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Reaction Behavior of Secondary Alcohols in Supercritical Water

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Benzhydrol and benzoin, which have two benzene subunits, a secondary hydroxy group, and no hydrogen atom on the β-position of the hydroxy group, were treated in supercritical water in the absence of an oxidizing agent or a catalyst. Water played a key role in the product distributions in these reactions. Each reaction proceeded smoothly to give larger amounts of oxidation products, benzophenone (**3**) and benzil (**6**), as well as smaller amounts of reduction products, diphenylmethane (**4**) and benzyl phenyl ketone (**7**), respectively, in the presence of water, while the ratios of **3**:**4** and **6**:**7** were almost 1:1 in both cases in the absence of water. The best yield of benzophenone (63%) was achieved by the reaction of benzhydrol at 460 °C for 180 min in 0.35 g mL^{-1} water density in the SUS 316 reactor. Hydrogen gas evolution was observed in the reaction of benzhydrol in a quartz tubular reactor.

Much attention has been paid to supercritical water (SCW) as a medium for chemical reactions, since it has quite unique properties, such as low polarity, high density, low viscosity, and high solubility of organic materials, which are tunable simply by changing temperature, pressure, and water density.[1] These unique properties have been exploited, for example, in the field of the waste treatment especially in the presence of a large excess amount of oxygen.[2] Recently, unique organic reactions in SCW, such as H–D exchange reaction in supercritical deuterium oxide,[3] Beckmann rearrangement of cyclohexanone oxime,[4] pinacol rearrangement of 2,3-dimethyl-2,3-butanediol,[4b,5] Cannizzaro reaction of formaldehyde[6] and benzaldehyde,[7] Heck reaction,[8] C–Si bond cleavage,[9] Claisen–Schmidt reaction,[10] and benzil–benzilic acid rearrangement,[11] have been also studied.

In related studies, we have reported a unique reaction of ethanol in SCW.[12] When ethanol was treated in SCW at 450–500 °C in the absence of an oxidizing agent or a catalyst, oxidation occurred to give acetaldehyde concomitant with hydrogen gas generation. Takahashi et al. proposed a water-catalyzed hydrogen formation mechanism consisting of an ethanol molecule and two water molecules for the transition state of the reaction based on theoretical calculations, in which two water molecules catalyzed the reaction by making an eight-membered ring bridging over two hydrogen atoms of the ethanol to give an H_2 molecule (Scheme 1).[13] Unfortunately, side reactions, such as dehydration, occurred to give ethene simultaneously, which hindered knowing the intrinsic alcohol oxidation ability of SCW. Alternative substrates with no side reaction should be considered to discuss the inherent oxidation ability of SCW.

Combining the advantages of the benzene subunit exhibiting high affinity to SCW[14] and secondary alcohol with no hydrogen atom on the β-position of the hydroxy group leading to dehydration, benzhydrol (**1**) and its related compound benzoin (**2**) were selected as substrates in order to evaluate the intrinsic alcohol oxidation ability of SCW. In this paper, we wish to report the alcohol oxidation property of supercritical water through secondary alcohols **1** and **2** (Chart 1).

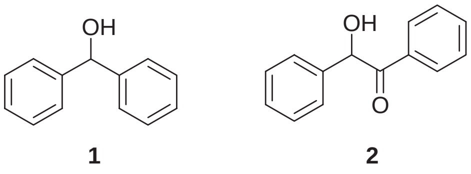
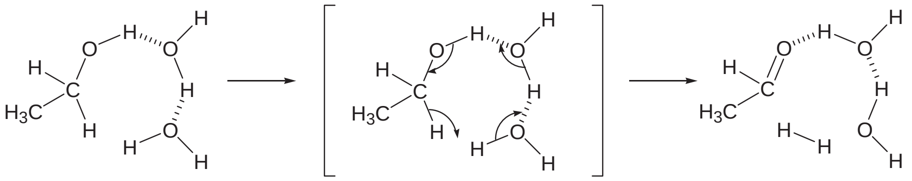


Chart 1.

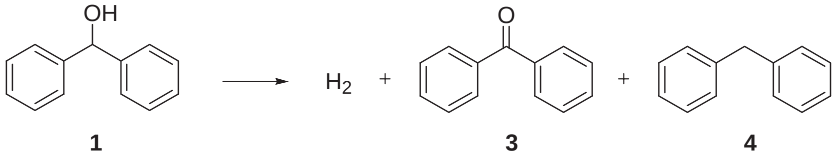


Scheme 1.

Table 1. Reaction of **1** in Supercritical Water[a)]

Entry	Mole of **1** /mmol	Temperature /°C	Water density /g mL^{-1} [b)]	Reaction time /min	Conversion /%	Product/%	
						3	**4**
1	0.272	380	0.35	180	19	6	4
2	0.272	400	0.35	180	26	16	5
3	0.272	420	0.35	180	77	46	4
4	0.272	440	0.35	180	87	53	9
5	0.272	460	0.35	180	>99	63	10
6	1.09	460	0.35	180	96	60	10
7	2.00	460	0.35	180	>99	60	17
8	0.272	460	0.35	20	38	16	<1
9	0.272	460	0.35	60	82	53	7
10	0.272	460	0.35	120	93	49	7
11	0.272	440	0	180	>99	48	53
12	0.272	440	0.05	180	86	50	29

a) Under N_2, in SUS 316 tubular reactor. b) Value of water density: water (g)/volume of the reactor (9.9 mL).



Scheme 2.

Table 2. Generation of Hydrogen Gas in Supercritical Water Reaction of **1**[a)]

Entry	Temperature /°C	Reaction time /min	Conversion[b)] /%	Products/%		
				H_2	**3**	**4**
1	422	10	≈1	0.6	2.4	1.5
2	420	60	7	1.2	5.1	2.8

a) Reaction conditions: 0.272 mmol of **1** and 0.34 mL of water in 1 mL quartz tubular reactor, water density 0.34 g mL^{-1}. b) Conversions was suppressed with low level to avoid explosion of the quartz tubings by inner pressure of generated hydrogen gas.

Results and Discussion

Reaction of Benzhydrol (1) in Supercritical Water. Alcohol **1** was treated in supercritical water in a SUS 316 tubular reactor under various conditions (Table 1).[15] Small amounts of benzophenone (**3**) and diphenylmethane (**4**) were produced at the temperature near the critical point (Entry 1). With an increase in the reaction temperature, the conversion of **1** and yields of **3** and **4** became higher (Entries 1–5). A remarkable change was observed at 420 °C (Entry 3). Concerning the reaction time, reaction almost finished within about 120 min (Entry 10). The required high temperature (>420 °C) as well as long reaction time (>120 min) suggests that the activation energy of this reaction is quite high. The best yield of **3** was achieved at 460 °C for 180 min (Entry 5). A higher concentration of alcohol **1** has almost no influence on the conversion of **1** and the yield of **3**, and a little influence on the yield of **4**, although the yields of **3** were higher than those of **4** in all cases (Entries 5, 6, and 7) (Scheme 2).

The role of water in the above reaction was examined by changing the water density. In the absence of water (Entry 11, pyrolysis), almost equal amounts of oxidation product **3** and reduction product **4** were obtained, suggesting that disproportionation between two molecules of alcohol **1** took place thermally. In the presence of water, however, the ratio of **3**:**4** always exceeded unity and increased with increasing water density (Entries 11, 12, and 4). Even within shorter reaction time (Entries 8, 9, and 10), the amount of **3** was always larger than that of **4** at 460 °C and 0.35 g mL^{-1} water density. These observations imply that a new reaction path other than the disproportionation occurs at higher water density and higher temperature. Water must play a key role in the new reaction.

Next, a quartz tubular reactor was adopted instead of the SUS 316 one to ascertain the evolution of hydrogen gas and to quantify the gaseous products. When alcohol **1** was treated in supercritical water at 420 °C in the quartz tubular reactor, evolution of hydrogen gas was observed, as expected, along with oxidation product **3** and reduction product **4** (Table 2). The material of the reactor, quartz or SUS 316, influenced the product distributions in SCW.[12] Thus, the product distributions of the reaction in the quartz tubular reactor were slightly different from those in the SUS 316 reactor in the present study. In other words, smaller ratios of **3**:**4** were obtained in the quartz tubular reactor than those in the SUS 316 reactor, although oxidation product **3** was the major product in both reactors. The amount of **3** was almost equal to the sum of obtained H_2 and **4**, showing no discrepancy supposing that reduction of **1** and/or **3** by the generated hydrogen gave **4** in the reaction system.[16] Prolonged reaction time led to higher conversion of **1** and higher yields of hydrogen and products **3** and **4** (Entry 2).[17] The yields of **3** were almost two times higher than those of **4** in both reactions.

Hatano et al. studied a similar reaction using the same substrate **1** in sub- and super-critical water in a steel bomb reactor.[18] They obtained the same products, **3** and **4**, as us, though the ratios of **3**:**4** were quite different from ours, almost 1:1 under all conditions they tested. No effect of water density on product distributions was observed in their experiments. They obtained ether **5** (Chart 2) from their reaction at 200 °C. When ether **5** was treated under supercritical conditions as a starting material, the corresponding product ratio of **3**:**4** was almost 1:1. They concluded, therefore, that equal amounts of **3** and **4** were derived from disproportionation of ether **5**, which was produced in an early stage of the reaction.[19] The proposed reaction mechanism would be quite reasonable if a 1:1 mixture of **3** and **4** were obtained even in our experiments. Our experiments always gave larger amounts of **3** than those of **4**. The low yield of **4** in our experiments could be attributed to the lability of **4** under the reaction conditions. A control experiment involving **4** in SCW (460 °C, 180 min, 0.35 g mL^{-1} water density), however, resulted in complete recovery of **4** (>99%), indicating that **4** was quite stable under the reaction conditions. Especially, it is noteworthy that the yield of **3** exceeded 50% to reach 63% under the reaction conditions of Entry 5 in Table 1. The observed temperature and water density dependence of the reaction (Table 1) and the evolution of hydrogen are of considerable importance for discussion of the reaction mechanism. In our experiment, the formation of ether **5** could be suppressed by hydrolysis of **5** itself under extreme supercritical conditions, even if ether **5** was generated in the reactions. It is difficult to put forward a conclusive discussion, though the crucial differences in the reaction behavior between the reported and ours could be attributed to the difference in the materials of the metal reactors. Although the reaction mechanism is not well understood, the water-catalyzed hydrogen formation mechanism[13] seems to be the most favourable one at present for our experiment in water.

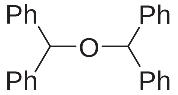


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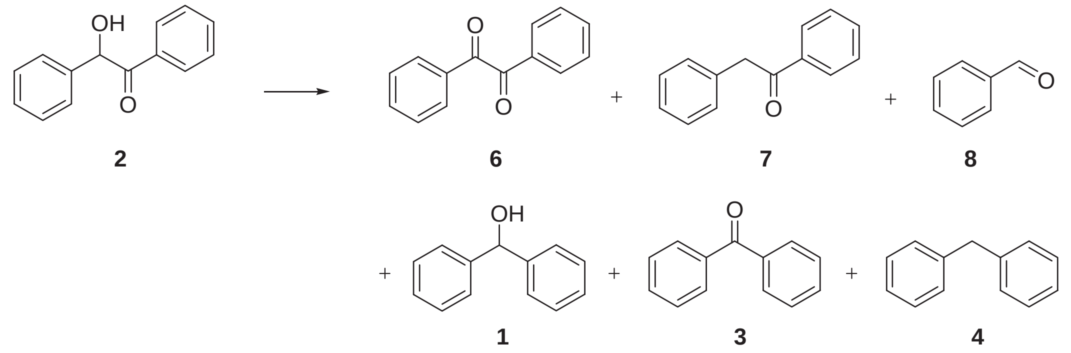
Chart 2.

Reaction of Benzoin (2) in Supercritical Water. The higher homologue benzoin (**2**) (Scheme 3), which also has two benzene subunits, a secondary hydroxy group, and a carbonyl group, was the next secondary alcohol to be treated in sub- and super-critical water (Table 3). Oxidation product benzil (**6**) and reduction product benzyl phenyl ketone (**7**) with small amounts of benzaldehyde (**8**), which can be derived from decomposition of **2**, **6**, and/or **7**, were obtained even at low temperatures (Entries 1 (300 °C) and 2 (340 °C)) and a short reaction time (10 min), indicating that the reactions of **2** in sub- and super-critical water proceeded easily as compared to those of **1**. Conversion of **2** and yields of **6** and **7** became higher with an increase in the reaction temperature (Entries 1, 2, and 6) and then saturated at 380 °C (Entry 10). A longer reaction time improved conversion of **2** as well as yields of **6** and **7**, though small amounts of **1**, which should be produced via benzil–benzilic acid rearrangement of **6**, followed by decarboxylation, as reported by Comisar and Savage,[11] and quite small amounts of benzophenone (**3**) and diphenylmethane (**4**) from **1**, as discussed previously, were obtained. Water density also played a crucial role in this reaction. In the absence of water (Entry 7, pyrolysis), however, reaction of **2** resulted in high conversion (95%) and almost the same total yield of the oxidation products (≈29%, defined as the sum of **6**, **1**, **3**, and **4**) and reduction product **7** (30%), which was quite similar to the results of the pyrolysis of alcohol **1** (Entry 11 in Table 1). Conversion of **2** as well as yields of **6** and **7** became lower with an increase in the water density (Entries 7–10 and 6), suggesting disproportionation of **2** was suppressed by water in the reaction. Again, in the presence of water, total yield of the oxidation products as defined above was always larger than the yield of reduction product **7** in every reaction.

As a conclusion, **2** had higher reactivity than **1** in sub- and super-critical water. The reaction of **2** in SCW was temperature- and time-dependent. Compound **2** reacted more rapidly with an increase in reaction temperature up to 380 °C. Longer reaction time caused higher conversion of **2** and higher yields of products. The total amount of oxidation product **6** and its secondary products (**1**, **3**, and **4**) was higher than that of reduction product **7** in the presence of water.

Reaction of Reference Compound Benzyl Alcohol (9) in SCW. The reaction behavior of benzyl alcohol (**9**) in SCW,



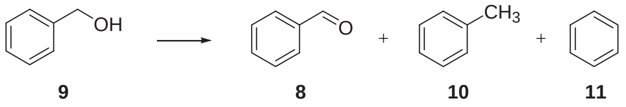
Scheme 3.

Table 3. Reaction of **2** in Subcritical and Supercritical Water[a)]

Entry	Temperature /°C	Water density /g mL^{-1} b)	Reaction time /min	Conversion /%	Product/%					
					6	**7**	**8**	**1**	**3**	**4**
1	300	0.35[c)]	10	42	8	2	1	<1	—[d)]	—[d)]
2	340	0.35[c)]	10	47	15	5	2	2	—[d)]	—[d)]
3	380	0.35	0[e)]	27	10	1	<1	<1	—[d)]	—[d)]
4	380	0.35	1	36	15	3	1	1	—[d)]	—[d)]
5	380	0.35	5	59	16	6	4	4	<1	<1
6	380	0.35	10	66	19	9	6	6	<1	<1
7	380	0	10	95	26	30	6	<1	<1	<1
8	380	0.05	10	81	19	16	12	<1	<1	<1
9	380	0.15	10	73	18	10	12	2	<1	<1
10	380	0.25	10	68	16	7	8	3	<1	<1
11	400	0.35	10	67	18	9	15	7	<1	<1

a) Reaction conditions: 0.236 mmol of **2**, water, under N_2 in SUS 316 tubular reactor. b) Value of water density: water (g)/volume of the reactor (9.9 mL). c) Reaction medium was not homogeneous, because reaction temperature was under the critical temperature of water. d) Not detected. e) As soon as the temperature reached 380 °C, the reaction was quenched by rapid cooling of the reactor in ice-water.

which is a primary alcohol, was compared to the reaction behavior of **1** and **2** (Scheme 4). When alcohol **9** was treated at 380–440 °C for 180 min in 0.35 g mL^{-1} water density in the SUS 316 reactor, oxidation product benzaldehyde (**8**) and reduction product toluene (**10**) were obtained (Table 4). Lower conversion of **9** than that of benzhydrol (**1**) under the same reaction conditions indicates that the reactivity of **9** is lower than that of **1**. Benzene (**11**) was also obtained in the reaction, which should be generated by thermal decomposition of **8**.[20] The total amount of the oxidation products **8** and **11** in this reaction is always larger than that of the reduction product **10**.



Scheme 4.

Conclusion

We demonstrated the reaction behavior of benzhydrol (**1**) and its higher homologue benzoin (**2**), both of which have two benzene subunits, a secondary hydroxy group, and no hydrogen atom on the β-position of the hydroxy group, in sub- and super-critical water without any oxidizing agents or catalysts. Oxidation product **3** and reduction product **4** were produced from the reaction of **1**. In the absence of water, almost a 1:1 (**3**:**4**) mixture was obtained, suggesting that disproportionation between two molecules of alcohol **1** occurred thermally. Higher yields of **3** than that of **4** were always achieved in water under all conditions examined. Efficient oxidation of **1** was achieved at 460 °C for 180 min in 0.35 g mL^{-1} water density in a SUS 316 reactor to give 63% of **3**. Water played a key role in this reaction. The ratio of **3**:**4** always exceeded unity and rapidly increased with an increase in the water density and temperature. Evolution of hydrogen gas was confirmed in the reaction of **1** in a quartz tubular reactor. In the reaction of **2**, the total yield of oxidation product **6** and its secondary reaction products **1**, **3**, and **4** was also higher than that of reduction product **7** in the presence of water. The fact of hydrogen gas evolution, water density dependence of alcohol reaction, and more oxidation products than reduction product in SCW suggests that the water-catalyzed hydrogen generation mechanism is favorable to explain the reaction behavior of alcohols in SCW.

Experimental

^{1}H NMR spectra were obtained on a Varian Unity Inova spectrometer operating 400 MHz. GC-MS analyses were performed on a Shimadzu GCMS-QP 5050. GC analyses were done on a Shimadzu GC-17A gas chromatograph with CBP-5 and/or DB-1 columns. Benzhydrol and benzyl alcohol were purchased from Nacalai Tesque Inc., and benzoin was purchased from Wako Pure Chemical Industries Ltd.

The relevant alcohol and reverse osmosis water, into which nitrogen gas had been bubbled for 30 min to remove the dissolved oxygen, were introduced into a SUS316 tubular reactor. The reactor was purged with N_2 for 10 min to remove the oxygen in the reactor and sealed with a screw cap, which was equipped with a thermocouple for measuring the reactor temperature. The reactor

Table 4. Reaction of **9** in Supercritical Water[a)]

Entry	Temperature /°C	Water density /g mL^{-1} b)	Reaction time /min	Conversion /%	Product/%		
					8	**10**	**11**
1	380	0.35	180	9	5	<1	—[c)]
2	400	0.35	180	18	10	2	<1
3	420	0.35	180	26	14	5	1
4	440	0.35	180	40	21	10	8

a) Reaction conditions: 1.09 mmol of **9**, water, under N_2 in SUS 316 tubular reactor. b) Value of water density: water (g)/volume of the reactor (9.9 mL). c) Not detected.

was then put in a molten salt bath, which was kept at an appropriate temperature, and heated for an appropriate time. It took about 20–30 s to raise the inner reactor temperature up to 380–460 °C. After the reaction, reactor was placed into an ice water bath to quench the reaction. When the reactor was completely cooled down, the screw cap was opened. The reaction mixture was extracted 3 times with ether. The organic phase was separated, and the solvent was evaporated in vacuo to give crude products. The crude products were purified by using silica gel chromatography (Wako C-200, ether and hexane) and GPC (JAI gel 1H and 2H, chloroform), if necessary. The products were identified using ^{1}H NMR and GC-MS by comparing the spectra with those of authentic samples. Conversion of the starting materials and yields of the products were determined using an internal standard method in the GC analysis. Heptadecane and dodecane were used as internal standards.

Reaction in quartz tubular reactor: To a quartz tubular reactor was added **1** (50 mg, 0.272 mmol) and water (0.34 mL). The quartz reactor, which had an inner volume of 1 mL, was sealed with a flame under N_2. The sealed quartz reactor was inserted into the SUS 316 reactor, which was filled with 4 mL of water, and then the SUS 316 reactor was closed tightly. The SUS 316 reactor with the small quartz reactor inside was heated at a desired temperature by the method similar to that described above. Evolved gases were identified and quantified with GC.[12]

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16 When alcohol **1** was treated with and without additional hydrogen gas in SCW (**1**: 0.054 mmol, H_2: 0 or 0.29 mmol, 440 °C for 180 min in 0.35 g mL^{-1} water density in SUS 316 reactor), no difference in the product distributions was observed between the reactions with and without additional hydrogen gas (with H_2, **3**: 24%, **4**: 15%; without H_2, **3**: 25%, **4**: 13%). But the possibility of the reduction of **1** not by hydrogen gas generated in situ but nascent hydrogen in the reaction conditions still remains. Reduction of **1** and **3** to give **4** in 15% aqueous formic acid or 15% aqueous sodium formate in supercritical conditions (460 °C, 60 min) was reported: A. R. Katritzky, E. S. Ignatchenko, S. M. Allin, R. A. Barcock, M. Siskin, C. W. Hudson, *Energy Fuels* **1997**, *11*, 160.

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