Selected Paper

Hot Water Induces an Acid-Catalyzed Reaction in Its Undissociated Form

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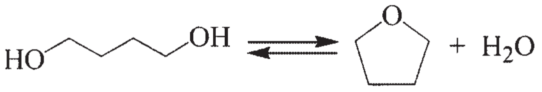
Hot water in its undissociated form has been kinetically proven to induce a chemical reaction that does not undergo under ambient conditions in the absence of a strong acid. The water-induced and acid-catalyzed rate constants were separately determined for the dehydration of 1,4-butanediol by varying the oxonium ion (H^+) concentration. It was found on the kinetic level over a wide range of temperature from moderate to supercritical that the undissociated form of water promotes the reaction at an effective acid concentration of 10^{-4}–10^{-6} M. A strong density dependence of the reaction rate constant was further observed under supercritical condition, and is related to the anomalous temperature dependence of the rate constant near the critical point.

Hot water has attracted much attention recently as a novel solvent for chemical processes of synthetic, environmental, or geological importance and as an environmentally benign alternative to harmful organic solvents.[1–20] Unlike ambient water, water under hydrothermal conditions mixes well with organic compounds. It also acts as a noncatalytic medium to often induce a chemical reaction that does not proceed without acidic or basic catalysts on a practically accessible time scale under ambient conditions. The noncatalytic reactivity in water under hydrothermal conditions is often presumed to be a catalytic effect of H^+ or OH^- produced by the autoprotolysis of water. Indeed, the ion product of water increases with the change of the thermodynamic state from ambient to hydrothermal, and $[H^+]$ and $[OH^-]$ grow correspondingly by one to two orders of magnitude.[21] On the other hand, the reaction rate constant is generally a strong function of the thermodynamics state, and $[H^+]$ or $[OH^-]$ may not be the sole factor to govern the reaction rate variation upon temperature elevation. Thus, quantitative kinetic measurements are necessary to identify the role of H^+ or OH^- in a noncatalytic reaction in hot water. In this paper, we focus on a model ether reaction under hydrothermal conditions, and scrutinize the contribution of H^+ in the noncatalytic kinetics.

The model chemical reaction treated in the present work is the conversion between 1,4-butanediol and tetrahydrofuran (THF), expressed as Scheme 1. The forward reaction is dehydration and the backward one hydrolysis. This reaction is a simplest reaction involving ether bonding. The ether bonding is a building component of coal and cellulose, and its reaction under hydrothermal conditions is important from energy and food concerns. Furthermore, the dehydration process in Scheme 1 is of synthetic utility for preparing an industrially important solvent, THF. Under ambient conditions, it is well known that both the forward and backward reactions in Scheme 1 need acid or metal catalysts.[22–25] In contrast, many ether reactions, including Scheme 1, are found to proceed under hydrothermal conditions without adding acids from outside.[2–5,7,13,16,18] Our purpose is to perform detailed kinetic analyses on the model reaction given by Scheme 1, rather than to add another example of noncatalytic reaction in hot water.



Scheme 1. Reaction of interest.

Our kinetic analysis of Scheme 1 is based on a general expression for the reaction rate constant of an acid-catalyzed reaction. When the concentration of the oxonium ion is $[H^+]$, the observed rate constant k_{obs} of an acid-catalyzed reaction is expressed as

$$k_{obs} = k_{water} + k_{acid}[H^+], \tag{1}$$

where k_{water} is the first-order rate constant under the hypothetical condition that H^+ is absent in the aqueous system, and k_{acid} is the second-order rate constant in the presence of H^+. A schematic illustration of Eq. 1 near $[H^+] = 0$ is given in Fig. 1. As illustrated, it should be emphasized that k_{water} is the limiting intercept in Eq. 1. Since H^+ is always present due to the autoprotolysis of water, $[H^+] = 0$ needs to be hypothetically set to define k_{water}. In the following, k_{water} and k_{acid} are called the water-induced and acid-catalyzed rate constants, respectively.[26] In a typical acid-catalyzed reaction at room temperature, k_{water} is too small to be detected on the practical time scale of seconds to days. In this case, k_{obs} is dominated by the second term of Eq. 1 and appears to be proportional to $[H^+]$. In contrast, when the undissociated form of water becomes kinetically manifest on a practically accessible time scale, the water-induced term k_{water} will be appreciably different from zero. A nonzero intercept is to be revealed, as illustrated in Fig. 1, in the plot of k_{obs} against $[H^+]$. On the basis of this idea, we determine both k_{water} and k_{acid} for the model reaction as functions of temperature by varying $[H^+]$ in the low-concentration range. The role of water as a solvent can then be clarified by decomposing k_{obs} into the k_{water} and k_{acid} terms at neutral (nonacidic) conditions, where no acid is added from outside and only the oxonium ion by the autoprotolysis of water is present. The determination of both k_{water} and

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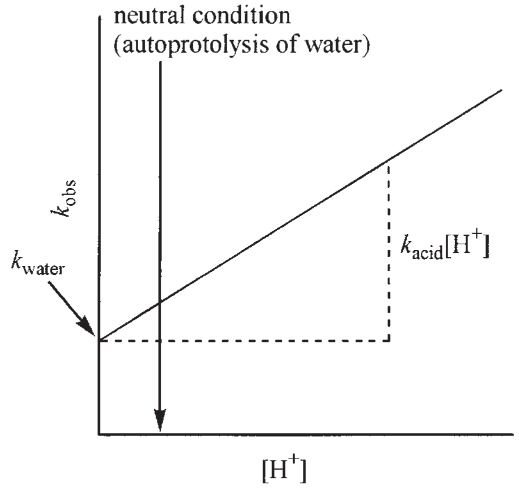

Fig. 1. Schematic illustration of the dependence of the observed rate constant k_{obs} on the oxonium ion concentration $[H^+]$ for an acid-catalyzed reaction. k_{water} is the limiting intercept under the hypothetical condition that H^+ is not present in the system. The acid-catalyzed part $k_{acid}[H^+]$ is proportional to $[H^+]$.

k_{acid} is possible under hydrothermal conditions since the water-induced path is thermally accelerated to a practically accessible rate.

The determination of the rate constant of a chemical reaction in hot water is often based upon a multistep kinetic scheme to fit the observed reaction profile. On the other hand, our model reaction given by Scheme 1 is suitable to single out the kinetic effect of H^+. It is found to involve no side reaction even when an acid is added from outside, and a simple kinetic analysis is possible with minimal reference to the detailed mechanism. In this paper, we present a kinetic analysis of the model reaction based on Eq. 1. An analysis based on Eq. 1 was also performed by Narayan and Antal for the dehydration of 1-propanol and by Taylor et al. for the hydrolysis of *tert*-butyl methyl ether.[3,4] They determined the dependence of the rate constant on the H^+ concentration and argued that the reaction is acid-catalyzed. We reveal, by using Eq. 1, that the reaction of interest is mainly water-induced. When the effect of an acid catalyst is to be examined, it is desirable to fix the thermodynamic state. Since the chemical reaction rate constants are generally strong functions of the temperature and pressure of the system, it is misleading to change the thermodynamic state in a discussion of the effect of the $[H^+]$ variation.

Experimental

The forward and backward reactions of Scheme 1 were studied kinetically under neutral and acidic conditions at temperatures of 150, 200, 240, 270, and 290 °C on the liquid branch of the saturation curve of water. In the kinetic measurements under acidic conditions, $[H^+]$ was controlled by adding HCl. The concentration of HCl was on the order of 10^{-4}–10^{-3} M (M = mol dm^{-3}), and HCl is fully dissociated in the temperature and concentration range of interest.[21,27] Nitric acid was also used to provide H^+ at 270 °C and 10^{-4} M; HNO_3 is considered to be fully dissociated in the experimental range.[28,29] It was then seen that the change in the anion did not cause any observable effect on the kinetics. The effect of acid on the kinetics was further studied at a supercritical state where the temperature was 400 °C and the water density was 0.4 g/cm^3. The concentration of HCl added was on the order of 10^{-5} M. In this case, HCl is only weakly dissociated and $[H^+]$ was estimated according to the dissociation constant of HCl.[21] The kinetic measurements at the neutral condition were further performed at subcritical states of 310, 330, 350, and 365 °C on the saturation curve and supercritical states of 385 and 400 °C with the water density ranging between 0.1 and 0.6 g/cm^3. A sealed tube of quartz was used as a vessel for the reaction. The sample set-up and the sample state along the temperature elevation are described in our previous papers.[30,31]

The solution of 1,4-butanediol in heavy water (D_2O) was sealed in a quartz tube with 1.5 mm i.d. at 1.0 M. 1,4-Butanediol, HCl, and HNO_3 were purchased from Nacalai, and D_2O (more than 99.9% purity) was from CEA, France. They were used without further purification. D_2O was employed as the solvent so that the identification of the reactant and product is convenient by the proton NMR measurement. We actually write the oxonium ion as H^+, rather than D^+, in the following unless any confusion will arise.[32] It should be noted that the ion product of D_2O is smaller than that of H_2O typically by an order of magnitude.[21] 1,4-Butanediol was chosen as the starting material, rather than THF, in the present study since THF is more abundant at equilibrium. The filling factor, which is defined as the ratio of the solution volume to the vessel volume at room temperature, was set to 50% for the samples reacted at temperatures of 350 °C or lower, and it was 40% for the samples reacted at 365 °C. The filling factor also determines the (water) density under the supercritical conditions,[30,31] and was set for the samples reacted at the supercritical temperatures according to the desired density. The length of the solution portion in each quartz tube was 4 cm for a quick, high-resolution NMR measurement. The total length of the quartz tube was then determined by the filling factor, and the reactor volume amounted to 0.12–0.71 mL, depending on the filling factor.

The high-temperature reaction was performed in an electric furnace. The sample was put into a furnace heated in advance at each reaction temperature. The temperature in the furnace was homogeneous within ±1 °C. The reaction time was in the range of 10^3–10^6 s. After the reaction time, the sample was removed from the furnace quickly and quenched in a cold-water bath. It took less than 60 s for the sample to heat up and cool down. Actually, the time scales for the sample heating and cooling were much shorter than those for the reactions at the thermodynamic states of interest. The sample was subjected to a proton NMR measurement (JEOL EX270 and ECA400), and the product and residual reactant were quantified; a solution of 1,3,5-trioxane in D_2O was sealed in a capillary and used as an external reference. The effects of the reactant concentration and the container surface on the rate constants were negligible within our experimental precision. This was confirmed by varying the reactant concentration and the quartz vessel diameter.[33,34]

Results and Discussion

In Fig. 2, the proton spectrum is shown as a function of time for the sample reacted at 350 °C. It is seen that the reaction in Scheme 1 was found to proceed reversibly without any added catalysts under hydrothermal conditions. Furthermore, no by-products were detected within our NMR precision and the mass balance was maintained throughout the reaction. This is a convenient property as a model reaction. At the supercritical temperature 400 °C, the pyrolytic reactions other than the dehydra-

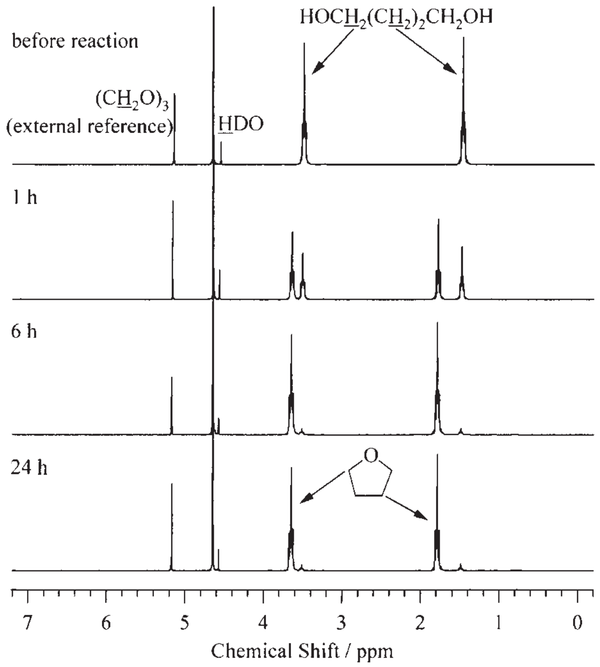

Fig. 2. The time evolution of the proton spectrum of the sample reacted at 350 °C without acids added from outside.

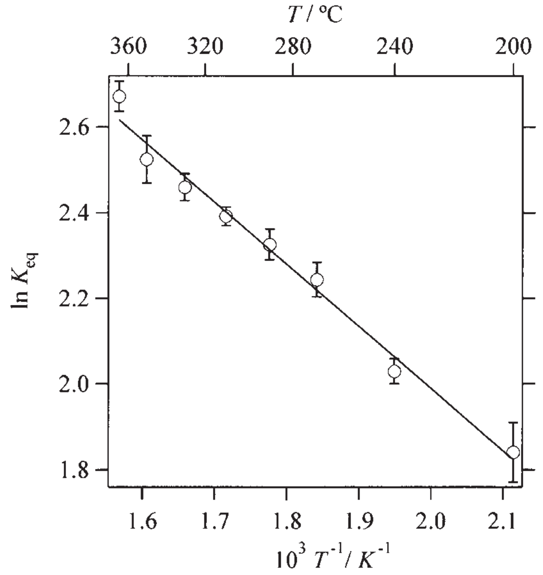

Fig. 4. The equilibrium constant K_{eq} of the reaction expressed as Scheme 1 as a function of the temperature T along the liquid branch of the saturation curve of water. The line is the linear fit of ln K_{eq} against $1/T$. The reaction is apparently endothermic.

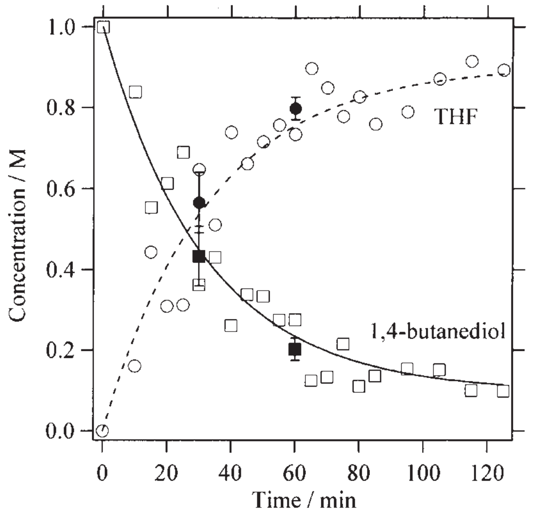

Fig. 3. The time evolution of the concentrations of 1,4-butanediol and THF at a temperature of 270 °C and an acid concentration of 0.9×10^{-4} M. The acid added from outside is HCl for the open symbols, and is HNO_3 for the filled symbols. The solid and dashed lines stand for the fits to the reversible first-order rate law.

tion were actually observed. The overall pyrolytic rate constant is then $\sim 10^{-5}$ s^{-1}, and its weight against the dehydration increases with the density reduction. The pyrolysis and dehydration was found to be comparable in rate at ~0.2 g/cm³.

Figure 3 illustrates the time dependence of the concentrations of 1,4-butanediol and THF at 270 °C and $[H^+] = 0.9 \times 10^{-4}$ M. It is evident that both the first-order rate constants for the dehydration and hydrolysis can be determined accurately from the time evolution of the proton spectrum. In addition, the equilibrium constant K_{eq} expressed as[35]

$$K_{\mathrm{eq}} = [\mathrm{THF}]/[\text{1,4-butanediol}], \qquad (2)$$

is given in Fig. 4 as a function of the temperature along the liquid branch of the water saturation curve. According to Fig. 4, THF becomes more favourable than 1,4-butanediol when the temperature is elevated. This behaviour is related to the hydrogen bonding ability of water with THF and 1,4-butanediol. Under ambient conditions, 1,4-butanediol is strongly hydrated at the two OH groups. The temperature elevation (and density reduction) then leads to the loss of the hydrogen bonding and lessens the relative stability of 1,4-butanediol. At the supercritical states, the equilibrium is too one-sided to determine the equilibrium constant K_{eq}. No 1,4-butanediol was found at equilibrium in our experimental precision.

Suppose in Eq. 1 that k_{water} is negligible compared to $k_{\mathrm{acid}}[H^+]$ in the experimental range of $[H^+]$. Note that $[H^+]$ is not zero even at the neutral condition, where no acid is added from outside and only H^+ produced by the spontaneous dissociation of the water molecule is present in the system. Under the proportionality supposition of the observed rate constant k_{obs} to $[H^+]$, since the ionization of the water molecule (D_2O) gives rise to 10^{-6} M of oxonium ion (D^+) at 270 °C in the neutral condition,[21] for example, the addition of 10^{-4} M HCl is to increase k_{obs} by two orders of magnitude. Figure 5(a) then illustrates the experimentally determined dependence of k_{obs} on $[H^+]$ for the dehydration of 1,4-butanediol to THF at temperatures of 150 and 270 °C on the water saturation curve. Evidently, k_{obs} in the $[H^+]$ range of $\sim 10^{-4}$ M is only 2 or 3 times as large as k_{obs} at the neutral condition. In other words, the intercept in the $[H^+]$ dependence of k_{obs} is evidently nonzero under our experimental conditions. According to the values of k_{water} and k_{acid} determined from Eq. 1, $k_{\mathrm{acid}}[H^+]$ contributes by less than ~5% to k_{obs} at the neutral condition when the temperature is lower than 290 °C on the saturation curve. Furthermore, Fig.

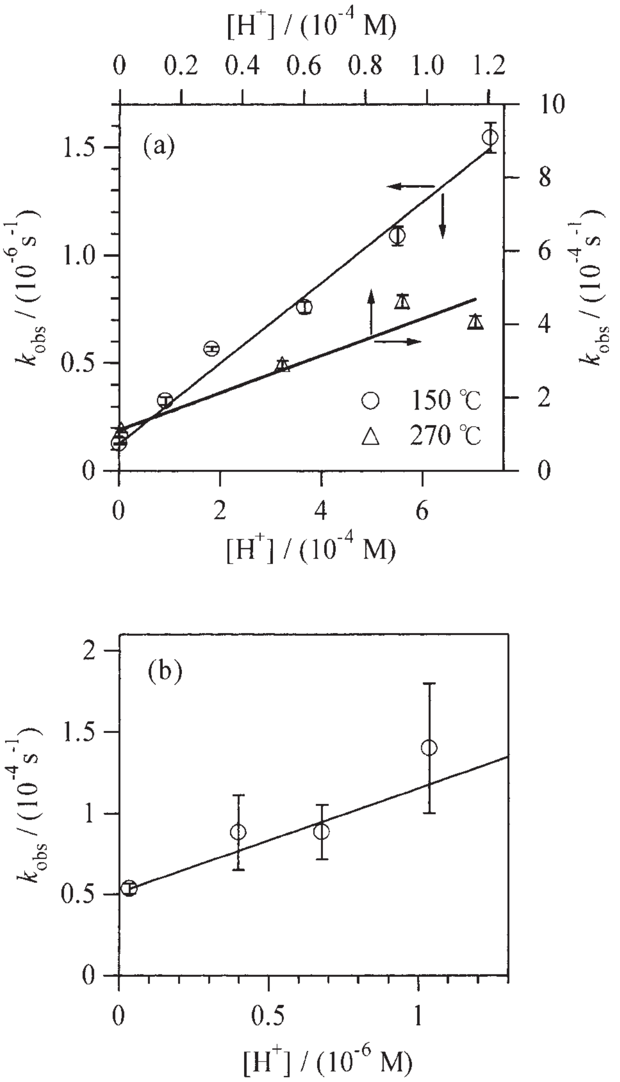

Fig. 5. The observed rate constant k_{obs} for the dehydration of 1,4-butanediol as a function of the oxonium ion concentration $[H^+]$ (a) at temperatures of 150 and 270 °C on the liquid branch of the water saturation curve and (b) at a supercritical state of 400 °C and 0.4 g/cm^3. The data at nearly zero $[H^+]$ correspond to the neutral (nonacidic) condition and $[H^+]$ is not exactly zero due to the autoprotolysis of water. The linear fits are shown by the lines. In (b), the fit to Eq. 1 gives $k_{water} = (5.1 \pm 0.3) \times 10^{-5}$ s^{-1} and $k_{acid} = (6.6 \pm 1.4) \times 10^{1}$ M^{-1} s^{-1}.

5(b) shows the $[H^+]$ dependence of k_{obs} at a supercritical state of 400 °C and 0.4 g/cm^3. In this case, HCl is only weakly dissociated and $[H^+]$ was evaluated from the ionization constant of HCl listed in Ref. 21. The situation is similar to that observed for Fig. 5(a). The presence of a nonzero intercept is evident in the $[H^+]$ dependence of k_{obs}, and $k_{water} \gg k_{acid}[H^+]$ holds at the neutral condition.[32] Within the fitting procedure of Fig. 5(b), $k_{acid}[H^+]$ contributes by ~5% to k_{obs} at the neutral condition. Therefore, Fig. 5 demonstrates that hot water accelerates the reaction even without the presence of H$^+$. Moreover, we confirmed that the dehydration does not proceed appreciably in the dilute gas condition even at high experimental temperatures of 350 and 400 °C. This shows that 1,4-butanediol does not dehydrate only by heat. The presence of the aqueous medium is necessary for dehydration. Water is thus revealed, at the level of kinetics, to promote the reaction in its undissociated form.

The transition state of the dehydration reaction along the water-induced path has been proposed by Takahashi through quantum-chemical calculations and found to be stabilized through strong coupling with the water molecule.[36] Actually, Takahashi showed that a water-wired form also appears in the ethanol oxidation in supercritical water and greatly reduces the electronic energy of the transition state.[37] It has been found that the hydration induces a large dipole moment for Takahashi's structure and leads to the further stabilization. In a subsequent paper, a full account of the quantum-chemical calculation of the transition state will be described and the effect of hydration is treated with the QM/MM (quantum mechanical-molecular mechanics) simulations and free energy calculations.[36] In this connection, it is also of theoretical interest to note under supercritical conditions that water controls the reaction pathway even at a density lower than 0.1 g/cm^3.[38]

In Fig. 6, we show k_{water}, k_{acid}, and k_{obs} at the neutral condition as functions of the temperature T along the liquid branch of the water saturation curve. As expected, k_{obs} increases with the temperature in the range of 150 to 330 °C. The further elevation of the temperature above 330 °C, however, causes an apparent reduction in the rate constant. The apparent inversion of the temperature dependence of k_{obs} at the neutral condition is consistent with the density dependence of the rate constants in supercritical water. The relationship for the rate constant between the strength of the density dependence and the apparent anomaly near the critical point is described parametrically in the Appendix.

When $[H^+]$ is varied at constant temperature and pressure, Eq. 1 shows that

$$[H^+]_c = k_{water}/k_{acid} \tag{3}$$

is the crossover concentration $[H^+]_c$ for the relative importance of the water-induced and acid-catalyzed paths; the water-induced path is more important when $[H^+] < [H^+]_c$ and the acid-catalyzed path is when $[H^+] > [H^+]_c$. From Figs. 5 and 6, it is seen over the entire temperature range, including a moderate temperature of 150 °C, that $[H^+]_c$ is on the order of 10^{-4}–10^{-6} M. In the thermodynamic range of Figs. 5 and 6, on the other hand, H$^+$ is present on the order of 10^{-8}–10^{-6} M by the autoprotolysis of water when no acid is added from outside. Thus, when H$^+$ is present only due to the autoprotolysis of water, $[H^+]_c \gg [H^+]$ holds and the water-induced path dominates over the acid-catalyzed. Actually, the strength of water to promote the reaction in its undissociated form can be parameterized by an effective acid concentration expressed as $[H^+]_c$. Figs. 5 and 6 show that the role of undissociated water to induce the reaction as an effective acid is not restricted to the high-temperature regime. The issue is only the time scale when the practical time scale of 10^4–10^6 s (hours to days) is concerned. At low temperatures, k_{water} is practically too small and a large amount of H$^+$ needs to be added to detect the reaction. In this case, the practical time scale of experiment requires a certain value of $[H^+]$ that is much larger than $[H^+]_c$, and the observed rate constant k_{obs} appears to be proportional to $[H^+]$. When the temperature is elevated, k_{water} increases to a practical-

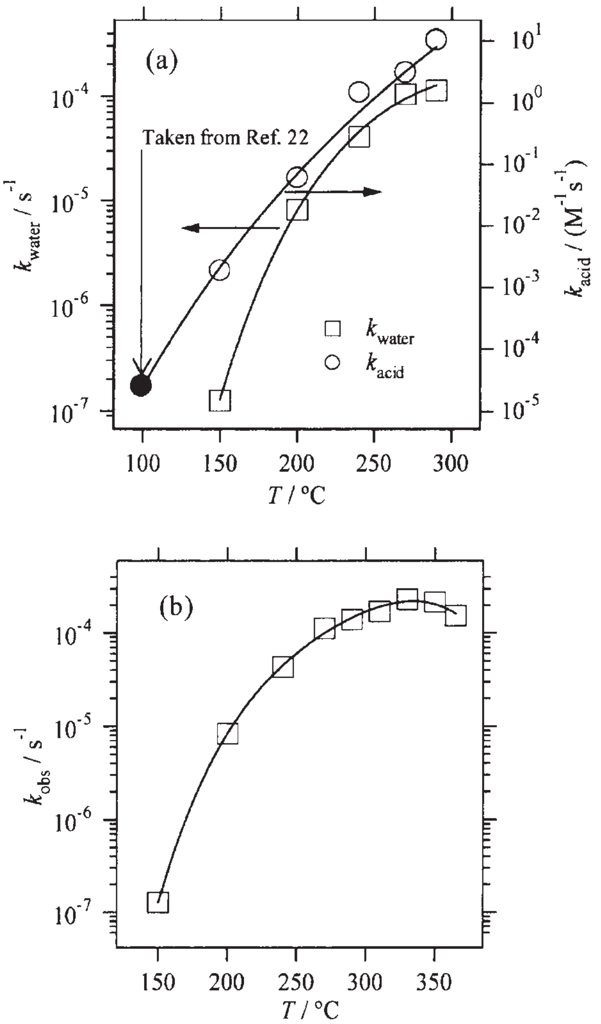

Fig. 6. (a) The water-induced rate constant k_{water} and the acid-catalyzed rate constant k_{acid} and (b) the observed rate constant k_{obs} at the neutral condition for the dehydration of 1,4-butanediol as functions of temperature along the liquid branch of the saturation curve. The lines are drawn just for the eye guide. k_{acid} obtained in the present work is extrapolated through an Arrhenius plot to the previous value at 100 °C.[22] It should be noted that the system is on the saturation curve and that the temperature variation accompanies the changes in both the density and the pressure. Along this temperature variation, the apparent activation energies for k_{water} and k_{acid} are 29 and 25 kcal/mol, respectively.

ly accessible value and the water-induced path becomes manifest on the time scale of 10^4–10^6 s. In other words, [H$^+$] resulting from the autoprotolysis of water is comparable to or smaller than $[H^+]_c$, and the intercept is evident in the plot of k_{obs} against [H$^+$] in the practical time scale.

In recent papers, Richter and Vogel investigated the dehydration of 1,4-butanediol to THF in an Inconel 625 vessel as a function of temperature at constant pressure, and found that the reaction rate constant involves a maximum around the critical temperature.[13,16] They then adopted the conventional acid-catalyzed mechanism of the dehydration (neglect of the first term in Eq. 1) and related their finding to the temperature dependence of [H$^+$] due to the autoprotolysis of water. When the thermodynamic condition is varied over a wide range, however, the acid-catalyzed rate constant k_{acid} itself in Eq. 1 changes drastically. Therefore, it may be quantitatively insufficient simply to compare the temperature and density dependence of the observed rate constant k_{obs} at the neutral condition only to that of [H$^+$].[39,40] To elucidate the effect of H$^+$ on the reaction, it is desirable to fix the temperature and density and to examine the rate of the dehydration against [H$^+$] according to Eq. 1, as done in the present work.

Hot water in noncatalytic conditions is also found to promote a chemical reaction, such as Cannizzaro-type disproportionation, that proceeds under ambient conditions in the presence of a base.[10,11,13,15,19,20] In particular, Adschiri et al. revealed, by examining the hydrolysis rate of a nitrile as a function of pH, that H_2O, rather than OH$^-$, is the predominant nucleophile under hydrothermal conditions.[10] The effective base concentration $[OH^-]_c$ of the undissociated form of water can also be defined by an equation similar to Eq. 3. We see according to Adschiri et al.'s results that $[OH^-]_c$ is on the order of 10^{-5} M. Actually, it is known that H_2O is a weak Lewis base and serves as a nucleophile even under ambient conditions.[24,25] On the other hand, several acid-catalyzed reactions are found to proceed under hydrothermal conditions without any acid catalysts.[2–9,13,14,16,18] In this work, we based our analyses on a well-defined kinetic expression given by Eq. 1, and revealed quantitatively the role of the undissociated form of water as an effective acid by controlling the H$^+$ concentration.

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Appendix

In Fig. 6, the observed rate constant k_{obs} at the neutral condition exhibits an inversion in the temperature dependence along the liquid branch of the saturation curve. In this Appendix, we show through a parameterization of the density and temperature dependence of k_{obs} that the inversion is related to the density reduction of water upon elevation of the temperature. It should be noted that the arguments in this Appendix refer only to the density and temperature dependence of the observed rate constant and are not affected by the molecular mechanism of the reaction. In Fig. 7, we show k_{obs} at the neutral condition as a function of the (water) density at fixed supercritical temperatures of 385 and 400 °C. The kinetic data shown in Fig. 7 can be parameterized by

$$k_{obs} = \rho^m \exp\left(-\frac{\Delta E}{RT}\right), \tag{4}$$

where ρ is the water density, R is the gas constant, T is the temperature, and ΔE is the apparent activation energy. In this equation, although we introduced a power m and an activation energy ΔE, we do not assume that m water molecules are involved in the reac-

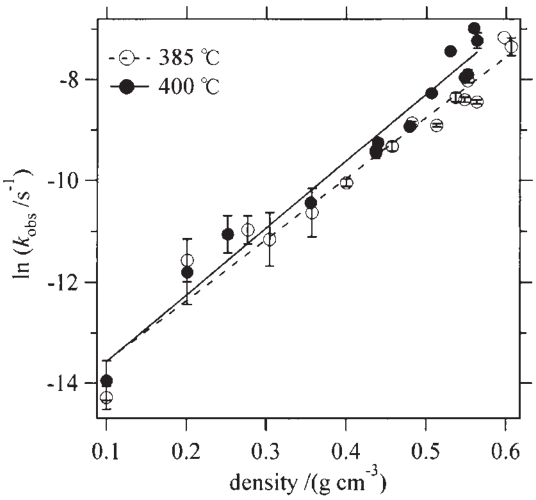

Fig. 7. The observed rate constant k_{obs} for the dehydration of 1,4-butanediol at supercritical temperatures of 385 and 400 °C against the density of water. The dashed and solid lines stand for the linear fits of $\ln k_{obs}$ against the water density at 385 and 400 °C, respectively.

tion. Eq. 4 is simply a fitting function. When Eq. 4 is transferred to the subcritical region, the temperature dependence along the saturation curve of water is given by

$$\frac{\partial \ln k_{obs}}{\partial T} = \frac{m}{T}\left(\frac{\partial \ln \rho}{\partial \ln T} + \frac{\Delta E}{mRT}\right). \tag{5}$$

The inversion of the temperature dependence of k_{obs} is observed at the T value where the right-hand side of Eq. 5 vanishes. Since $\partial \ln \rho / \partial T$ is negative along the liquid branch of the saturation curve and ΔE is positive, the inversion temperature is lower when m is larger. Actually, given that $\partial \ln \rho / \partial T$ diverges at the critical point, the inversion temperature is always present when ΔE and m are positive. In our case, Fig. 7 provides $m = \sim 4$ and $\Delta E < \sim 170$ kJ/mol. The inversion temperature is then inferred from Eq. 5 to be lower than 360 °C, which is in agreement with the one observed in Fig. 6. According to the discussion in this Appendix, the increase of k_{obs} with the density as parameterized by Eq. 4 leads, in general, to an inversion of the temperature dependence on the saturation curve. The inversion is simply related to the divergent nature of $\partial \ln \rho / \partial T$ toward the critical point. In this sense, the phenomenological inversion of the temperature dependence of the reaction rate constant does not mean an "anomalous" feature of a reaction near the critical point, but reflects the general feature near the critical point that the density varies strongly with the temperature along the saturation curve.

The dielectric constant ε and the ion product of water (pK_w) are increasing functions of the density of water in the supercritical condition. The near-critical inversion of their temperature dependence along the saturation curve is then derived from an argument similar to the one given above. Thus, a correlation of the rate constant to ε and/or pK_w can be seen, especially when the near-critical inversion is emphasized. The presence of correlation does not necessarily mean, however, the presence of causality. To examine the role of H^+ on the rate constant, in particular, a systematic investigation is needed for the [H^+] dependence of the rate constant, as done in the present work.

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32 Since the ion product is different between H_2O and D_2O, it is possible that the ionization constant of DCl is different from that of HCl. In the present work, we assume that DCl is fully dissociated under the condition that HCl is fully dissociated. At the supercritical condition, HCl and DCl are not fully dissociated in our concentration range and the abscissa of Fig. 5(b) needs to be treated with care. We used the ionization constant of HCl and the ionic product of H_2O to identify $[H^+]$ in Fig. 5(b) since the values for the deuterated compounds were not available. This identification leads to an underestimate of k_{acid} since a deuterated acid typically involves a smaller ionization constant than the protonic counterpart. The k_{water} value is not affected in Fig. 5(b), however, when the change of the ionization constant upon deuteration is the common to water and hydrogen chloride. If k_{water} value is not affected by deuteration, the value of $k_{acid}[H^+]$ at the neutral condition is not, either, of course. Thus, it is considered that the relationship $k_{water} \gg k_{acid}[H^+]$ at the neutral condition is valid even when D_2O is employed as the solvent.

33 As described in Ref. 34, the saturated concentration of the dissolved quartz is at most 10^{-4} in mole fraction in the present experimental conditions. The dissolved quartz is usually present in the hydrated form H_2SiO_3 and produces H^+ by ionization. It can be shown by virtue of the extrapolation of the data listed in Ref. 21, however, that $[H^+]$ from the dissolved quartz is smaller by orders of magnitude than $[H^+]$ from the autoprotolysis of water.

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36 H. Takahashi et al. in preparation. Of course, the number of water molecules involved in the transition state is not necessarily equal to the reaction order against the water density. The reaction rate is affected by the hydration of the reactant and transition state due to the surrounding water molecules.

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39 In this connection, it is of interest to note the following. When the density is varied from 0.1 to 0.6 g/cm^3 at a fixed supercritical temperature of 400 °C, $[H^+]$ from the autoprotolysis of water increases by six orders of magnitude. The observed rate constant k_{obs} of the dehydration is shown in Fig. 7, on the other hand, to grow only by three orders of magnitude. Thus, if the reaction is acid-catalyzed and k_{water} is negligible in Eq. 1, then k_{acid} needs to reduce by three orders of magnitude upon the density variation.

40 We do not attempt to write the water-induced term k_{water} in the form of $k_{water} = k[H_2O]$, where k is a second-order rate constant. This is because the water molecule contributes to k_{water} not only as a reactant but also through solvation. Indeed, Fig. 7 shows that k_{water} is nonlinear with respect to $[H_2O]$, when k_{water} is considered dominant in the observed rate constant k_{obs}. In this case, the k derived from the form of $k_{water} = k[H_2O]$ is dependent on $[H_2O]$ and does not lead to a clearer representation of the water density dependence.