J. Phys. Chem. A **2004,** *108,* 11635−11643

Mechanisms and Kinetics of Acetaldehyde Reaction in Supercritical Water: Noncatalytic Disproportionation, Condensation, and Decarbonylation

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Received: August 27, 2004; In Final Form: October 26, 2004

Noncatalytic reaction pathways and their rates of acetaldehyde were determined in the neat system and in supercritical water at 400 °C and the density of 0.1−0.6 g/cm^3. In supercritical water, acetaldehyde undergoes five types of reactions: (i) decarbonylation into methane and carbon monoxide, (ii) self-disproportionation producing ethanol and acetic acid, (iii) cross-disproportionation generating ethanol and carbonic acid, (iv) condensation forming crotonaldehyde, and (v) the subsequent polymerization of crotonaldehyde or its decarbonylated monomer. Reactions i and iv proceed irrespective of the presence of water, while water suppresses reaction i. Reactions ii and iii are characteristic of aldehyde under hydrothermal conditions. Although reaction ii produces the same products as the classical Cannizzaro reaction, it does not require any added catalysts. Reaction iii manifests the role of formic acid as a reducing aldehyde. Actually, it is shown that reaction iii involves a larger weight than reaction ii and leads to the excess production of ethanol. The rates of these reactions are sensitive to the water density, and path weight control is thus possible through variation of the thermodynamic conditions. New reaction mechanisms are proposed for the present set of high-temperature processes.

Introduction

Unlike ambient water, hot water mixes well with organic compounds. It can thus induce noncatalytic chemical reactions of organics that never take place without acidic, basic, or metallic catalysts under ambient conditions.[1−22] To control hydrothermal reactions in a manner friendly to the earth, we need a systematic investigation on each functional group. Aldehydes are important in laboratorial and industrial processes as solvents and synthetic starting materials. Conventionally, they are transformed in the presence of catalysts into alcohols, carboxylic acids, alkanes, alkenes, acetals, and so on. In particular, it is well-known that alcohols can be prepared from the corresponding aldehydes through hydrogenation, Cannizzaro, or Grignard reaction.[23] Under hydrothermal conditions, detailed information about the noncatalyzed reaction pathways of aldehyde is required for both scientific and industrial purposes. This is one of a series of papers on the noncatalytic reactions of aldehydes in hot water studied by the application of NMR.[19−22] Here, we have attempted to elucidate the reaction kinetics and mechanisms of acetaldehyde in supercritical water.

In our previous communications,[20,22] the simplest aldehyde, formaldehyde, was investigated in subcritical water at 250 °C using a quartz tube that has no catalytic effect. It has been found to undergo two types of noncatalytic disproportionation reactions that are expressed as follows:

$$2\mathrm{R{-}CHO} + \mathrm{H_2O} \rightarrow \mathrm{R{-}CH_2OH} + \mathrm{R{-}COOH} \tag{1}$$

$$\mathrm{R{-}CHO} + \mathrm{H_2O} + \mathrm{HCOOH} \rightarrow \mathrm{R{-}CH_2OH} + \mathrm{H_2O} + \mathrm{CO_2} \tag{2}$$

When R is H, eq 1 is the self-disproportionation of two formaldehydes to generate methanol and formic acid and eq 2 is the cross-disproportionation between formaldehyde and formic acid to produce methanol and carbonic acid ($CO_2 + H_2O$). Equation 2 is called cross-disproportionation because it involves two different kinds of aldehydes; formic acid is hydroxyl aldehyde (HO−CHO). Methanol is actually yielded in excess to formic acid, and its yield reaches as much as ∼70%. The excess generation of methanol was confirmed later also in supercritical water.[7] This is in sharp contrast to the conventional cross-Cannizzaro reaction with *formaldehyde* in the presence of a large amount of base catalyst like OH^-.[23] In the cross-disproportionation in supercritical water, not formaldehyde but *formic acid* has been used to reduce the aldehyde to alcohol and is itself oxidized to carbonic acid, leading to carbon dioxide and water. In addition, it has been shown that the aromatic aldehyde benzaldehyde transforms into benzyl alcohol and benzoic acid at a ratio of 2.5:1.0.[19] In this reaction, formic acid is considered to be produced from benzaldehyde ($R = C_6H_5$) through a two-step reaction represented by eqs 3 and 4:

$$\mathrm{R{-}CHO} \rightarrow \mathrm{R{-}H} + \mathrm{CO} \tag{3}$$

$$\mathrm{CO} + \mathrm{H_2O} \rightarrow \mathrm{HCOOH} \tag{4}$$

The first is the decarbonylation of benzaldehyde, and the second, the assumed conversion of the generated CO to formic acid through hydration.[19,21] The noncatalytic synthesis of formic acid from CO by eq 4 was confirmed recently in subcritical water.[6] It is thus expected qualitatively that the noncatalytic cross-disproportionation reaction pathway expressed as eqs 2−4 is common to the aldehyde family in hot water. However, the reaction is complex enough that it involves the paths given by eqs 1−4 at least (and is proven later to involve more). Further progress can be achieved only through quantitative and comprehensive elucidation of the reaction pathways. For this purpose, it is necessary to focus on an aldehyde with an R group which is simple enough but can be differentiated from the CHO moiety. We pay attention to acetaldehyde, the simplest member of aliphatic aldehydes with α-hydrogen.

10.1021/jp046117h CCC: $27.50 © 2004 American Chemical Society
Published on Web 12/08/2004

Under ambient conditions, it is well-known[23] that the main reaction pathway of acetaldehyde in the presence of base catalysts is the aldol (condensation) reaction:

$$2CH_3CHO \xrightarrow[OH^-]{} CH_3CH(OH)CH_2CHO \rightarrow CH_3CH{=}CHCHO + H_2O \quad (5)$$

In contrast, it has previously been reported in a short communication that acetaldehyde undergoes noncatalytic self-disproportionation (eq 1) and cross-disproportionation (eq 2) and decarbonylation (eq 3) in supercritical water at 400 °C; the products were analyzed only at a long reaction time of 4 h.[21] The condensation products were not detected in the previous observation. It is then considered that the condensation products, acetaldol and crotonaldehyde, are short-time-lived under supercritical water conditions (400 °C) and that the intermediate species are further transformed through decarbonylation like eq 3 and some polymerization. To establish the detailed reaction pathways, here, we have performed a quantitative study by NMR of all the products except solid polymers over a wide range of time. We have attempted to identify the key intermediates in eq 4, CO and HCOOH, and such aldol condensation products as those involved in eq 5. After the reaction, such gaseous products as CH_4, CO, and CO_2 are distributed among the liquid and gas phases in the reaction vessel; CH_4 and CO are exclusively present in the gas phase. Thus, not only liquid-phase products but also gas-phase ones are observed here to elucidate the mechanisms of the noncatalytic reactions of acetaldehyde in supercritical water. Furthermore, the solid polymers are examined on the production mechanism based on the mass balances for carbon and hydrogen.

One of the most important features of hydrothermal reactions is that water behaves as a reactant as well as a solvent, as can be seen in eqs 1, 2, and 4. Indeed, water is a reactive species at high temperatures which readily causes hydration, hydrolysis, and dehydration. As a solvent, supercritical water can stabilize polar transition states by solvation and accelerate noncatalytic reactions.[16,17] Thus, the reaction pathways and rates should be different between the reactions with and without water; this potentiality allows us to enhance a target reaction pathway and suppress the others. The control of competitive reaction pathways is essential for the development of supercritical water chemical engineering. Hence, to elucidate how water affects the titled reactions of acetaldehyde, we compare reaction products and their time dependences with and without water.

Experimental Section

Acetaldehyde (CH_3CHO, 99%) was purchased from Merck Co., and ^{13}C enriched acetaldehyde ($^{13}CH_3{}^{13}CHO$, 99.9%; ^{13}C enrichment, 99.27%) was from ISOTEC Co. They were used without further purification. The ^{13}C enriched acetaldehyde was employed for reliable quantification of carbon monoxide and carbon dioxide by NMR. Water was distilled three times after being ion exchanged by a Milli-Q lab filter (Millipore). Sodium benzoate (99.5%) was obtained from Nacalai, and its solution in D_2O (99.9% D) was used as an external reference for NMR observation. A sealed tube of quartz was used as a vessel for the reaction.

The solution of acetaldehyde in H_2O was loaded in a quartz tube of 1.5 mm i.d. and 3.0 mm o.d. The sample was sealed after the air in the reactor was replaced by argon. The filling factor, which is defined as the ratio of the solution volume to the vessel volume at room temperature, determines the water density under homogeneous supercritical conditions, and it was varied from 0.1 to 0.6. This means that the water density for the supercritical water is 0.1−0.6 g/cm^3. The detailed analysis of the hydrothermal reaction is performed at 0.5 g/cm^3. The solution was prepared under ambient conditions so that the initial concentration of acetaldehyde is set to 0.125 and 0.5 M (M = mol/dm^3) under supercritical conditions. In this scheme, the concentration of a sample under ambient conditions is given by the target concentration under supercritical conditions divided by the filling factor, that is, respectively, 0.25 and 1.0 M for the sample reacted at 0.5 g/cm^3. For comparison, the neat reaction was also examined at 400 °C. In this case, no water solvent was added in the sample and the density of acetaldehyde was set to 0.125 and 0.5 M before the reaction, in accordance with those for the supercritical water reaction.

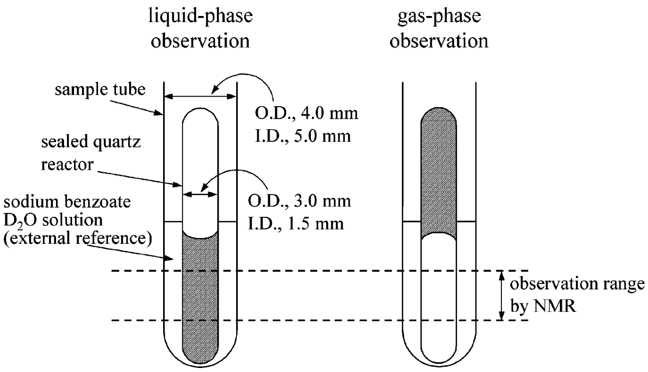


Figure 1. Schematic illustration of the sample setup for the liquid- and gas-phase NMR observations. When the gas phase is measured, the vessel is turned upside down. In this case, the liquid phase stayed at the top due to the surface tension and its interfering signal is absent with a far enough meniscus from the rf coil center.

The reaction temperature was fixed at 400 °C. The sample was put into a programmable electric furnace kept at 400 °C; the temperature was controlled within ±1 °C. In the sample vessel, the system is homogeneous during the reaction. After a reaction time, the sample was removed quickly from the furnace and quenched in a cold-water bath. It took <30 s for the sample to cool. Actually, the time scales for heating and cooling the sample are shorter than those for the reactions at the thermodynamic states of interest. After the sample is cooled, the liquid and gas phases coexist in the sample vessel. The liquid and gas phases were separately subjected to ^1H and ^{13}C NMR measurements at room temperature using ECA400N, ECA400W, and ECA500W (JEOL) through a method illustrated in Figure 1, and the products and residual reactant were quantified. The concentrations of carbon monoxide and carbon dioxide could be determined with precision, since the ^{13}C enriched acetaldehyde was used for their quantification.

Results and Discussion

First, we show what kinds of products are generated in the neat reactions and supercritical water reactions of acetaldehyde according to the ^{13}C and ^1H NMR spectroscopic analyses at a fixed reaction time of 20 min. The identification of the reaction products is followed by the analysis of the time evolution of the reactant and the major and minor products detected at different initial concentrations. The reaction mechanisms of the supercritical water reactions of acetaldehyde are discussed on the basis of the product distributions and rate constants determined.

Neat Reactions. As can be seen in Figure 2a, such gases as methane and carbon monoxide are produced by neat reactions

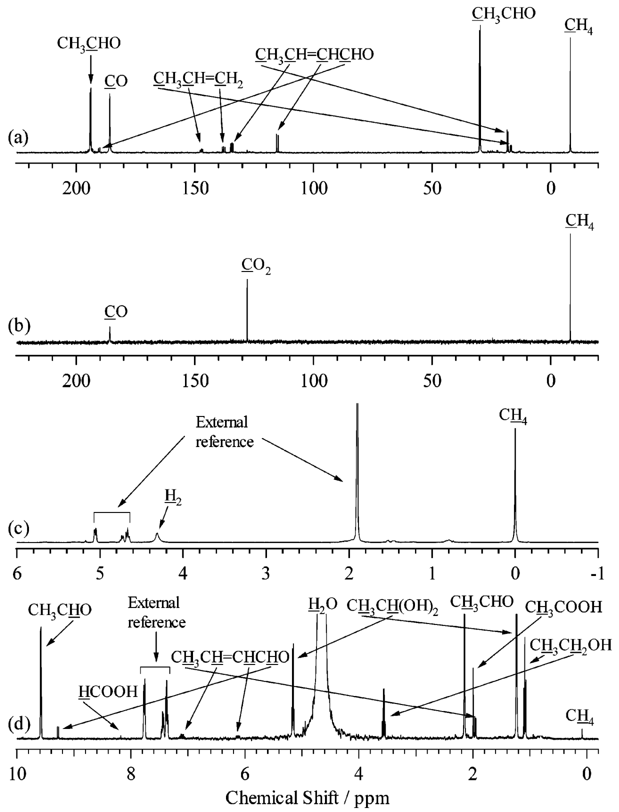


Figure 2. NMR spectra for the reaction products of acetaldehyde after being treated at 400 °C for 20 min. Part a represents the ^{13}C spectrum for the neat reaction without solvent water. Parts b, c, and d represent the gas-phase ^{13}C, gas-phase ^{1}H, and liquid-phase ^{1}H spectra for the reaction in supercritical water at 0.5 g/cm^3, respectively. The acetaldehyde sample used is enriched by ^{13}C in parts a and b and is naturally abundant in parts c and d. The initial concentration is 0.5 M under the reaction conditions. The neat reaction spectrum (a) was obtained by a high-temperature measurement at 150 °C; under these conditions, the sample system is homogeneous. In the ^{1}H spectra, sodium benzoate solution was employed as an external reference for the quantification of the species of interest. $CH_3CH(OH)_2$ is the hydrated form of CH_3CHO and is a reactant.

of acetaldehyde at 400 °C. When no solvent water is added, they are detected as the main products. Thus, the decarbonylation reaction of acetaldehyde proceeds under neat conditions as follows:

$$CH_3CHO \rightarrow CH_4 + CO \qquad (3')$$

The C2 molecule (acetaldehyde) is thermally fragmented into the two C1 molecules without catalysts. In the fragmentation induced by rotational proton transfer, one (methane) is more reduced and the other (carbon monoxide) is more oxidized; this can be called an “intramolecular disproportionation”. For the reaction mechanism, we consider that both the C−C bond scission and the rotational proton transfer from the polarized carbonyl carbon to the methyl carbon take place simultaneously; as a result of the strong coupling of anharmonic vibrations of many degrees of freedom, some vibrations associated with bond formation and breakage can be significantly softened. The concerted proton transfer is expected to be induced by the thermally excited vibration involving the methyl-carbon, carbonyl-carbon, and aldehyde-hydrogen groups at high temperatures. As shown in conventional studies, a homolytic C−C bond-breakage process may be considered because of the presence of such minor products as propane, ethane, ethylene, carbon dioxide, and hydrogen molecules. However, the total yields of these minor products are negligible and below 10% at 60 min in the neat reaction at 0.125 and 0.5 M, respectively.

The reaction mechanism considered on the basis of the experimental observation is in conformity with the optimized structure of the transition state elucidated by the recent ab initio molecular orbital calculation of the singlet-state potential energy surface (S_0).[24,25] The bond scission is possible without resorting to an intersystem crossing to the triplet state (T_1); some radical mechanisms can be realized however photochemically. The reaction mechanism is thus not radical but ionic irrespective of the presence of water. This seems to be characteristic of aldehydes; see the mechanistic transition from the radical to the ion in the study of the hydrolysis of *tert*-butyl chloride as a consequence of the increase in the density (hydration) of supercritical water.[26] It has been revealed that the motion along the reaction coordinate from the reactant to the transition state essentially involves two motions; one is the rotation of H around the carbonyl carbon toward the methyl carbon, and the other is the simultaneous C−C bond elongation. It is therefore concluded that the decarbonylation of acetaldehyde is induced by the thermal excitation of concerted vibrations as mentioned above.

As shown in Figure 2a, some other byproducts are detected. They are crotonaldehyde and propene produced by the following reactions:

$$2CH_3CHO \rightarrow (CH_3CH(OH)CH_2CHO) \rightarrow CH_3CH{=}CHCHO + H_2O \qquad (5')$$

$$CH_3CH{=}CHCHO \rightarrow CH_3CH{=}CH_2 + CO \qquad (3'')$$

Crotonaldehyde is generated by the quick dehydration reaction of acetaldol which is formed by the bimolecular thermal condensation of acetaldehyde without any base catalysts. Furthermore, crotonaldehyde is decarbonylated to propene and carbon monoxide, as is the parent aldehyde. The condensation is considered to take place in an acetaldehyde dimer with their aldehyde-group planes in parallel and their dipoles antiparallel. The condensation mechanism must be unique and different from the ordinary one that requires a base catalyst and solvent to generate the carbanion under ambient conditions.[23] The intermolecular C−C bond is formed accompanying the proton transfer from the methyl carbon in one aldehyde to the polarized carbonyl oxygen in the other. In a sense, this is similar to the mechanism of the intramolecular disproportionation mentioned above. The concerted proton transfer is expected to be induced by the thermal excitation of strongly coupled vibrations of H−C−C=O in the dimer at high temperatures; a key role is played by the acidic character of carbonyl α-protons.

The products discussed above can be compared with those reported for the neat reaction undergone in a silica vessel at 523 °C at a pressure much lower than the atmospheric.[27,28] Hydrogen, acetone, ethane, ethylene, and carbon dioxide were reported to be formed as minor products from the methyl and formyl radicals produced by the homolytic decomposition of acetaldehyde. According to the radical chain mechanism proposed, the stable main products can be considered to be methane and carbon monoxide. The products reported correspond to our products except for acetone. The absence of the condensation products, crotonaldehyde and propene, can be explained by considering the marked effect of the initial concentration on the intermolecular reaction. We confirmed that the yields of the condensation products are reduced by ~70%

as the initial concentration of acetaldehyde decreases from 0.5 to 0.125 M. This indicates that the bimolecular reaction, condensation, is suppressed by the decrease of the initial concentration of acetaldehyde, which leads to the lowering of the yield of propene. Although acetone was reported in the previous work[27,28] as the low-yield product according to the gas-chromatographic analysis, it was not detected in this work. In conclusion, there are two types of thermal reaction pathways of acetaldehyde, decarbonylation and condensation. The former is a unimolecular bond-breaking reaction, whereas the latter is a bimolecular bond-forming reaction. Thus, the weight of these reaction pathways is dependent significantly on the initial concentration of acetaldehyde.

Hydrothermal Reactions. Now, we examine how the reaction products are modified by the presence of hot water. As can be seen in Figure 2b−d, the products are generated in the following decreasing order: methane > carbon dioxide > hydrogen > carbon monoxide > ethanol > crotonaldehyde > acetic acid > formic acid. Methane is produced in the largest amount. This indicates that the decarbonylation of acetaldehyde (eq 3′) proceeds also in supercritical water through the mechanism of intramolecular disproportionation considered for the neat reaction. It is to be noted, however, that carbon dioxide as well as carbon monoxide is formed in supercritical water. In a separate experiment, we confirmed that acetic acid is stable at 400 °C; that is, neither CO_2 nor methane is produced by the high-temperature treatment of acetic acid under the present conditions. The emergence of carbon dioxide and hydrogen and the relative deficiency of carbon monoxide can be explained by the conversion to formic acid and its decomposition into carbon dioxide and hydrogen as follows:

$$CO + H_2O \rightarrow HCOOH \tag{4}$$

$$HCOOH \rightarrow CO_2 + H_2 \tag{6}$$

In a recent study,[6] we found that formic acid is formed as an intermediate product of the water-gas-shift reaction.

In the supercritical water reaction, carbon dioxide, ethanol, acetic acid, and formic acid are generated in addition to the products of the neat reaction mentioned above, but propene is not observed. The presence of ethanol and acetic acid shows that the noncatalytic bimolecular self-disproportionation reaction between acetaldehyde and its hydrated form takes place in supercritical water as follows:

$$\begin{aligned} 2CH_3CHO + H_2O &\rightarrow [CH_3CH(OH)_2 + CH_3CHO] \\ &\rightarrow CH_3CH_2OH + CH_3COOH \end{aligned} \tag{1′}$$

Here, it is speculated that the hydrated form (1,1-ethanediol) of acetaldehyde is involved in the noncatalytic disproportionation. The disproportionation reaction, where the one reactant is reduced and the other is oxidized, is achieved by the simultaneous transfers of H from CH_3CHO to $CH_3CH(OH)_2$ and OH from $CH_3CH(OH)_2$ to CH_3CHO; the dimer would be formed with the methyl groups facing in the opposite directions. Rotational proton transfer and softening of coupled vibrations play a key role in controlling the noncatalytic disproportionation in supercritical water, as in the case of the aldol condensation in the neat reaction.

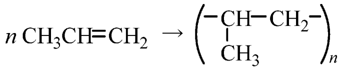
As can be seen in Figure 1d, however, ethanol is produced as ∼3 times as large as acetic acid, in sharp contrast to the 1:1 alcohol/acid ratio in the self-disproportionation reaction. This implies that ethanol production involves another reaction pathway in addition to the self-disproportionation of acetaldehyde. The additional production can be made possible by the cross-disproportionation reaction given by

$$\begin{aligned} &CH_3CHO + \\ &\quad H_2O + HCOOH \rightarrow [CH_3CH(OH)_2 + HCOOH] \\ &\qquad \rightarrow [CH_3CH_2OH + HOCOOH] \\ &\qquad \rightarrow CH_3CH_2OH + CO_2 + H_2O \end{aligned} \tag{2′}$$

Formic acid, the hydroxyl “aldehyde”, reduces the hydrated form (1,1-ethanediol) of acetaldehyde to ethanol and is itself oxidized to carbon dioxide. This implies that formic acid is a stronger reducing reagent than acetaldehyde in hot water. The reaction requires water; water behaves as a reactant as well as a solvent. The mechanism is presumed to be the simultaneous transfers of H from HCOOH to $CH_3CH(OH)_2$ and OH from $CH_3CH(OH)_2$ to HCOOH like the self-disproportionation.

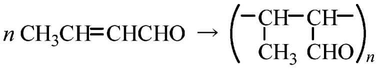
The two types of disproportionation reactions are common to other aldehydes in hot water. In recent studies,[19,20,22,29] we found that formaldehyde and benzaldehyde are transformed into the corresponding alcohol and carboxylic acid without any catalysts; the alcohols are yielded in excess to the carboxylic acids. This indicates that the simultaneous transfers of H and OH take place for any type of aldehyde including aromatic. Formaldehyde is more reactive for the disproportionations than the other aldehydes. This is consistent with the higher population of the hydrated form in the hydration equilibrium.

Crotonaldehyde is generated as a minor product as in the case of the neat reaction. This indicates that the proton transfer required for condensation can be activated irrespective of the presence of water in the vicinity of the acetaldehyde dimer. The sum of carbon monoxide and carbon dioxide generated is larger in amount than methane. Thus, carbon monoxide is produced also by the decarbonylation of crotonaldehyde as in the neat reaction. In the supercritical water reaction, however, the decarbonylation product, propene, was not observed. This suggests that the decarbonylation product further transforms readily into a polymeric one such as polypropylene through the following reaction:

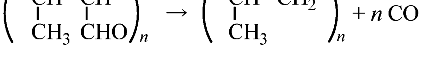


$$n\,CH_3CH{=}CH_2 \rightarrow \left(-\underset{\displaystyle CH_3}{CH}-CH_2-\right)_n \tag{7}$$

The polymerization is considered to take place also by crotonaldehyde; the polymer contains carbonyl groups and can be decarbonylated by the following reactions:



$$n\,CH_3CH{=}CHCHO \rightarrow \left(-\underset{\displaystyle CH_3}{CH}-\underset{\displaystyle CHO}{CH}-\right)_n \tag{8}$$



$$\left(-\underset{\displaystyle CH_3}{CH}-\underset{\displaystyle CHO}{CH}-\right)_n \rightarrow \left(-\underset{\displaystyle CH_3}{CH}-CH_2-\right)_n + n\,CO \tag{9}$$

The time dependence of the amount of these polymers will be discussed later in a quantitative manner.

All reaction pathways of acetaldehyde in supercritical water in the absence of catalysts can be summarized as in Figure 3. Acetaldehyde can have four types of reaction pathways, such as decarbonylation, self- and cross-disproportionations, and condensation, in supercritical water. The competitive reaction scheme is further confirmed below quantitatively on the basis of the time evolution.

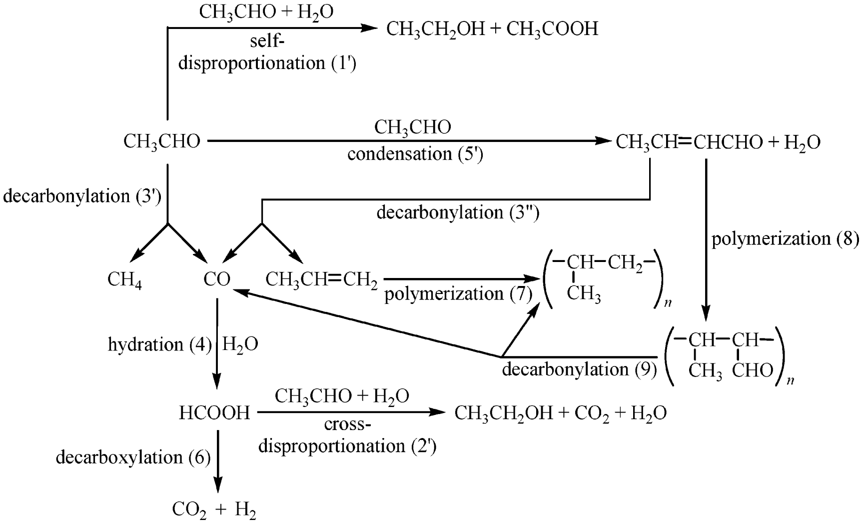


Figure 3. Noncatalytic reaction pathway of acetaldehyde in supercritical water. The numbers in parentheses denote the equation numbers of the reactions in the text.

Time Evolution of Products and Kinetic Analysis. We can confirm the reaction schemes considered above by inspecting how the concentrations of acetaldehyde and the products vary with time in the neat and supercritical water reactions. As shown in Figure 3, there are two types of neat reaction pathways of acetaldehyde, decarbonylation and condensation; the former and the latter are uni- and bimolecular reactions, respectively. The weights of the reaction pathways are therefore expected to be dependent on the concentration of acetaldehyde. We examine the time evolution of acetaldehyde and its products at different initial concentrations of 0.125 and 0.5 M. As can be seen in Figure 4a and b, the increase of the initial concentration spreads the distribution of the products. Such decarbonylation products as carbon monoxide and methane are generated equally at the lower initial concentration, whereas the former is more than the latter at the higher initial concentration. The yields of carbon monoxide and methane are indeed nearly equal (within an error of ~10%) to the amount of decreased acetaldehyde. The excess carbon monoxide is due to the decarbonylation of the condensation product, crotonaldehyde. The production of crotonaldehyde and propene is evidently enhanced by the increase of the initial concentration, as expected. The enhancement of the condensation leads to the relative decrease of the methane production, as can be seen from Figure 4b.

Carbon monoxide is produced by the decarbonylation reactions of both acetaldehyde and crotonaldehyde. This is why the amount of carbon monoxide is the largest (see Figure 4a and b) and why the yield of carbon monoxide is equal to the sum yield of methane and propene. At the higher initial concentration, however, the sum decreases by ~20% due to such reactions as polymerization and transformation to minor products involved. Thus, the total mass in the gas and liquid phases is kept constant at low concentrations but not at high concentrations.

To see how the weights of the reaction pathways and the rates are modified by hot water, we compare the time evolutions with and without water at a low (0.125 M) and a high (0.5 M) initial concentration (Figure 4c and d). The yield of methane as the main product is reduced by the presence of water; the yield at 60 min is ~35% in the neat reaction, whereas it is ~25% in the supercritical water reaction whatever the concentration of aldehyde. This can be caused by the suppression of the reactive vibrating mode by water. If only the decarbonylation takes place as in the neat reaction, methane and carbon monoxide should be equally generated. However, carbon monoxide is converted into carbon dioxide and hydrogen in hot water. As discussed below, this is caused by the transformation of carbon monoxide into formic acid (eq 4) followed by the decomposition to carbon dioxide (eq 6).[6]

The slowdown of the decarbonylation of acetaldehyde induced by water can be quantitatively shown by a comparative study of the rate constants with and without water. At the lower initial concentration, the rate constant for the single decarbonylation path can be determined; see Figure 4a and c. The first-order rate constants listed in Table 1 are determined by monitoring the concentrations of (i) methane, (ii) the sum of carbon monoxide and carbon dioxide, or (iii) acetaldehyde; among these methods, the first one (i) is the most reliable. The rate constant is found to be reduced by a factor of ~0.6 by the presence of water. The value calculated by the decrease of acetaldehyde is somewhat larger than those estimated on the basis of methane and carbon monoxide. This is caused by the slight contributions of condensation and disproportionation.

To elucidate the mechanism of the conversion of carbon monoxide to carbon dioxide in supercritical water, we normalize their time-dependent yields by that of methane at the low and high concentrations; see Figure 5. Assume that only acetaldehyde is subjected to the decarbonylation and that the decarbonylation product, carbon monoxide, is quickly transformed into carbon dioxide via formic acid, as seen in eqs 4 and 6. Under these assumptions, the decrease in carbon monoxide should be symmetric to the increase in carbon dioxide and the sum of the normalized yield is equal to unity. Especially, the normalized yields for carbon monoxide and carbon dioxide are equal to zero and unity, respectively, in the long-time (equilibrium) region (>120 min). At the lower concentration, this is the case. The evolution of carbon dioxide is almost symmetric to the depletion of carbon monoxide. Thus the rate of the conversion of carbon monoxide to carbon dioxide is indeed fast. Strictly speaking, however, the long-time yield of carbon dioxide slightly and significantly exceeds unity, respectively, at the low and high concentrations, as an indication of the contribution of the decarbonylation other than the parent molecule, acetaldehyde; crotonaldehyde makes such a contribution (see eqs 3″ and 9). The time scale of the conversion of carbon monoxide to carbon dioxide explains why the carbon monoxide is not observed in the previous study,[21] as mentioned in the Introduction. As can be seen in Figures 4 and 5, a reaction time of 4 h used for the analysis is long enough for the complete

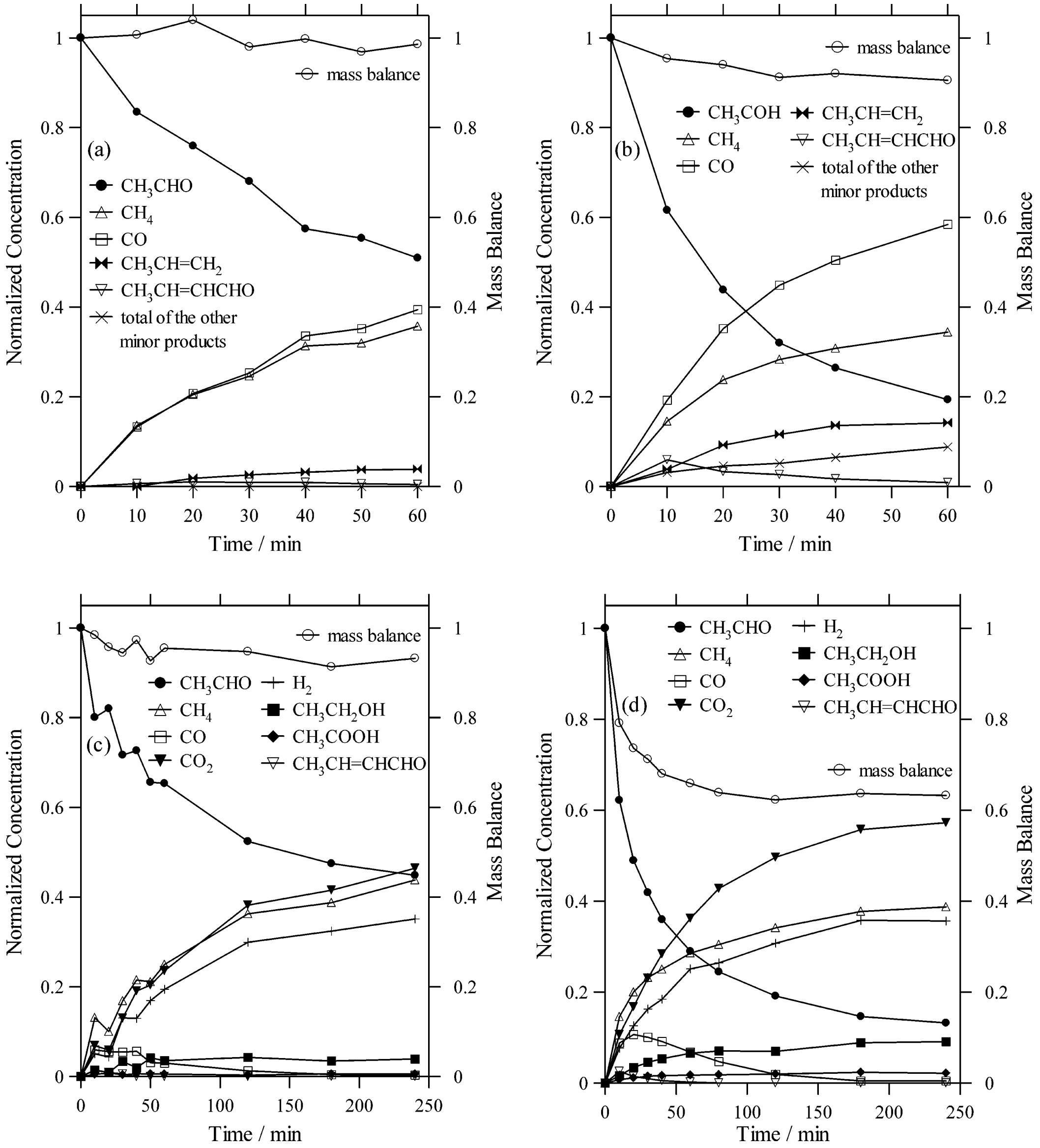


Figure 4. Time evolution of the concentrations of acetaldehyde and the products treated at 400 °C. Parts a and b represent the neat reaction at initial concentrations of 0.125 and 0.5 M, respectively. Parts c and d represent the hydrothermal reaction at a water density of 0.5 g/cm^3 and initial concentrations of 0.125 and 0.5 M, respectively. The normalized concentration denotes the concentration of the compound of interest divided by the initial concentration of acetaldehyde. The proton mass balance denotes the ratio of the hydrogen amount in acetaldehyde and the products except H_2 at a specified reaction time to the initial amount in acetaldehyde. The exception of H_2 is because its hydrogen atom is the water origin.

TABLE 1: Rate Constants of the Decarbonylation of Acetaldehyde under Neat and Hydrothermal Conditions at 400 °C and 0.5 g/cm^3

	rate constant/s^{-1}	
compound used for calculation	neat	hydrothermal
methane	1.6×10^{-4}	8.8×10^{-5}
carbon monoxide	1.7×10^{-4}	9.7×10^{-5}[a]
acetaldehyde	2.1×10^{-4}	1.4×10^{-4}

[a] The rate constant was calculated by the sum of carbon monoxide and carbon dioxide.

conversion. Thus, both carbon monoxide and the intermediate, formic acid, were not observed there.

Although the decarbonylation discussed above is a first-order reaction, the self- and cross-disproportionations are considered to be second-order ones; see the reaction scheme in Figure 3 and the rate equations (eqs 13 and 14) in the Appendix. The higher reaction order of the disproportionations is indicated by the strong dependence of the ethanol production on the concentration of acetaldehyde, as can be seen in Figure 4c and d. Ethanol is generated more than acetic acid. This is because ethanol is produced by both the self- and cross-disproportionations. It is interesting to see which pathway is more important in the ethanol production. This can be elucidated by analyzing the ratio of ethanol to acetic acid; acetic acid is generated only from the self-disproportionation. The production ratio of ethanol/acetic acid is increased during the course of the reaction time. The ratio is ~2 at the shortest time (10 min) and ~4 at the longest (240 min). The rate law and kinetic analyses are presented in the Appendix, and the cross-disproportionation is found to be faster than the self-disproportionation. The rate constant of the cross-disproportionation (k_c) is larger than that of the self-disproportionation (k_s), and the cross-disproportionation is more important even though the concentration of formic acid is much lower than that of acetaldehyde. The larger reactivity of formic acid than acetaldehyde can be explained by considering that the hydroxyl group on the carbonyl carbon intensifies the polarization of formic acid and stabilizes the negative partial charge in the transition state. The larger

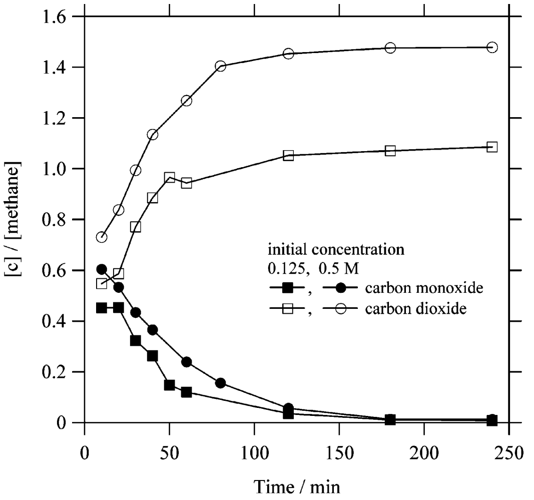


Figure 5. Time dependence of the concentrations of carbon monoxide and carbon dioxide normalized by the methane concentration at initial acetaldehyde concentrations of 0.125 and 0.5 M in supercritical water at 400 °C and 0.5 g/cm^3. [c] denotes the concentration of carbon monoxide or carbon dioxide.

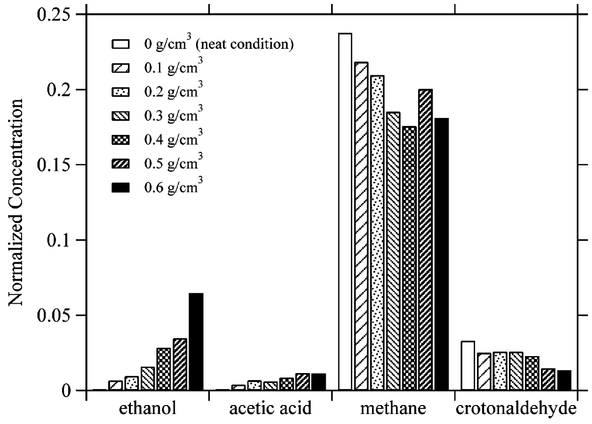


Figure 6. Product concentrations in various water densities at a fixed supercritical temperature of 400 °C, reaction time of 20 min, and initial concentration of 0.5 M. The normalized concentration denotes the concentration of the compound of interest divided by the initial concentration of acetaldehyde.

contribution of the cross-disproportionation with formic acid is common to other aldehydes.[19,21,29] For example, in the case of formaldehyde, the rate constants of the self- and cross-disproportionations are respectively determined as 1×10^{-4} and 1×10^{-3} M^{-1} s^{-1} at 225 °C on the water saturation curve.[29]

The self- and cross-disproportionation reactions require water as a reactant as well as a solvent, as shown in eqs 1′ and 2′. Therefore, they are expected to be enhanced as the supercritical water density is increased, in contrast to the decarbonylation of acetaldehyde. We examine the water density dependence of the product yields at fixed parameters of a supercritical temperature of 400 °C, reaction time of 20 min, and initial concentration of 0.5 M. As can be seen in Figure 6, the yields of ethanol and acetic acid increase with the water density, whereas those of methane and crotonaldehyde show decreasing tendency. The increasing rate of ethanol is larger than that of acetic acid; the yield ratio change by the density elevation from 0.1 to 0.6 g/cm^3 is ~10 for ethanol, whereas it is ~3 for acetic acid. This indicates that both the self- and cross-disproportionations are accelerated. Furthermore, the production ratio of ethanol/acetic acid is increased to ~6 from ~2 by the density elevation. Thus, the importance of the cross-disproportionation increases as the water density is elevated. This is considered to be caused since the hydration of carbon monoxide into formic acid is promoted with water density. On the other hand, the yield of methane seems to be constant in the medium densities of 0.3−0.6 g/cm^3.

Before going to the conclusion, now we consider a remaining problem concerning the relation between the polymerization of crotonaldehyde and its decarbonylation. The solid polymer formed was not identified here[30] but can be estimated according to the ^{1}H and ^{13}C NMR measurements for the other products detected in the gas and liquid phases by assuming the mass balances for carbon and hydrogen. As can be seen in Figure 4d, the total mass (hydrogen-based) obtained by the NMR measurements decreases steeply in the early reaction stage (<80 min) due to the polymerization of crotonaldehyde. The amount of polymerized crotonaldehyde can be obtained by using the following quantities expressed in terms of the monomer unit:

$$A = \frac{(4[\mathrm{CH_3CHO}]_0 - y)}{8} \tag{10}$$

where

$$y = \sum [j] n_j \tag{11}$$

and

$$B = [\mathrm{CO}] + [\mathrm{CO_2}] - [\mathrm{CH_4}] \tag{12}$$

Here, [j] denotes the molar (M) concentration of the species j; for example, $[\mathrm{CH_3CHO}]_0$ is the initial concentration of acetaldehyde. The quantity n_j denotes the number of hydrogen atoms contained in the detected species j; for example, n_j is taken to be 8 (not 6) for the monomer unit (crotonaldehyde) because of the release of one molecule of water. The quantity A indicates the amount of polymerized crotonaldehyde (see eqs 7 and 8) determined by the undetected hydrogen atoms, expressed in terms of two acetaldehydes. The amount of polymers without aldehyde groups can also be computed from the gas products (carbon-based), as shown by the quantity B in eq 12. Since carbon monoxide is produced by the decarbonylation reactions of acetaldehyde, crotonaldehyde, and its polymer and since CO is converted to CO$_2$, the sum of CO and CO$_2$ subtracted by CH$_4$ is equal to the amount of the solid polymers decarbonylated. The quantity A is always larger than or equal to the quantity B. In the limits of the complete decarbonylation, A and B are equal.

To examine how the polymers mentioned above are produced, we plot A and B calculated from Figure 4d (the initial acetaldehyde concentration is 0.5 M, and the water density is 0.5 g/cm^3) against time for comparison in Figure 7. The curve for A initially rises and reaches a plateau after a long enough time to consume the monomer, crotonaldehyde. Since A includes all kinds of polymers irrespective of decarbonylation, in fact, A is larger than B, until they finally become equal. Their agreement implies that the decarbonylation from polymers is completed; a variety of polymers are finally reduced to polypropylene.

Conclusions

We have found that acetaldehyde in supercritical water undergoes such new reactions as noncatalytic self- and cross-disproportionations, condensation, and decarbonylation. The decarbonylation generates carbon monoxide, which is transformed into formic acid in the presence of water, and formic acid, hydroxyl aldehyde, which is subjected to the cross-

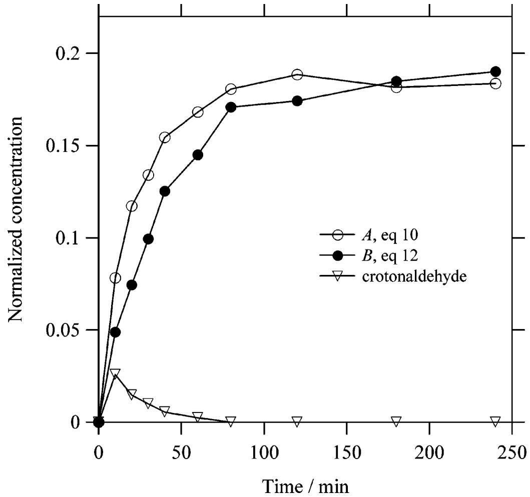


Figure 7. Time evolution of the amount of polymerized crotonaldehyde (quantity *A*), polymers without aldehyde groups (quantity *B*), and crotonaldehyde.

disproportionation. Supercritical water acts as a reactant as well as a solvent in the self- and cross-disproportionations.

In the self- and cross-disproportionations, ethanol production is found to be increased with an increase in the supercritical water density or initial concentration of acetaldehyde. Acetic acid is produced only through the self-disproportionation, and the production ratio of ethanol/acetic acid exceeds 2. This is a clear indication of the higher reactivity against acetaldehyde of formic acid (cross-disproportionation) than that of acetaldehyde (self-disproportionation). The dimer of acetaldehyde, where the carbonyl groups face in opposite directions, is considered for the interpretation of the reaction mechanism. The disproportionation reactions are achieved by the simultaneous rotational transfers of H from CH_3CHO or HCOOH to $CH_3CH(OH)_2$ and OH from $CH_3CH(OH)_2$ to CH_3CHO or HCOOH. Softening of coupled vibrations and simultaneous rotational proton transfer play a key role in controlling the noncatalytic disproportionation.

The bimolecular condensation reaction leading to crotonaldehyde can take place even in the absence of catalysts and solvent water. For the reaction mechanism, a dimer of acetaldehyde with antiparallel dipoles is considered to be formed, in contrast to the conventional idea about a complex between the catalyst-induced carbanion and the positively polarized carbonyl carbon. The concerted proton transfer from the methyl carbon in one aldehyde to the polarized carbonyl oxygen in the other is expected to be induced by the thermal excitation of strongly coupled vibrations of H−C−C=O in the dimer at high temperatures.

The decarbonylation and condensation occur even under neat gas conditions. For these reactions, not a radical but an ionic reaction mechanism is concluded here. The presence of solvent water decelerates the decarbonylation of acetaldehyde; the rate constant decreases by a factor of 0.6. This is caused by the suppression of the low-frequency concerted motion corresponding to the reaction coordinate for the simultaneous C−C bond scission and rotational proton transfer from the aldehyde group to the methyl group. Thus, the bond-breaking in acetaldehyde is not simply pyrolytic. The reaction pathways found here are in sharp contrast to the conventional notion that high-temperature reactions in the absence of solvent are essentially radical-based.

Acknowledgment. This work was supported by the Grant-in-Aid for Scientific Research 15205004 from Japan Society for the Promotion of Science and by the Grant-in-Aid for Creative Scientific Research 13NP0201 and the Grant-in-Aid for Scientific Research on Priority Area 15076205 from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Appendix: Kinetic Equations

As can be seen in Figure 3, acetaldehyde undergoes two types of ethanol production reactions; one is the self-disproportionation and the other is the cross-disproportionation with formic acid. In this appendix, we show through an estimate of relative rate constants based on the rate equations that the cross-disproportionation reaction is faster than the self-disproportionation. The rate equations for the production of ethanol and acetic acid are expressed as follows:

$$\frac{\mathrm{d}[\mathrm{CH_3CH_2OH}]}{\mathrm{d}t} = k_\mathrm{s}[\mathrm{CH_3CHO}]^2 + k_\mathrm{c}[\mathrm{CH_3CHO}][\mathrm{HCOOH}] \tag{13}$$

$$\frac{\mathrm{d}[\mathrm{CH_3COOH}]}{\mathrm{d}t} = k_\mathrm{s}[\mathrm{CH_3CHO}]^2 \tag{14}$$

where k_s and k_c represent the rate constants of the self- and cross-disproportionations, respectively. Thus, the production ratio of ethanol to acetic acid can be expressed as follows:

$$\frac{[\mathrm{CH_3CH_2OH}]}{[\mathrm{CH_3COOH}]} = \frac{\int_0^t \mathrm{d}t(k_\mathrm{s}[\mathrm{CH_3CHO}]^2 + k_\mathrm{c}[\mathrm{HCOOH}][\mathrm{CH_3CHO}])}{\int_0^t \mathrm{d}t(k_\mathrm{s}[\mathrm{CH_3CHO}]^2)} \tag{15}$$

Since the concentration of formic acid is much smaller than that of acetaldehyde during the course of the reaction time ($[\mathrm{HCOOH}] \ll [\mathrm{CH_3CHO}]$), eq 15 can be transformed into the following inequality as expressed by the ratio of the rate constants:

$$\begin{aligned}\frac{[\mathrm{CH_3CH_2OH}]}{[\mathrm{CH_3COOH}]} &<< \frac{\int_0^t \mathrm{d}t(k_\mathrm{s}[\mathrm{CH_3CHO}]^2 + k_\mathrm{c}[\mathrm{CH_3CHO}]^2)}{\int_0^t \mathrm{d}t(k_\mathrm{s}[\mathrm{CH_3CHO}]^2)} \\ &= 1 + \frac{k_\mathrm{c}}{k_\mathrm{s}}\end{aligned} \tag{16}$$

From Figure 4d, it is seen that the yield ratio of ethanol/acetic acid is 2−4 throughout the observed reaction time. Thus, the rate constant ratio ($k_\mathrm{c}/k_\mathrm{s}$) is much larger than 1−3. This is a clear indication of the larger rate constant of the cross-disproportionation (k_c) than that of the self-disproportionation (k_s).

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(30) At the concentrations studied here, solid polymers could not be analyzed by NMR because of the small amount. When the initial concentration of acetaldehyde was increased to 1 M, however, yellow liquid polymers were produced to an observable amount. In the broad ^{1}H spectrum, there are observed protons attached to olefinic (6.5−7.1 ppm) and saturated (0.5−3.0 ppm) carbons; correspondingly, the broad ^{13}C spectrum indicates the presence of olefinic (114−150 ppm) and saturated (6−55 ppm) carbons. The polymers thus produced are considered to be generated at the high concentration by consecutive condensation reactions followed by decarbonylation. Thus, at the lower concentrations of our interest, the polymerization schemes given by eqs 7−9 are reasonable on the basis of the mass balance.