CC}[HCOOH]_{eq}/(1 + K_{CC}[HCOOH]_{eq})$. In other words, the value of $K_{CC}[HCOOH]_{eq}/(1 + K_{CC}[HCOOH]_{eq})$ is an upper bound for the lactic acid yield at a given temperature and initial formic acid concentration. The lactic acid formation is favored by increasing the values of K_{CC} and $[HCOOH]_{eq}$. When we make the lactic acid yield larger than 50%, for example, $K_{CC}[HCOOH]_{eq} > 1$ is a necessary condition according to (16). Table 3 lists the values of $K_{CC}[HCOOH]_{eq}/(1 + K_{CC}[HCOOH]_{eq})$ when the initial formic acid concentration is 2.0 M and the filling factor η (the volume ratio of the solution to the total sample tube) at room temperature is 0.7; at a reaction temperature of 225 °C, η becomes ~0.8 due to the expansion of liquid. We discuss how to evaluate K_{CC} and $[HCOOH]_{eq}$ below.

The value of K_{CC} can be obtained from the van't Hoff plot of K_{CC} listed in Table 2. $[HCOOH]_{eq}$, on the other hand, can be approximated by the formic acid concentration equilibrated with carbon monoxide, as discussed in Appendix A. This approximation is valid because the formic acid is added in excess in the reaction mixture and the decarbonylation is the dominant reaction of formic acid. Therefore, $[HCOOH]_{eq}$ in (16) can be expressed as follows (see Appendix A for the derivation):

$$[HCOOH]_{eq} = \frac{[HCOOH]_0}{K_{deCO}\left(\frac{1-\eta}{\eta}K_D + 1\right) + 1} \qquad (17)$$

Here, K_{deCO} is the equilibrium constant of the formic acid decarbonylation. K_D denotes the concentration ratio of carbon monoxide in the gas phase to the liquid phase of the sample and η is the filling factor of the sample at the reaction temperature. Equation 17 indicates that an upper bound of the lactic acid formation (16) at a given temperature can be tuned by the initial formic acid concentration and the sample filling factor. Especially, when the filling factor is tuned so that η may be close to 1 at the reaction temperature, $[HCOOH]_{eq}$ reaches its maximum $[HCOOH]_0/(K_{deCO} + 1)$ at a given initial formic acid concentration and temperature.

Now let us show how the lactic acid yield can be maximized. By satisfying (12) and (13), we can make the initial rate of the lactic acid formation faster than the cross-disproportionation and the aldol condensation. Figure 5a,b shows how the lactic acid yield, the ethanol yield, and the loss of mass balance at 225 °C after 2 h are varied with 1/[HCl] and $[CH_3CHO]_0/[HCOOH]_0$, respectively. As 1/[HCl] decreases, the path weight of the lactic acid formation against the cross-disproportionation increases. As $[CH_3CHO]_0/[HCOOH]_0$ decreases, the path weight of the lactic acid formation against the aldol condensation increases. These trends can be understood according to (12) and (13). The path selection between the lactic acid formation and the cross-disproportionation is achieved by tuning the HCl concentration because the acid catalyzes only the former reaction (see eqs 1 and 2 and Figure 5a). In the case of the path selection between the lactic acid formation and the aldol condensation, the former selection can be done by lowering the concentration of acetaldehyde at a fixed formic acid concentration because the reaction order of acetaldehyde is first in the lactic acid formation and second in the aldol condensation; see eqs 1 and 3 and Figure 5b.

Here we examine the temperature dependence of k_{CC}^f/k_{CD} and k_{CC}^f/k_A in (12) and (13). As seen in Table 3, the value of k_{CC}^f/k_A increases drastically from 1×10^{-3} to 2×10^{-1} by the temperature elevation from 150 to 300 °C. At low temperatures, thus the aldol condensation is to be dominant; the situation comes back to the textbook knowledge on the reactions of aldehydes with α-hydrogens at room temperature.[16,24,25] The temperature dependence of k_{CC}^f/k_A indicates that the crossover of the reaction dominance occurs by the temperature elevation; as the temperature increases, the C−C bond formation starts to compete with the aldol condensation and finally becomes dominant. Thus, (13) is less satisfied at low temperatures. At 150 °C, for example, [HCOOH] needs to be at least 1000 times larger than $[CH_3CHO]$, which is totally unsuitable for practical use. In contrast, [HCOOH] needs to be only 5 times larger than $[CH_3CHO]$ at 300 °C. The value of k_{CC}^f/k_{CD} does not vary significantly (3−10 M^{-1}) in the temperature range 150−300 °C. Thus (13) determines the lower bound of the temperature suitable for the selective formation of lactic acid.

Now let us discuss the maximization of the lactic acid yield for a specific example. When 0.01 M of acetaldehyde reacts with 2.0 M of formic acid, the value of $[CH_3CHO]_0/[HCOOH]_0$ is 5×10^{-3}. The value of k_{CC}^f/k_A, on the other hand, is 4×10^{-3}, 9×10^{-3}, 2×10^{-2}, and 5×10^{-2}, respectively, at 175, 200, 225, and 250 °C (see Table 3). In this case (13) is satisfied when the temperature is higher than ~200 °C. In such a temperature region, 0.6 M of HCl (1/[HCl] ≈ 1.7) is enough for the path selection as seen from (12) and Table 3. Although (13) governs the lower bound of the reaction temperature for the selective formation of lactic acid, the upper bound of the temperature is determined by (16). With the initial formic acid concentration $[HCOOH]_0$ of 2.0 M and the filling factor η of 0.7 at room temperature, the value of $K_{CC}[HCOOH]_{eq}/(1 + K_{CC}[HCOOH]_{eq})$ is 0.93, 0.74, 0.49, and 0.22 at 200, 225, 250, and 275 °C, respectively. These values are the upper bound for the lactic acid yield as shown by (16). When we wish to achieve the lactic acid yield higher than 50%, therefore, the reaction temperature should be lower than ~250 °C. Thus the optimum reaction temperature for the lactic acid formation is located in the range of 200−250 °C.

We examined the lactic acid yield in the reaction of acetaldehyde (0.01 M) and formic acid (2.0 M) with HCl (0.6 M) experimentally. Figure 5c shows when the lactic acid yield attains a maximum value at 200, 225, and 250 °C with the sample filling factor η of 0.7 at room temperature. The reaction is successfully controlled, and a high lactic acid yield of ~60% is achieved at 200 and 225 °C. At 250 °C, the lactic acid yield drops to ~45% as predicted. The lactic acid yield is almost the same at 200 and 225 °C, but it took only 120 min to reach the equilibrium of lactic acid formation at the higher temperature, 225 °C, which is one-seventh of the reaction time required at 200 °C. Thus 225 °C is found to be the most suitable temperature for the maximization of the lactic acid yield. According to (16) and (17), we can maximize the lactic acid yield by tuning the sample filling factor η so that it may be close to 1 at a given temperature and initial formic acid concentration. The sample filling factor $\eta = 0.70$ and 0.83 at room temperature correspond to $\eta = 0.84$ and 0.99 at 225 °C, respectively. Thus selecting such a high value as 0.83 for η at room temperature, we have achieved a maximum lactic acid yield of 68% as seen in Figure 5c.

The acid-catalyzed lactic acid formation in hydrothermal conditions is novel in that lactic acid, an important industrial material, forms without any organic solvents or metal catalysts. We have shown how we can control the reaction paths for the lactic acid formation by tuning the filling factor, the acid, and reactant concentrations. It is to be noted that even in the reaction of aldehydes with α-hydrogens, we can select the reaction path for the acid-catalyzed lactic acid formation and subdue the aldol condensation. The amination of lactic acid results in the formation of alanine. Alanine and lactic acid are essential chemicals to living things. The hydrothermal lactic acid formation proposes a new method for green lactic acid formation, and this hydrothermal process can be a step toward the chemical evolution to amino acids in the primitive ocean under suitable acidity conditions.

4.2. Ethanol Formation. Finally, let us discuss the path selection for the ethanol formation. The cross-disproportionation proceeds without acid whereas the lactic acid formation and the aldol condensation do not. Thus ethanol can be maximized simply when the reaction of acetaldehyde proceeds under an excess amount of formic acid. For example, when acetaldehyde (0.3 M) and formic acid (2.0 M) are reacted at 225 °C, a high ethanol yield of 75% is achieved within 8 h. Formic acid reduces aldehyde into corresponding alcohol in a high yield without catalysts. Today's environmental issues call for green methods of energy source production. As an environmentally benign method of alcohol production, the cross-disproportionation of aldehyde and formic acid can be one of possible answers to this issue.

5. Conclusions

In this work, the reaction of acetaldehyde and formic acid in acidic hydrothermal condition is studied. Acetaldehyde is found to exhibit the acid-catalyzed lactic acid formation, the cross-disproportionation, and the aldol condensation. The lactic acid formation is a chemical evolution from C2 to C3 compounds in acidic hydrothermal conditions and is a novel reaction in that the reaction proceeds without any organic solvents or metal catalysts. The lactic acid formation from acetaldehyde and formic acid reported here elucidates the generality of the hydrothermal C−C bond formation from aldehyde and formic acid.[9,13] In the cross-disproportionation, formic acid reduces acetaldehyde without any catalysts. This reaction is important as a green method for alcohol production.

The equilibrium constant of the lactic acid formation and the rate constants of the lactic acid formation, the cross-disproportionation, and the aldol condensation are determined in the temperature range 200−250 °C. The reaction order of acid is found to be unity in the lactic acid formation, as is the case of the glycolic acid formation. For the hydrothermal C−C bond formation between aldehyde and formic acid, a reaction mechanism is proposed in which aldehyde, formic acid and proton form a six-membered ring. The rate constants and the equilibrium constant allow us to quantitatively control the reaction pathways for the lactic acid formation and for the ethanol formation, respectively, by tuning the reactant concentrations, the sample filling factor, and the temperature. The lactic acid yield of 68% is achieved by the reaction of acetaldehyde (0.01 M) and formic acid (2.0 M) in the presence of HCl (0.6 M) at 225 °C with the sample filling factor of 0.83. The high yield of ethanol (75%) is achieved by the reaction of acetaldehyde (0.3 M) and formic acid (2.0 M) at 225 °C.

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Appendix A: Formic Acid Decarbonylation

To perform the kinetic analysis and the pathway control of the reaction between acetaldehyde and formic acid, it is important to know how formic acid is depleted during the reaction. Here, we clarify the time dependence of formic acid concentration in the gas−liquid coexisted system. To clarify what reaction formic acid exhibits, we have analyzed the reaction of ^{13}C-enriched acetaldehyde (0.05 M) and an excess amount of ^{13}C-enriched formic acid (2.0 M) with HCl (0.6 M) at 225 °C. After 2 h of reaction, 66% of formic acid reacted where ∼64% is consumed by the formic acid decarbonylation[8,14] and ∼2% by the acetaldehyde reactions (eqs 1–3).[34] The decarbonylation of formic acid is thus the dominant reaction of formic acid in acidic hydrothermal conditions. The rate equation of the formic acid decomposition involving the phase equilibrium is expressed as

$$\frac{\mathrm{d}[\mathrm{HCOOH}]}{\mathrm{d}t} = -k_{\mathrm{deCO}}[\mathrm{HCOOH}][\mathrm{HCl}] + \frac{k_{\mathrm{deCO}}}{K_{\mathrm{deCO}}}[\mathrm{CO}]_{\mathrm{liq}}[\mathrm{HCl}] \quad (18)$$

where k_{deCO} and $[\mathrm{CO}]_{\mathrm{liq}}$ are the rate constant of the decarbonylation of formic acid and the concentration of carbon monoxide in the liquid phase, respectively. Note that only the decarbonylation of formic acid is taken into account; the reaction of acetaldehyde (eqs 1–3) have little effect on the time evolution of formic acid that is present in excess. K_{deCO} is the equilibrium constant of the formic acid decarbonylation expressed as[14]

$$K_{\mathrm{deCO}} = \frac{[\mathrm{CO}]_{\mathrm{liq,eq}}}{[\mathrm{HCOOH}]_{\mathrm{eq}}} \quad (19)$$

The values of K_{deCO} and k_{deCO} are obtained by the interpolation of the data from ref 14. We introduce the partition coefficient K_{D} as the ratio of the concentrations of carbon monoxide in the gas ($[\mathrm{CO}]_{\mathrm{gas}}$) and liquid ($[\mathrm{CO}]_{\mathrm{liq}}$) phase as

$$K_{\mathrm{D}} = \frac{[\mathrm{CO}]_{\mathrm{gas}}}{[\mathrm{CO}]_{\mathrm{liq}}} = \frac{k_{\mathrm{H}}}{RTd_T} \quad (20)$$

where k_{H} and d_T are the Henry constant and the molar concentration of liquid water at temperature T on the saturation curve, respectively. R is the gas constant. To determine the value of K_{D}, the values of k_{H} and d_T are obtained from refs 35 and 36 as described in ref 14. K_{D} is determined as 28.5, 22.0, 16.6, and 12.4 at 175, 200, 225, and 250 °C, respectively. $[\mathrm{CO}]_{\mathrm{gas}}$ can be expressed as

$$[\mathrm{CO}]_{\mathrm{gas}} = \frac{\eta}{1-\eta}([\mathrm{HCOOH}]_0 - [\mathrm{HCOOH}] - [\mathrm{CO}]_{\mathrm{liq}}) \quad (21)$$

where η is a filling factor of the sample (the volume ratio of the solution to the total sample tube) at the reaction temperature. Using eq 21 and the definition of K_{D}, we can express $[\mathrm{CO}]_{\mathrm{liq}}$ as

$$[\mathrm{CO}]_{\mathrm{liq}} = \frac{[\mathrm{HCOOH}]_0 - [\mathrm{HCOOH}]}{\frac{1-\eta}{\eta}K_{\mathrm{D}} + 1} \quad (22)$$

From eqs 18 and 22, [HCOOH] is obtained as a function of time and initial concentration $[\mathrm{HCOOH}]_0$ as follows:

$$[\mathrm{HCOOH}] = \frac{[\mathrm{HCOOH}]_0}{Q+1}\left(1 + Q\exp\frac{-(Q+1)k_{\mathrm{deCO}}[\mathrm{HCl}]t}{Q}\right) \quad (23)$$

where

$$Q = K_{\mathrm{deCO}}\left(\frac{1-\eta}{\eta}K_{\mathrm{D}} + 1\right) \quad (24)$$

In the limit of $t \rightarrow \infty$, the formic acid concentration $[\mathrm{HCOOH}]_{\mathrm{deCO}}$ at equilibrium of the decarbonylation is given by

$$[\mathrm{HCOOH}]_{\mathrm{deCO}} = \frac{[\mathrm{HCOOH}]_0}{K_{\mathrm{deCO}}\left(\frac{1-\eta}{\eta}K_{\mathrm{D}} + 1\right) + 1} \quad (25)$$

This is used for the discussion of the C−C bond formation pathway control in section 4.1.

In section 4.1, we used $[\mathrm{HCOOH}]_{\mathrm{deCO}}$ for $[\mathrm{HCOOH}]_{\mathrm{eq}}$, the formic acid concentration at the equilibrium of the lactic acid formation, in (16). This can be done only when the decarbonylation of formic acid is dominant, and when the formic acid decarbonylation equilibrates before the lactic acid formation equilibrates. The former condition is confirmed by the independent experiment using ^{13}C-enriched formic acid as mentioned above. As for the latter condition, the value of $Q\exp(-(Q + 1)k_{\mathrm{deCO}}[\mathrm{HCl}]t/Q)$ in eq 23 is 0.001−0.04 and negligibly small at 200−250 °C when the lactic acid formation equilibrates; for example, t is ∼650 min at 200 °C and ∼20 min at 250 °C in the reaction with acetaldehyde (0.05 M), formic acid (2.0 M), and HCl (0.6 M). This means that the formic acid decarbonylation is close enough to the equilibrium. Therefore, we can use eq 17 safely.

Appendix B: Rate Determination

We explain here how to determine the rate constants of the lactic acid formation $k_{\mathrm{CC}}^{\mathrm{f}}$ and the cross-disproportionation k_{CD}. At the beginning of the reaction, there is no contribution of backward reaction of the lactic acid formation, and we can neglect the second term on the right-hand side of eq 5.[37] Thus we can integrate the rate equations of the lactic acid formation (eq 5) and the cross-disproportionation (eq 6), respectively, as

$$[\mathrm{CH_3CH(OH)COOH}]_t = k_{\mathrm{CC}}^{\mathrm{f}}[\mathrm{HCl}]^m \int_0^t [\mathrm{CH_3CHO}][\mathrm{HCOOH}]\,\mathrm{d}t \tag{26}$$

$$[\mathrm{CH_3CH_2OH}]_t = k_{\mathrm{CD}} \int_0^t [\mathrm{CH_3CHO}][\mathrm{HCOOH}]\,\mathrm{d}t \tag{27}$$

Here, $[\mathrm{CH_3CH(OH)COOH}]_t$ and $[\mathrm{CH_3CH_2OH}]_t$ denote the concentrations of lactic acid and ethanol, respectively, at reaction time t. To calculate eqs 26 and 27 in the early reaction stage, we approximate the time evolution of $[\mathrm{CH_3CHO}]$ as $[\mathrm{CH_3CHO}]_0\exp(-At)$ by the fitting; A is the apparent rate constant for the multistep consumption of acetaldehyde. We applied the approximation to the beginning of the reaction until the acetaldehyde concentration decreases by ~25%. A is obtained by plotting the acetaldehyde concentration against the reaction time. Because we already obtained the evolution of formic acid as a function of time (eq 23) in Appendix A, eqs 26 and 27 are rewritten, respectively, as

$$[\mathrm{CH_3CH(OH)COOH}]_t = k_{\mathrm{CC}}^{\mathrm{f}}[\mathrm{HCl}]^m \int_0^t [\mathrm{CH_3CHO}]_0 \times \exp(-At) \times \frac{[\mathrm{HCOOH}]_0}{Q+1}\left(1 + Q\exp\frac{-(Q+1)k_{\mathrm{deCO}}[\mathrm{HCl}]t}{Q}\right)\mathrm{d}t \tag{28}$$

$$[\mathrm{CH_3CH_2OH}]_t = k_{\mathrm{CD}} \int_0^t [\mathrm{CH_3CHO}]_0 \times \exp(-At) \times \frac{[\mathrm{HCOOH}]_0}{Q+1}\left(1 + Q\exp\frac{-(Q+1)k_{\mathrm{deCO}}[\mathrm{HCl}]t}{Q}\right)\mathrm{d}t \tag{29}$$

where $Q = K_{\mathrm{deCO}}\{[(1-\eta)/\eta]K_{\mathrm{D}} + 1\}$ as shown in eq 24. From eqs 28 and 29, we obtain

$$[\mathrm{CH_3CH(OH)COOH}]_t = \frac{k_{\mathrm{CC}}^{\mathrm{f}}[\mathrm{HCl}]^m[\mathrm{HCOOH}]_0}{Q+1} \times \left\{\frac{[\mathrm{CH_3CHO}]_0}{A}(1-\exp(-At)) + \frac{[\mathrm{CH_3CHO}]_0 Q^2}{(Q+1)k_{\mathrm{deCO}}[\mathrm{HCl}] + AQ} \times \left(1 - \exp\left(-\frac{(Q+1)k_{\mathrm{deCO}}[\mathrm{HCl}] + AQ}{Q}t\right)\right)\right\} \tag{30}$$

$$[\mathrm{CH_3CH_2OH}]_t = \frac{k_{\mathrm{CD}}[\mathrm{HCOOH}]_0}{Q+1} \times \left\{\frac{[\mathrm{CH_3CHO}]_0}{A}(1-\exp(-At)) + \frac{[\mathrm{CH_3CHO}]_0 Q^2}{(Q+1)k_{\mathrm{deCO}}[\mathrm{HCl}] + AQ} \times \left(1 - \exp\left(-\frac{(Q+1)k_{\mathrm{deCO}}[\mathrm{HCl}] + AQ}{Q}t\right)\right)\right\} \tag{31}$$

The value of $k_{\mathrm{CC}}^{\mathrm{f}}[\mathrm{HCl}]^m$ is obtained from eq 30 and the experimental plot of lactic acid yield against the reaction time. Likewise, k_{CD} is obtained from eq 31 and the experimental plot of ethanol yield against the reaction time. The reaction order of lactic acid formation with respect to acid m is determined at first by varying the acid concentration as shown in Figure 6.

In the case of aldol condensation, $[\mathrm{CH_3CHO}]$ is approximated by $[\mathrm{CH_3CHO}]_0\exp(-At)$ in the early stage of reaction until the acetaldehyde concentration decreases by ~30%. Thus the integration of eq 7 is expressed as

$$([\mathrm{CH_3CHO}]_{\mathrm{loss}} + 2[\mathrm{CH_3CH{=}CHCHO}])_t = k_{\mathrm{A}}[\mathrm{HCl}]^n \int_0^t [\mathrm{CH_3CHO}]_0^{\,2}\exp(-2At)\,\mathrm{d}t \tag{32}$$

From eq 32, we obtain

$$([\mathrm{CH_3CHO}]_{\mathrm{loss}} + 2[\mathrm{CH_3CH{=}CHCHO}])_t = \frac{k_{\mathrm{A}}[\mathrm{HCl}]^n[\mathrm{CH_3CHO}]_0^{\,2}}{2A}(1-\exp(-2At)) \tag{33}$$

The value of $k_{\mathrm{A}}[\mathrm{HCl}]^n$ is obtained from eq 33 and the experimental plot of the acetaldehyde amount consumed by the aldol condensation against the reaction time. The reaction order of aldol condensation with respect to acid n is determined at first by varying the acid concentration as shown in Figure 6.

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(27) In the present reaction condition, no methane is observed. Thus the decarbonylation of acetaldehyde ($CH_3CHO \rightarrow CH_4 + CO$) is not the cause of low mass balance.

(28) If the polymerization of acetaldehyde is the cause of loss in mass balance, lowering the initial acetaldehyde concentration should improve the mass balance. Indeed, by lowering the acetaldehyde concentration form 0.3 to 0.1 M with the fixed concentrations of formic acid (2.0 M) and HCl (0.3 M), mass balance increased from ∼30 to 42% at 225 °C. Also, in the former study of formaldehyde, an aldehyde without α-hydrogen, no oil formation or sharp reduction of mass balance were observed under acidic hydrothermal condition.[9,13].

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(30) To confirm that lactic acid has no other reactions than the backward reaction of eq 1, we have examined the reaction of 0.1 M of ^{13}C-enriched sodium L-lactate ($CH_3CH(OH)^{13}COONa$) in the presence of HCl (0.6 M) at 225 °C.^{13}C-enriched sodium L-lactate (99 atom % and 20% in H_2O) is obtained from Euriso-top and used as received. Though sodium salt is used instead of lactic acid due to the availability, this difference is trivial in our reaction condition because sodium lactate is converted to lactic acid by the strong acid, HCl. The products after 3 h of reaction are, in the decreasing order: $CH_3CH(OH)COOH$ (56) > CH_3CHO (41) > HCOOH (33) > CO (11) > CH_3COOH (1). The numbers in parentheses are product yields (%); note that the sum of the yield exceeds 100% because a part of lactic acid decomposes to acetaldehyde and formic acid. The sum of formic acid and its decomposition product, carbon monoxide, is almost equal to the acetaldehyde yield. This means that lactic acid first decomposes into acetaldehyde and formic acid and then a part of formic acid decarbonylates to produce carbon monoxide.[8,14] Mass balance is maintained through the reaction within an error of 3%. It is therefore concluded that lactic acid has no other reactions in acidic hydrothermal conditions.

(31) No polymerization of lactic acid occurs in the present reaction condition. The aldol condensation is thus the only cause of the oil formation in the reaction of acetaldehyde with HCl.

(32) In the cross-disproportionation, we confirmed that the reaction is of zeroth order with respect to the acid.

(33) Morooka, S. , Ph D. thesis, Kyoto University, 2008.

(34) The formic acid decarboxylation is not observed in the present reaction condition because the decarboxylation is too slow to be observed in the reaction time scale of our interest. For example, the decarboxylation proceeds in the order of 100 h at 240 °C,[14] and our experiments are in the order of ∼80 min at 250 °C.

(35) Fernández-Prini, R.; Alvarez, J. L.; Harvey, A. H. *J. Phys. Chem. Ref. Data* **2003**, *32*, 903.

(36) The International Association for the Properties of Water and Steam (IAPWS) Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use.

(37) In the determination of $k^{f}_{CC}[HCl]^{m}$, we confirmed that the ratio of the backward reaction to that of forward is less than 5% in the time region of interest.

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