

REVIEW

# Effects of water on reactions for waste treatment, organic synthesis, and bio-refinery in sub- and supercritical water

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Received 10 April 2013; accepted 11 June 2013  
Available online 15 July 2013

**Current research analyzing the effects of water in the field of homogeneous and heterogeneous reactions of organics in sub- and supercritical water are reviewed in this article. Since the physical properties of water (e.g., density, ion product and dielectric constants) can affect the reaction rates and mechanisms of various reactions, understanding the effects that water can have is important in controlling reactions. For homogeneous reactions, the effects of water on oxidation, hydrolysis, aldol condensation, Beckman rearrangement and biomass refining were introduced including recent experimental results up to 100 MPa using special pressure-resistance equipment. For heterogeneous reactions, the effects of ion product on acid/base-catalyzed reactions, such as hydrothermal conversion of biomass-related compounds, organic synthesis in the context of bio-refinery, and hydration of olefins were described and how the reaction paths are controlled by the concentration of water and hydrogen ions was summarized.**

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**[Key words:** Supercritical water; Subcritical water; Supercritical water oxidation; Hydrothermal reaction; Gasification; Organic synthesis; Bio-refinery; Acid/base-catalyzed reaction]

Supercritical water, defined as water above its critical point (374°C, 22.1 MPa), has been attracting attention as an environmentally benign reaction medium for the past 3 decades. Its application in the field varies widely, e.g., destruction of hazardous materials (1–3), organic synthesis (1,4–6), synthesis of inorganic materials (7,8), recovery of valuables from wastes (9,10), recycling of polymers (9), energy recovery of biomass (1,11–13).

The advantages of applying supercritical water as a reaction medium for these processes are that it is inexpensive, non-toxic and non-flammable, however, the most important aspect is its physical and transport properties. The various properties of water, e.g., density, dielectric constant, viscosity, ion product ( $K_w$ ), diffusion coefficient, vary over a wide range depending on the temperature and pressure. The solubility of organics and inorganics also changes with the changing properties of water. These properties of water sometimes affect reaction kinetics and mechanisms in various manners and make it possible to control reactions. Some of the properties of water as a function of temperature at various pressures are shown in Fig. 1A–C (14,15). The value of water density decreases with increasing temperature, increases with increasing pressure, and above the critical temperature ( $T_c$ ), it is possible to change the density by controlling the pressure at a constant temperature. The dielectric constant also decreases with increasing temperature, and the value of the dielectric constant is about 2 at

420°C and 25 MPa, which corresponds to that of hexane. In contrast, the value of the ion product does not show constant decrease with temperature, but has a maximum at around 300°C. Furthermore, these specific trends of the physical properties of water can be controlled continuously without phase change in the supercritical region. Therefore, it is necessary to understand the effects of the properties of water on reactions in supercritical water by controlling the conditions precisely.

In this review article, the effects of water on both homogeneous and heterogeneous reactions in sub- and supercritical water are summarized, including our recent research progress. In the first section, we focus on the effect of water on homogeneous reactions in sub- and supercritical water, especially decomposition and oxidation reactions of organics without using a solid catalyst. In the latter section, the researches on the effects of water on bio-refinery and organic synthesis using solid acid/base catalysts are reviewed as a typical example of controlling a reaction path using the ion product.

## HOMOGENEOUS REACTIONS IN SUB- AND SUPERCRITICAL WATER

**Overview of the effects of water on homogeneous reactions** There have been many previous studies of homogeneous reactions in supercritical water, and the kinetics of these reactions is one of the main areas of discussion. Several sets of data have implied that the reaction rate can be affected by changes in the

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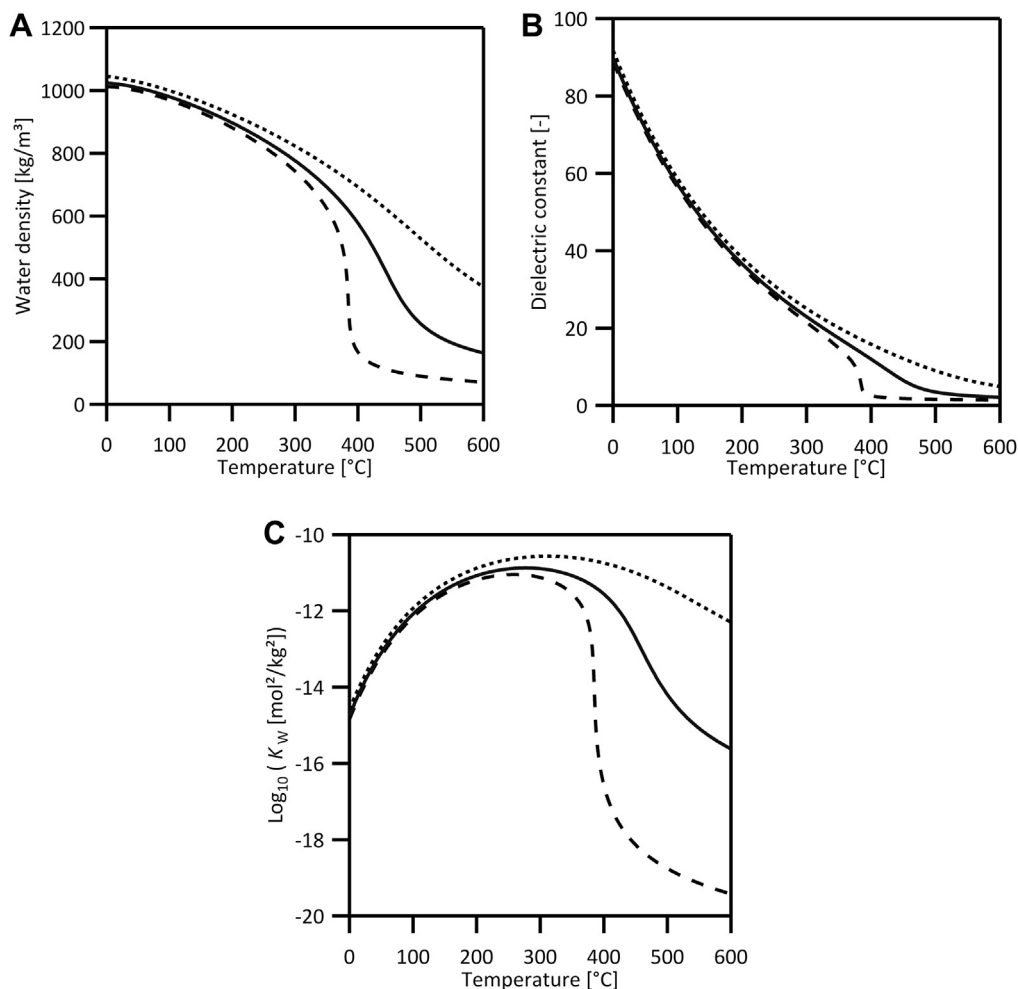


FIG. 1. Properties of water as a function of temperature. (A) Density (14), (B) dielectric constant (14), (C) ion product (15). Dashed line: 25 MPa; solid line: 50 MPa; dotted line: 100 MPa.

water properties. In supercritical water oxidation, for example, it has been reported that the decomposition rate of compounds such as CO (16,17), methanol (18,19), and phenol (20) is a function of water density. Several reports have indicated that other types of reactions such as hydrolysis (21–33), dehydration (34–36), and other organic reactions (37–47) are also affected by water density. Table 1 summarizes the experimental conditions of selected previous reports on the effects of water density on reactions in sub- and supercritical water. The role of water in these reactions was discussed in some reviews (4,48,49). Water can influence reactions by participating in the reaction as a reactant or as a catalyst, contributing to changes in the free energy of activation through solute–solvent interactions and solvent reorganization, phase behavior, solute solvent collisions, diffusion limitations and cage effects. Each of these effects has been thoroughly discussed in the literature. Although such work succeeded in explaining many of the effects of water on the reaction kinetics qualitatively or partly quantitatively, the details of the effects of water have not been completely understood. Kruse and Dinjus (4,49) pointed out that the knowledge of microscopic structuring (e.g., hydrogen bonds and solvation structure) is still poor, although several experimental results are available. They also said that more knowledge about solvation effects in hot-compressed water is needed to get a better understanding of the impact of water's properties on chemical reactions, and that for a kinetic description, the kinetic parameter, e.g., the activation volumes of single reaction steps, including its dependence on density and temperature, is necessary.

**Catalytic effects of water on reactions** Recently, it has been indicated by quantum chemical calculation that, in the gas phase, water reduces the activation energy by participating in a reaction involving hydrogen transformation, e.g., decomposition of formic acid (38,50–55), aldol condensation (56), ethanol oxidation (57,58) and hydrolysis of amide (59). One or two water molecules participate in these reactions and form activation complexes. By forming complexes, the activation energies are reduced. Fig. 2 shows one of the calculated results of formic acid decomposition (38). Such an effect of water participating in the activation complex is called as catalytic effect, water-assisted reaction, or concerted mechanism. In formic acid decomposition, for example, the catalytic effect qualitatively accounted for differences in selectivity and activation energies in the absence and presence of water. However, the catalytic effect cannot explain the experimentally observed pressure dependence of formic acid decomposition in supercritical water (37). Although the water concentration is higher in a high pressure condition, formic acid decomposition is suppressed at a pressure that is higher than the critical pressure. This discrepancy suggests that the water around solutes (reactants) affects the reaction. Honma and Inomata (60) investigated the role of local structure on formic acid decomposition in supercritical water with quantum mechanics/molecular mechanics (QM/MM) simulation and suggested that a particular solvation structure, e.g., hydrogen bonds around formic acid, determines the pathway to promote or restrict the reaction. Quantitative evaluation has not yet been conducted due to the mismatch of conditions between experiments and theoretical

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