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Structure and Base Catalysis of Supercritical Water in the Noncatalytic Benzaldehyde Disproportionation Using Water at High Temperatures and Pressures**

Yutaka Ikushima,* Kiyotaka Hatakeda, Osamu Sato, Toshirou Yokoyama, and Masahiko Arai

The physicochemical characteristics of water are greatly changeable by varying the pressure or temperature under supercritical conditions,[1] and supercritical water (scH_2O) offers exiting possibilities for the development of new chemical processes.[2] Furthermore, scH_2O is a suitable medium in connection with "green" (environmentally friendly) technology because water is the most environmentally acceptable and naturally abundant solvent. However, the microscopic characteristics of scH_2O, including the structure which is closely related to chemical reactivity in scH_2O, are not sufficiently well understood. Hence a better understanding of the structure and nature of scH_2O leads to marked improvements in practical applications such as in the mechanical, chemical, and geothermal industries.

Currently in organic synthesis, a matter of primary interest is the promotion of reaction rates by more "green" chemical processes. Recently we reported an interesting finding that scH_2O itself successfully functions as an acid in accelerating pinacol/Beckmann rearrangements.[3] Bröll et al. have briefly reported a base-catalyzed Cannizzaro-type disproportionation of formaldehyde in scH_2O carried out without a base catalyst.[4] In addition, our in situ Raman spectroscopy measurements have indicated that the extent and strength of hydrogen bonding of scH_2O are very different to those in heated and ambient H_2O.[5] This suggests a pronounced stimulation of the breakdown of monomeric water molecules under supercritical conditions, which would account for the acid and base difunctionality of scH_2O. We have further studied the base function of scH_2O by conducting a base-catalyzed disproportionation of benzaldehyde in the absence of any base catalysts. The rate of such a noncatalytic disproportionation in scH_2O has been found to be several-hundred-fold larger than in the conventional catalytic reactions, whereas the rates of these reactions in hot water (below 300 °C), even at high pressures, are extremely small. In addition, the participation of the OH^- ion, the not $OH^\bullet$ radical, in the reaction is strongly suggested from GC-MS and NMR spectroscopic analysis of the benzyl alcohol product in the disproportionation using [D6]benzaldehyde as a reactant.

We first demonstrate that the reaction of benzaldehyde to benzyl alcohol and benzoic acid proceeds in scH_2O even in the absence of any base catalysts. Figure 1 shows the background corrected IR spectra for reaction mixtures in scH_2O (397 °C) and hot water (277 °C) at a constant pressure of 25 MPa along with those for ordinary benzyl alcohol and benzaldehyde aqueous solutions. These measurements were performed by real time, in situ FT-IR spectroscopy for benzaldehyde in H_2O introduced into a high-pressure, high-temperature, flow reactor at a constant residence time of 105.0 s. The spectrum obtained in scH_2O (trace D),shows a new intense band at 1002 cm^{-1}, not present in that of the benzaldehyde solution (trace A). This strong band can be assigned to the CO stretching vibration(ν_1) of the benzyl alcohol formed, and is not observed in the hot water (trace C) or ordinary water (trace A) phases. We have further analyzed the absorption bands around 1700 cm^{-1} (not shown) can be assigned to the CO stretching vibrations of benzaldehyde and benzoic acid, in which the ν_1 frequency of benzoic acid is somewhat higher than that of benzaldehyde. In the scH_2O an intense band at 1702 cm^{-1} nearly coincides with that of the authentic benzoic acid sample, showing unambiguously that benzoic acid is produced in addition to benzyl alcohol. Detailed analysis of

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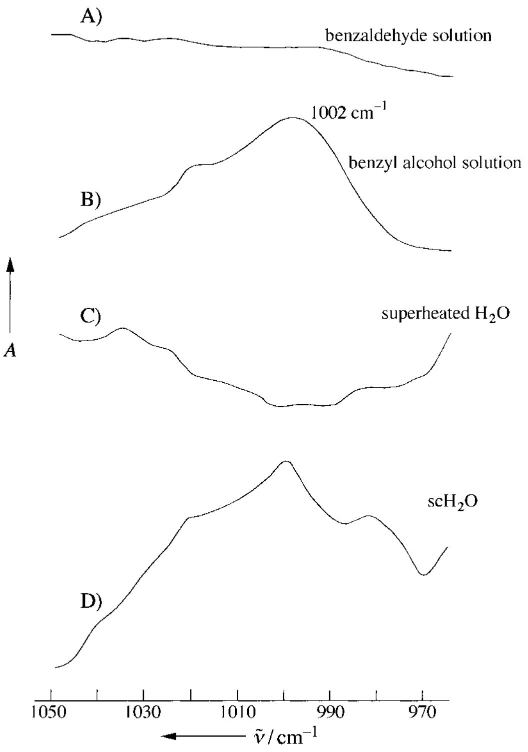
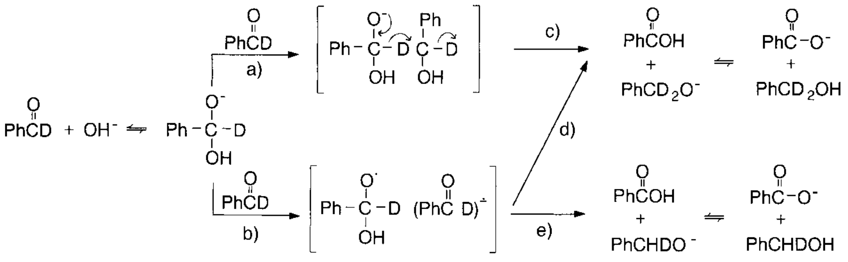


Figure 1. Infrared spectra of aqueous solutions of A) benzyldehyde 20 °C, 0.1 MPa, B) benzyl alcohol 20 °C, 0.1 MPa; and of reaction mixtures in the aqueous, noncatalytic disproportionation of benzaldehyde C) superheated H_2O, 277 °C, 25 MPa, D) scH_2O, 397 °C, 25 MPa. The band at 1002 cm^{-1} is assigned to CO stretching vibration (ν_1) of benzyl alcohol.

the reaction mixture by GC-MS and NMR spectroscopy at the end of the reaction supported the formation of benzyl alcohol and benzoic acid in scH_2O. Hence this in situ observation has first demonstrated the disproportionation of benzaldehyde to benzyl alcohol and benzoic acid in scH_2O without base catalysts.

To explore what kind of species causes the "noncatalytic" disproportionation in scH_2O, we attempted the disproportionation of [D6]benzaldehyde in scH_2O at 397 °C and 25 MPa. The benzyl alcohol product in the disproportionation was analyzed by GC-MS of the product mixture containing benzaldehyde and the alcohol, and also by ^1H NMR spectroscopy of the isolated alcohol product. We observed well-defined fragment ions such as $C_6D_5CD_2OH^+$ (m/z 115), $C_6D_5CDOH^+$ (m/z 113), $C_6D_5CDO^+$ (m/z 112), $C_6D_5CO^+$ (m/z 110), $C_6D_5CD_2^+$ (m/z 98), $C_6D_5CD^+$ (m/z 96), and $C_6D_5C^+$ (m/z 94) characteristic of [α-$^2H_2$]benzyl alcohol according to the reported analysis,[6] whereas signals from the fragments corresponding to the ionized products of [α-^2H]benzyl alcohol were negligible. In addition, the identification by ^1H NMR supports the result from the GC-MS analysis. A generally postulated mechanism for the disproportionation involves a pre-equilibrium addition of OH^- to the [α-^2H]benzaldehyde and a rate-determining intermolecular hydride transfer, followed by the production of [α^2H_2]benzyl alcohol (Scheme 1, pathway a–c),[7a,f] or an intervention of radical intermediates leading to the formation of [α-$^2H_2$]benzyl alcohol (Scheme 1, pathway b–d)[7b,c] or the formation of [α-^2H]benzyl alcohol (Scheme 1, pathway b–e).[7d,e] The OH^- ion and/or $OH^\bullet$ radical species are thus expected to cause this disproportionation using scH_2O alone, and undoubtedly arise from the H_2O molecule itself although H_2O at ambient conditions does not provide the benzylic hydrogen of the product.[8] The OH^- ion is required to form the product alcohol in any reaction mechanisms,[7] and the participation of the OH^- ion in the disproportionation using scH_2O has been clearly demonstrated. On the other hand, the formation of [α-^2H]benzyl alcohol was not identified in this experiment, and one can eliminate completely the possibility of participation of the $OH^\bullet$ radical, that is, the breakdown of the H_2O molecule to $H^\bullet$ and $OH^\bullet$ radicals under supercritical conditions on the assumption that the disproportionation using scH_2O follows reported mechanisms.[7]

Our in situ FT-IR measurements enable us to carry out a kinetic analysis. The extent of the conversion of benzaldehyde in the disproportionation reaction changes in proportion to an increase in the absorbance of the benzyl alcohol formed. In this study pseudo second-order rate constants have been determined at temperatures of 20–427 °C and pressures of 0.1–25 MPa by assuming that excess OH^- is evolved.[9] The extinction coefficient of the ν_1 band of benzyl alcohol determined through the Lambert–Beer law was assumed to be independent of temperature. Pressure differences did not influence the absorbance at temperatures of 20–200 °C.



Scheme 1. A postulated mechanism for the disproportionation of [D6]benzaldehyde in scH_2O; d) $D^\bullet$ transfer; e) $H^\bullet$ transfer.

Figure 2 shows the pseudo second-order rate constants (k_{p2}) under various conditions: scH_2O, hot water, and concentrated aqueous NaOH solution. A dramatic enhancement in the reaction rate is seen on carrying out the reaction in scH_2O in the absence of any base catalysts. The reaction in scH_2O at 25 MPa and 427 °C (Figure 2 g) is about 600 times faster than in 2 M NaOH at 60 °C (Figure 2 a).[9] The reaction is greatly accelerated by raising the temperature in the scH_2O region; however, in hot water below 300 °C even at such high pressures the reaction was not observed to occur for residence time from 12 to 360 s. The change in the molecular extinction coefficient of benzyl alcohol with water density might influence the rate constants. Recent experimental data show that the extinction coefficient of triplet anthracene in scH_2O decreases with increasing density, by a factor of about 3–4 in the density range of 0.12 to 0.62 g cm^{-3} (ref [10]); however, we

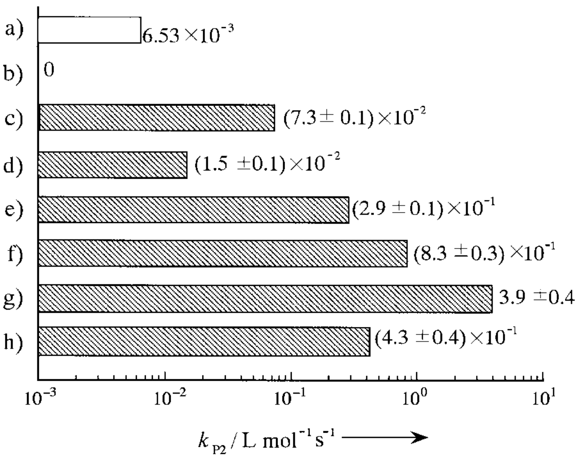


Figure 2. The pseudo second-order rate constants (k_{p2}) of the disproportionation of benzaldehyde. The base catalyst and its concentration, solvent, pressure, and temperature are a) 2 M NaOH aq. solution, 60 °C;[9] b) no catalyst, hot water, 25 MPa, 300 °C; c) no catalyst, hot water, 25 MPa, 352 °C; d) no catalyst, hot water, 19.1 MPa, 377 °C; e) no catalyst, scH_2O, 25 MPa, 377 °C; f) no catalyst, scH_2O, 25 MPa, 397 °C; g) no catalyst, scH_2O, 25 MPa, 427 °C; h) no catalyst, scH_2O, 22.1 MPa, 377 °C. For our data 95 % confidence limits are provided.

think that this change is not so large when compared with the marked enhancement of the rate of reaction, by one or two orders of magnitude, when using scH_2O, and does not prevent us from concluding that the use of scH_2O can significantly promote the rate of organic synthesis. Under the conditions used, the substrate can be soluble in the solvent at high pressures and temperatures. Increasing the pressure and temperature increases the density of H_2O and so decreases the concentration of substrate in the constant volume of reaction mixture. This will have a negative effect on the rate of reaction and so the enhanced reactivity of scH_2O is of great significance.

The change in hydrogen bonding is presumed to be a key factor for clarifying the temperature and/or pressure dependence of the rate of the disproportionation. It was demonstrated that the extent of hydrogen bonding is reducing uniquely near the critical point (critical pressure), where dimers and/or monomers are predominant,[11] but monomers, in part, are further broken into H^+ and OH^- ions by the large fluctuations in the water structure.[5, 11d] That is, the "local" H^+ or OH^- ion concentration would be extremely high when the transferring ion species cannot escape, leading to the maximized rate near the critical pressure. Hence such an acceleration of the disproportionation is quite peculiar to the supercritical state, and it is highly possible that the "specific breakdown" of H_2O to H^+ and OH^- ions under supercritical conditions occurs.

Figure 3 shows the change in the rate constant with temperature at a fixed pressure of 25 MPa, together with the extent of the disappearance of hydrogen bonding (1-η) of water determined by our Raman spectroscopic data.[5] The rate constant increases with increasing temperature above the near-critical region despite the loss in OH^- ion activity anticipated from the Raman data.[5] The significant increase in the rate constant with increasing temperature from 397 to 427 °C at 25 MPa is because of an increase in thermal energy; however, hot water did not show any reactivity below 320 °C, whereas a marked increase in the rate with increasing temperature was observed in the near-critical region. Thus, the rate of reaction did not show a monotonous temperature dependence, being in agreement with the 1-η values up to approximately 400 °C. Furthermore, even though such a specific breakdown really occurs near the critical point, extensive spectroscopic data[5, 11] suggest that the dispersed phase beyond the critical point contains low aggregates including monomeric water molecules. Hence, the excellent performance of the base-catalyzed disproportionation from the near-critical to supercritical region might be related not only to the thermal energy contribution but also to monomer-like water molecules that do not break completely into H^+ and OH^- ions but polarize extremely in the supercritical state. There is still a possibility that the reaction mechanisms using scH_2O might be different from those reported.[7] Microscopic dynamic behavior of water molecules in a shorter time domain is in any event more important when discussing the specific reactivities. We have successfully used the 1-η value to correlate the acid/base reactivity of scH_2O. Another possible parameter is the ion product of water (K_w) value; however, detailed measurements have not yet been made for scH_2O near the critical region, where interesting reaction results have been obtained.

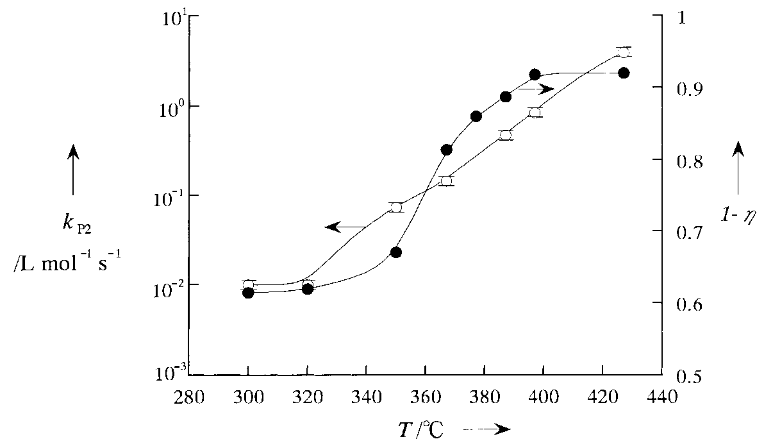


Figure 3. Relationship between the extent of disappearance of hydrogen bonding, 1-η (●) and the pseudo second-order rate constant, k_{p2} (○) for the benzaldehyde disproportionation as a function of temperature at a fixed pressure of 25 MPa. For k_{p2} values, 95 % confidence limits are given by bars.

Experimental Section

The reactions were performed under ambient to scH_2O conditions using a high-pressure, high-temperature flow-reaction system with a short-path-length (20 μm) FT-IR cell operable at 500 °C and 50 MPa. Details of the FT-IR system used are described elsewhere.[3b] An aqueous solution of benzaldehyde (0.05 M) was introduced into the system in the range of flow rates of 0.07 to 0.7 mL min^{-1} (the residence time from 12 to 360 s) using a high-pressure liquid pump, pressure control was achieved by a back-pressure regulator. The temperature was then raised to the desired value. Once stabilized, 50 spectra (4 cm^{-1} resolution) were accumulated in one destination file. Each file was rationed against the spectrum of pure H_2O under the same conditions. Furthermore, all of the products were qualitatively identified by using ^{1}H NMR spectroscopy and GC-mass spectrometry.

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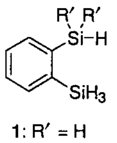
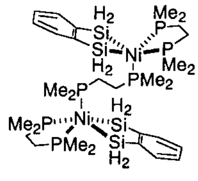
Isolation of Dinuclear (μ-Silylene)(silyl)nickel Complexes and Si–Si Bond Formation on a Dinuclear Nickel Framework[**]

Shigeru Shimada, Maddali L. N. Rao,
Teruyuki Hayashi, and Masato Tanaka[*]

Palladium and platinum complexes are versatile catalysts for the transformation of organosilicon compounds.[1] However, the utility of nickel complexes has not been as well established.[2] The understanding of the structure and the reactivity of silylnickel species[3] is indispensable for the development of new catalytic methodologies. Although a number of mononuclear silylmetal complexes are known for all Group 10 metals, structurally characterized silylene-bridged dinuclear complexes have been reported only for platinum[4] and palladium.[5, 6] These dinuclear species are considered to play important roles in catalytic processes. For example, silylene-bridged Pt_2Si_2 rings are potential key intermediates in the platinum-catalyzed dehydrocoupling of hydrosilanes.[4b–d] Here we report on the reaction of 1,2-disilylbenzene (**1**) with nickel(0) complexes, which led to the isolation of the dinuclear (μ-silylene)(silyl)nickel(III) complexes $[\{1,2\text{-}C_6H_4(SiH_2)(SiH)\}_2Ni_2(R_2PCH_2CH_2PR_2)_2]$ (R = Me or Et), which contain the first structurally characterized four-membered Ni_2Si_2 rings. The short contact between the SiH_2 and μ-SiH moieties revealed by X-ray crystallography suggests the possibility of Si–Si bond formation, which indeed takes place in a similar reaction of 1-(dimethylsilyl)-2-silylbenzene (**2**) with $[Ni(dmpe)_2]$ (dmpe = 1,2-bis(dimethylphosphanyl)ethane).



1: R′ = H
2: R′ = Me



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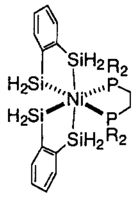
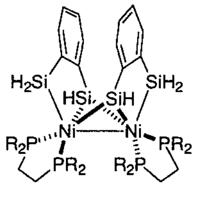
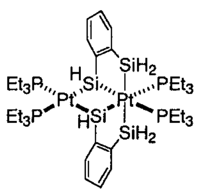


4a: R = Me
4b: R = Et

Previously, we reported that treatment of **1** with $[Ni(dmpe)_2]$ results in the dimeric bis(silyl)nickel(II) complex **3** and the first tetrakis(silyl)nickel(IV) complex **4a**.[7] A similar reaction under somewhat different conditions led to the formation of a new dimeric Ni^{III} complex. While studying **3** by variable-temperature NMR spectroscopy in [D_8]toluene, we observed, upon heating the solution to 80 °C, a color change from pale yellow to orange and the emergence of new weak signals in the ^{1}H and ^{31}P NMR spectra. Further heating at 110 °C for 30 min gave a new complex **5a**, which could be isolated as orange crystals (34%) by crystallization from benzene. The similar complex **5b**, ligated by 1,2-bis(diethylphosphanyl)ethane (depe), was also obtained directly from **1** and $[Ni(PEt_3)_2(depe)]$ (**1**:Ni = 1:1.05); the reaction proceeded even at room temperature and gave **5b** as the main product (49% yield). The ^{29}Si NMR spectrum of the crude mixture showed the presence of the tetrakis(silyl)nickel(IV) complex **4b** as a side product [$\delta = -2.11$ (dd, $^{2}J(\text{Si},\text{P}_{cis}) = 20$, $^{2}J(\text{Si},\text{P}_{trans}) = 101$ Hz), 3.03 (t, $^{2}J(\text{Si},\text{P}) = 16$ Hz)].



5a: R = Me
5b: R = Et



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