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The first ESR observation of radical species in subcritical water

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ABSTRACT

Triphenylmethanol was treated in subcritical and supercritical water. A radical species, triphenylmethyl radical, was directly generated from triphenylmethanol in subcritical and supercritical water without using any radical initiator. The radical formation was confirmed by direct electron spin resonance (ESR) measurement in high-temperature and high-pressure subcritical water and by capturing the radical intermediate using hydrogen donors in supercritical water.

1. Introduction

Subcritical water (sub-CW) and supercritical water (SCW) have attracted much attention in recent years not only from the view point of green chemistry but also their unique properties, such as low viscosity, high density, low polarity, and high water solubility of organic compounds.[1] Recently, sub-CW and SCW have been used as reaction media and reaction catalysts for organic reactions, such as H–D exchange reaction in supercritical deuterium oxide,[2] the Beckmann rearrangement of cyclohexanone oxime,[3] pinacol rearrangement of 2,3-dimethyl-2,3-butanediol,[3] the Cannizzaro reaction of formaldehyde[4] and benzaldehyde,[5] the Heck reaction,[6] C–Si bond cleavage,[7] benzil–benzilic acid rearrangement,[8] and the Claisen–Schmidt reaction.[9] More recently, unique reactions such as the oxidation of alcohols to obtain the corresponding aldehydes or ketones without the use of any oxidizing reagent or catalyst have been reported.[10,11] All the above-mentioned examples are concerned with ionic reactions that are catalyzed by H^+ and/or OH^- ions generated from water in situ[2–9] or by hydrogen bonding between the substrates and two water molecules to achieve an eight-membered ring transition state of the reaction.[10–13]

On the other hand, radical reactions are another common feature of the reactions that occur particularly in less dense SCW[14] as exemplified in the waste treatment of polymers and hazardous compounds in the presence of a large amount of oxygen.[15] Addition of hydrogen peroxide,[16] pulse radiolysis of water,[17] and acoustic cavitation[18] are also used to generate radical species in SCW. Although radical generation in water using these approaches is relatively easy, little is known about the direct observation of radical species generated in sub-CW and SCW. In this study, we report the generation of radical species from triphenylmethanol (**1**), direct observation of radical species in sub-CW using ESR, and the reaction behavior of the generated radical species in SCW.

2. Results and discussion

The triphenylmethyl radical is considered one of the most stable radicals. We selected this radical to investigate the reaction behavior of radical(s) generated in sub-CW and SCW, because of the following reasons: (i) the radical has no hetero bond that can be easily cleaved under the drastic reaction conditions of sub-CW and SCW; (ii) the benzene moieties of the radical are known to exhibit an attractive interaction with water molecules of sub-CW and SCW;[19] and (iii) the radical has a highly symmetrical structure, which simplifies the analysis of reaction products. Although there are several precursors from which the triphenylmethyl radical can be obtained, **1** seems to be one of the most suitable substrates, since the cleaved OH species and water molecules has very similar structural analogy and the cleaved OH would adapt to the surrounding water molecules.

Two possibilities exist when the carbon–OH bond of **1** is cleaved (Scheme 1). One is the ionic (heterolytic) fission of the bond to generate a triphenylmethyl cation and a hydroxyl anion. The other is the radical (homolytic) fission of the bond to generate triphenylmethyl and hydroxyl radicals. Another radical fission to generate diphenylhydroxymethyl and phenyl radicals is also possible. Semi-empirical molecular orbital calculations (AM1)[20] were performed to estimate the bond dissociation energies of the C–OH and C–Ph bonds of **1** in vacuum and in water (Scheme 1). The hydration effect was also considered using COSMO method in the calculations.[21] The bond dissociation energy for the ionic fission in water to generate triphenylmethyl and hydroxyl ions was calculated to be 71 kcal/mol, while those for the radical fissions to generate diphenylhydroxymethyl and phenyl radicals, and triphenylmethyl and hydroxyl

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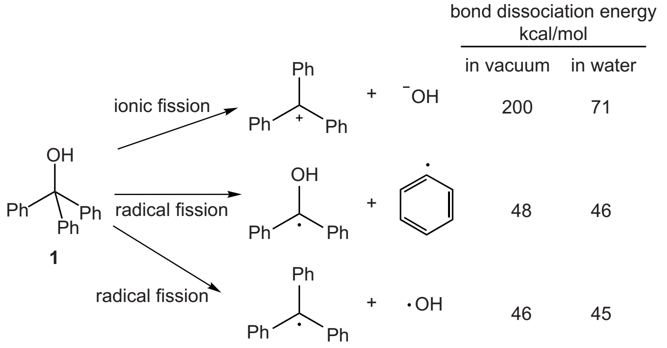


Scheme 1. Ionic and radical fissions of C–OH and C–Ph bonds of **1** and their bond dissociation energies in vacuum and in water calculated by MOPAC (AM1/COSMO method).

radicals were 46 and 45 kcal/mol, respectively. The corresponding dissociation energies in vacuum were calculated to be 200, 48, and 46 kcal/mol, respectively. Based on these calculations, the radical fissions would be more plausible than the ionic fission.

ESR spectroscopy is well known to be one of the most powerful methods to detect radical species directly. However, the glass sample tubings as well as the ESR instrument itself must tolerate the drastic conditions of such high-temperature and high-pressure. A commercial ESR instrument was modified to be equipped with the temperature control unit, which maintains the sample temperature being high by blowing the temperature controlled N_2 gas. We succeeded in observing the ESR signals of **1** in sub-CW (300 °C) using a quartz sample tubing instead of glass ones. As seen in Figure 1, characteristic ESR signals were observed, which clearly indicate the formation of radical species in the sub-CW. Due to the uncertainty of the hyperfine structures of the observed ESR signals, it is difficult to put forward a conclusive discussion of the radical species. However, the observed signals could be derived from triphenylmethyl radicals generated in sub-CW, since the signal shape and coupling constant (a=0.22 mT) are similar to the reported shape and value in toluene (a_p^H=0.286 mT).[22] To our knowledge, this is the first successful example of the direct ESR measurement of radical species in sub-CW.

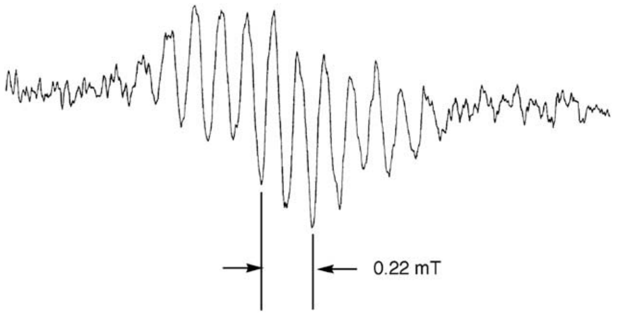
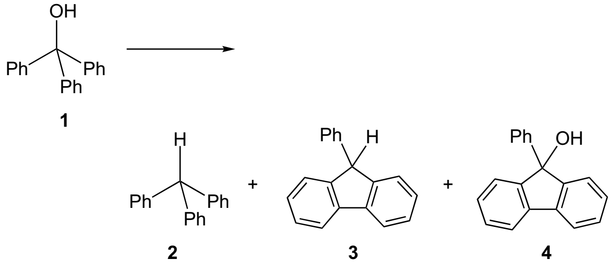


Figure 1. ESR spectrum of **1** in subcritical water (2.3 μmol of **1**/46 μL of water at 300 °C).



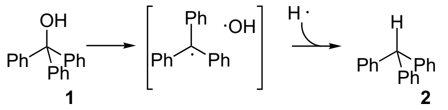
Scheme 2. Reaction of **1** in supercritical water.

Table 1
Reaction of **1** in supercritical water with and without hydrogen donor[a]

Entry	Hydrogen donor	Time (min)	Recovery (%)	Yield (%)		
			1	2	3	4
1	no	30	9	26	42	9
2	**5**[b]	20	1	>99	0	0
3	**6**[b]	30	0	96	3	0

[a] Reaction conditions: 0.192 mmol of **1**, 380 °C, 0.35 g/mL water density.
[b] An equimolar amount of hydrogen donor (0.192 mmol) was used.

When alcohol **1** was treated with SCW in an SUS316 batch type tubular reactor in a preparative scale,[23] the reaction proceeded smoothly to provide 26% of reduction product triphenylmethane (**2**), 42% of dehydrated cyclization product 9-phenylfluorene (**3**),[24] and 9% of 9-phenyl-9-fluorenol (**4**) with 9% recovery of substrate **1** (Scheme 2 and entry 1 in Table 1). If these products are derived from the radical intermediate(s), as suggested by the ESR measurement, it is reasonable to use a hydrogen donor such as 9,10-dihydroanthracene (**5**) or 2,5-di(*tert*-butyl)-1,4-hydroquinone (**6**) to trap the radical intermediate(s). When alcohol **1** was treated with SCW (380 °C, 0.35 g/mL water density) in the presence of an equimolar amount of hydrogen donor **5** or **6**, (almost) qualitative amount of reduction product **2** was obtained in each case (entries 2 and 3 in Table 1). These results clearly indicate that the reaction proceeds via the triphenylmethyl radical intermediate, and that the radical easily abstracts a hydrogen atom of the hydrogen donors coexisting in the reaction system to give the reduction product **2**, as shown in Scheme 3.[25] If no other hydrogen source was available, however, the radical would abstract a hydrogen atom from the other molecules instead to afford the same reduction product **2** or the radical would be submitted to further reactions to yield **3** and **4**.



Scheme 3. Plausible reaction pathway of **1** to give **2** in supercritical water.

To clarify the overall reaction behavior of compound **1** in SCW, the reaction temperature and water density were varied, as shown in Table 2. In the presence of water, the recovery of substrate **1** decreased with increasing temperature and the (almost) complete consumption of **1** was achieved at above 400 °C (entries 3–6). Reduction product **2** and dehydrated cyclization product **3** were obtained at all test temperatures. Yield of **2** increased gradually with increasing temperature, although the yield of **3** almost saturated at around 400 °C (entries 3–6). Cyclization product **4** having an OH group was produced only at low temperatures (<380 °C) with a low yield (9%) (entries 1 and 2).[26] Formation of **2** was almost independent

Table 2
Reaction of **1** in subcritical and supercritical water[a]

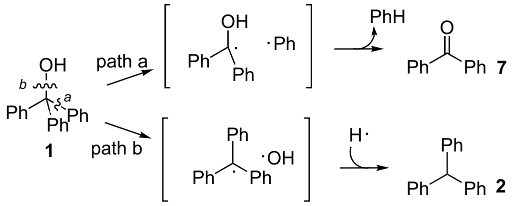
Entry	Temp (°C)	Reaction time (min)	Water density (g/mL)	Recovery (%)	Yield (%)			
				1	2	3	4	7
1	330	30	0.35	36(9)	16(2)	26(10)	9(4)	0
2	380	30	0.35	9(5)	26(3)	42(6)	9(3)	0
3	400	30	0.35	0	27(1)	56(5)	0	0
4	420	30	0.35	2(1)	31(3)	47(4)	0	0
5	440	30	0.35	1(2)	37(5)	44(19)	0	0
6	460	30	0.35	0	38(1)	47(1)	0	0
7	420	30	0	16(3)	36(5)	0	0	11(2)

[a] Recovery and yields are mean values of at least three runs. Standard deviation is given in parentheses.

of the water density (entries 4 and 7). Interestingly, benzophenone (**7**) was obtained instead of **3** and **4** in the absence of water.

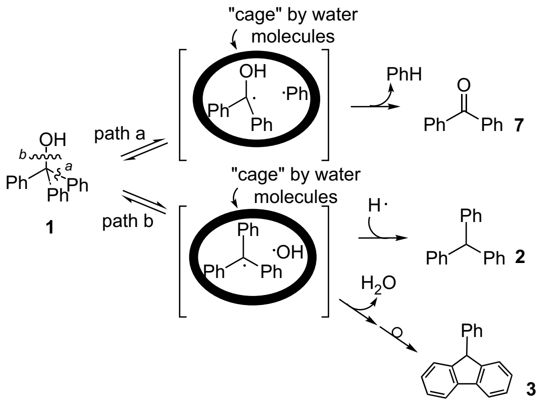
2.1. Reaction pathway

Considering the experimental data, we propose the following reaction pathway. In the case of simple pyrolysis (no water), homolytic fission would occur to give radical species via both *path a* and *path b* (Scheme 4). *Path a* should lead to the formation of diphenylhydroxymethyl and phenyl radicals. Benzophenone (**7**) should be formed if a hydrogen atom of the diphenylhydroxymethyl radical is abstracted.[27] On the other hand, *path b* should lead to the formation of triphenylmethyl and hydroxyl radicals. Then, reduction product **2** should be produced if the triphenylmethyl radical abstracts a hydrogen atom from the other molecules that might be derived from the residues such as decomposed products.



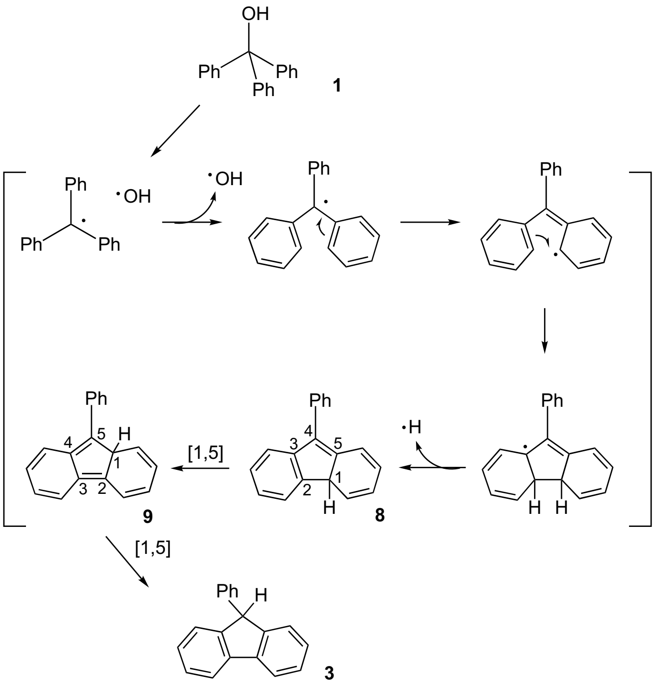
Scheme 4. Plausible reaction pathways of **1** in the absence of water.

The presence of water, however, changes the reaction behavior (Scheme 5). When an organic compound is immersed in SCW, water molecules surround and strongly solvate the organic molecule to form a water 'cage' around it.[28] The cage in which the radical species would be generated should lengthen the lifetime of the radical species by suppressing the diffusion process of the organic molecule. This should promote the recombination of the radical species and prevent the reaction from proceeding through *path a* to lead to **7**.[29]



Scheme 5. Plausible reaction pathways of **1** in the presence of water.

Moreover, the cage should also prevent the radical intermediates, triphenylmethyl and hydroxyl radicals, from diffusing in *path b*. Now, if a hydrogen atom is supplied from outside, the triphenylmethyl radical would abstract the hydrogen atom to afford reduction product **2**, particularly in the presence of hydrogen sources such as the hydrogen donors. Instead, if the fairly reactive hydroxyl radical abstracts a hydrogen atom of the triphenylmethyl radical, dehydrated cyclization product **3** should be obtained (Scheme 5). The reaction pathway to give **3** from the triphenylmethyl radical is shown in Scheme 6. The triphenylmethyl radical would rearrange and cyclize successively to give intermediate **8**, which would undergo a [1,5] hydrogen shift twice to give **3**, as demonstrated by Miyagawa et al.[30] and Shi et al.[31]



Scheme 6. Reaction pathway of triphenylmethyl radical giving **3**.

3. Conclusion

We successfully observed the ESR signals of a radical species of triphenylmethyl radical in sub-CW generated from triphenylmethanol. The water density of the reaction media played a crucial role in the generation of radical species. In the absence of water, benzophenone was obtained along with a large amount of triphenylmethane, while dehydrated cyclization product **3** was obtained as the main product along with **2** in the presence of water.

4. Experimental section

4.1. Materials and methods

GC analyses were done on a Shimadzu GC-17A equipped with a CBP-5 glass capillary column. GC–MS analyses were performed on a Shimadzu QP5050. ^{1}H NMR spectra were recorded on a Varian Unity Inova 400 spectrometer. ESR spectrum was recorded on a JEOL JES-RE-2X-ESR spectrometer. Triphenylmethanol (**1**), triphenylmethane (**2**), 9,10-dihydroanthracene (**5**), *n*-heptadecane, and *n*-heneicosane were purchased from Nacalai Tesque, Inc. 9-Phenyl-9-fluorenol (**4**) was purchased from Aldrich. 2,5-Di(*tert*-butyl)-1,4-hydroquinone (**6**) was purchased from Wako Pure Chemicals Industries, Ltd. Reverse osmotic water was used as a reaction medium in all reactions.

4.2. Reaction of triphenylmethanol (1) in water

Alcohol **1** (50 mg, 0.192 mmol) and water (N_2 bubbled) were introduced into an SUS316 tubular reactor of 10.0 mL inner volume. The reactor was purged by N_2 and sealed with a screw cap, which was equipped with a thermocouple for the measurement of the reactor temperature. The reactor was then put in a melting-salt bath, which was kept at an appropriate temperature, and heated for an appropriate time. It took about 20–30 s for the inner reactor temperature to be raised up to 380–460 °C. The reaction was quenched by placing the reactor into an ice-water bath. After the reactor was completely cooled, the screw cap was opened and the reaction mixture was extracted with ether. The organic phase was separated and the solvent was evaporated in vacuo to give the crude products. The products were purified further by GPC (JAI gel 1H+2H, chloroform), if necessary, and were identified by comparing their ^{1}H NMR and GC–MS spectra with those of authentic samples. Recovery of **1** and yields of the products were determined by internal standard method on GC and/or integration ratio of signals on ^{1}H NMR spectra. *n*-Heptadecane and *n*-heneicosane were used as internal standards for GC measurements.

4.3. Measurement of ESR spectra

Alcohol **1** (0.60 mg, 2.3×10^{-6} mol) and 0.046 mL of water (N_2 bubbled) was placed in a quartz tubing (o.d.: 2.7 mm, i.d.: 1.5 mm). The tubing was sealed (ca. 8 cm height) after the air was replaced by argon. Pressure resisting test of the sample quartz tubings was performed by heating at 300 °C for 5 min before use. The tubing was allowed to measure the ESR spectra at 300 °C. The sample tubing was heated by blowing the temperature controlled N_2 gas in a double quartz tubing of high-temperature unit.

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23. Same products, **2**, **3**, and **4**, were obtained in both sub-CW and SCW as shown in Table 2. Taking into account that physical properties of sub-CW and SCW, such as density, polarity, and ion product, change continuously between sub-CW and SCW in accordance with the temperature, we think it would be possible to discuss the reaction mechanism in sub-CW and SCW conditions in the same manner.
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25. Two electron transfer followed by proton shift from hydrogen donor, **5** or **6**, to **1** could be possible to afford the reduction product, however the calculated energies (AM1) necessary for the first electron transfer processes from **5** and **6** to **1** are quite larger (183 and 165 kcal/mol, respectively) than the bond dissociation energy for the homolytic fission of **1** (46 kcal/mol, Scheme 1).
26. When alcohol **4** was treated in SCW (420 °C, 30 min, 0.35 g/mL water density), 41% of **3** along with 48% recovery of **4** were obtained. Although the reaction pathway to give **4** from **1** is not clear yet, **4** could be derived from **3** by attack of the generated hydroxyl radical two times.
27. Formation of benzopinacol could be possible, if the reaction proceeds via the radical species. When benzopinacol was exposed to high-temperature (250 °C, GC measurement), disproportionation occurred to give almost equal amounts of benzophenone (**7**) and benzhydrol. Judging from this result, benzopinacol cannot be stable under the reaction conditions even if it is formed by coupling of two diphenylhydroxymethyl radicals in the reaction.
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