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Roles of Water for Chemical Reactions in High-Temperature Water

Naoko Akiya[†] and Phillip E. Savage*

Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan 48109-2136

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I. Introduction

High-temperature water (HTW), which we define broadly herein as liquid water above 200 °C and supercritical water ($T > 374$ °C, $P > 218$ atm), is attracting attention as a medium for organic chemistry. Chemistry in HTW is important from both scientific and engineering standpoints. For example, consider geochemical reactions in HTW.[1] The conversion of kerogen into petroleum occurs in HTW in the presence of clay minerals.[2,3] Reactions in hydrothermal vents are suggested to have contributed to the origin of life.[4−6] There has also been much previous research in the application of HTW as a reaction medium for chemical synthesis, materials synthesis, waste destruction, plastics recycling, coal liquefaction, and biomass processing.[7−11] The use of HTW for these reactions has been motivated by the desire to create cleaner, safer, and more environmentally benign chemical processes.

HTW exhibits properties that are very different from those of ambient liquid water, as will be discussed in more detail in section II. HTW has a lower dielectric constant, fewer and weaker hydrogen bonds, and a higher isothermal compressibility than ambient liquid water. Small organic compounds become increasingly soluble in HTW and completely miscible in SCW.[12,13] The solubility of most gases in liquid water initially decreases as the temperature is increased above ambient, but a minimum is soon reached, and then the gas solubility increases. For oxygen, for example, this minimum in solubility occurs around 100 °C.[14] Moreover, the ion product (K_w) for high-temperature liquid water is about 3 orders of magnitude higher than that for ambient liquid water. These properties of HTW vary with temperature and pressure (or density) over wide ranges at nearcritical and supercritical conditions. Consequently, HTW can support ionic, polar nonionic, and free-radical reactions. The relative rates of these different classes of reactions can be very sensitive to the reaction conditions. The state-sensitive nature of the solvent properties can give rise to marked temperature and density effects on the reaction kinetics, as observed experimentally for numerous reactions in HTW.

A successful application of HTW as a reaction medium requires the right combination of the chemistry and the reaction environment that HTW provides. At times water is not an inert medium but an active participant in the reaction. One must understand the interactions between the reacting system and the water medium to exploit fully the unique properties of HTW and to maximize control over the HTW-mediated processes. Individual water molecules can participate in the reaction as reactants or as catalysts. Water can contribute to the changes in the free energy of activation through solute−solvent interactions and solvent reorganization. Water can also influence reactions through phase behavior, solute−solvent collisions, diffusion limitations, and cage effects.

There have been few studies in the literature that closely examined the different potential influences of HTW on chemical reactions. Although the existing

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* To whom correspondence should be addressed. Phone: (734) 764-3386. E-mail: psavage@umich.edu.
[†] The Dow Chemical Company, 2301 Brasozport Blvd., Freeport, TX 77541.

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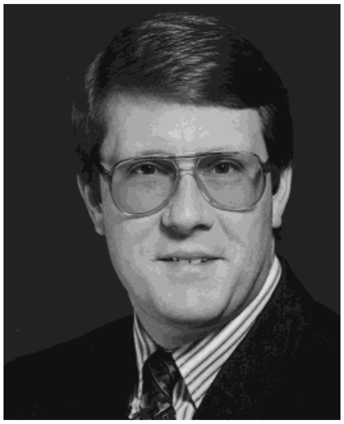
Naoko Akiya is a senior research engineer at the Dow Chemical Company in Freeport, TX. She joined Dow Chemical in mid 2001. She received her B.S. degree in 1996 from Rice University in Houston, TX. She received her M.S. degree in 1999 and Ph.D. degree in 2001 from the University of Michigan in Ann Arbor, MI. All of her degrees are in Chemical Engineering. Her graduate study, conducted under the direction of Professor Phillip Savage, focused on elucidating the roles of water on model chemical reactions in high-temperature water, using a combination of experimental and molecular modeling tools.



Phillip Savage is Professor of Chemical Engineering at the University of Michigan. He received his B.S. degree from Penn State in 1982 and his M.Ch.E. (1983) and Ph.D. (1986) degrees from the University of Delaware. All of his degrees are in Chemical Engineering. Phil's research focuses on the rates and mechanisms of organic chemical reactions that are of environmental significance. Current projects deal with reactions that can be used for environmentally benign chemical synthesis and for waste treatment. His research group uses experiments, mechanistic modeling, molecular simulation, and computational chemistry to explore different reaction systems. Most of the group's recent work has dealt with homogeneous catalysis in high-temperature water and oxidation in supercritical water. In addition to his research activities and classroom teaching at Michigan, Phil is also a co-lecturer in continuing education courses on the topics of kinetics, catalysis, and reaction engineering.

reviews and overviews of reactions in aqueous media[7−11,15−19] include some discussions of solvent effects, in none of these reviews is the focal point the role of the reaction medium. Thus, previous treatments of this topic are neither complete nor critical. This article presents the first comprehensive review and analysis of the roles of water for organic chemical reactions in HTW. The literature in this area is diverse and fragmented. Publications have appeared in chemical engineering, physical chemistry, chemical physics, fuel science, and geochemistry journals. In this review, we tie this fragmented literature together for the first time. Our goal is to provide a critical evaluation of all published information, so that those active in or entering this field can identify the roles and effects of water that are likely to be important for a particular chemistry at a particular set of reaction conditions.

II. Properties of HTW

HTW is structurally different from ambient liquid water, especially at supercritical states. This difference gives rise to properties that are unique to HTW. The structural and physical properties of pure water at elevated temperatures and pressures have been determined with a variety of experimental and computational techniques.[20−52] These data provide important clues for understanding the solvent effects on chemical reactions in HTW.

Pair correlation functions, which measure the spatial correlation of fluid density, are commonly used to decipher fluid structures. Experiments and computer simulations have consistently shown that the appearance of the oxygen−oxygen (or center-of-mass) correlation function for water changes with temperature and density.[20,21,23,25−28,33,35,36,39,43,46,49−51] Figure 1 shows that with increasing temperature, the nearest-neighbor peak ($r_{OO} \sim 3$ Å) becomes smaller and shifts toward larger distances whereas the second-neighbor peak ($r_{OO} \sim 4.5$ Å) becomes smaller and then disappears. These changes reflect the loss of the tetrahedral coordination in ambient liquid water, because of the reduced extent of the hydrogen-bond network in HTW. Figure 2 shows that with decreasing density, at near-critical temperatures and higher, the nearest-neighbor peak becomes larger whereas the second-neighbor peak becomes smaller and disappears. These changes indicate that the structure of HTW approaches that of a simple gas with decreasing density.

Hydrogen bonding is the source of many of the unique properties of liquid water. In general, the hydrogen bonding in water becomes weaker and less persistent with increasing temperature and decreasing density, as shown in Figure 3. Although the precise temperature and density dependence of hydrogen bonding in water has been the subject of debate for many years, numerous experiments and computer simulations have established that a reduced but nonzero extent of hydrogen bonding exists in HTW, even at supercritical temperatures (as high as ~800 K) and gaslike densities (as low as ~0.1 g/cm^3).[21−23,25−27,29,30,34−39,41,44,45,49−51] The persistence of hydrogen bonds in HTW is manifested in the hydrogen-bond peak of the oxygen−hydrogen correlation function that does not disappear at these conditions. For example, water at 773 K and ~0.1 g/cm^3 retains 10−14% of the hydrogen bonds that exist at ambient conditions, whereas water at 673 K and ~0.5 g/cm^3 retains 30−45%.[44]

Unlike the infinite percolating network of hydrogen bonds found in ambient liquid water, the hydrogen-bond network in HTW exists in the form of small clusters of hydrogen-bonded water molecules, with the cluster size distribution being state-dependent.[24,27,29,30,49] With increasing temperature and decreasing density, the average cluster size decreases.

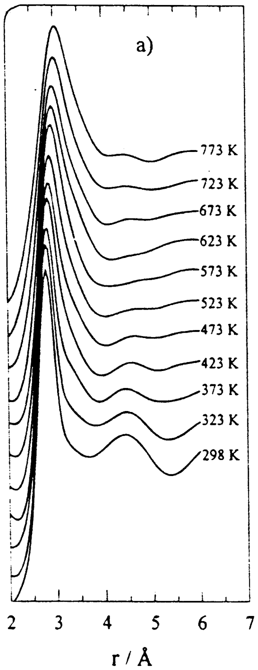


Figure 1. Molecular pair correlation functions of liquid and supercritical water at a constant pressure of 100 MPa. (Reprinted with permission from ref 21. Copyright 1995 American Chemical Society.)

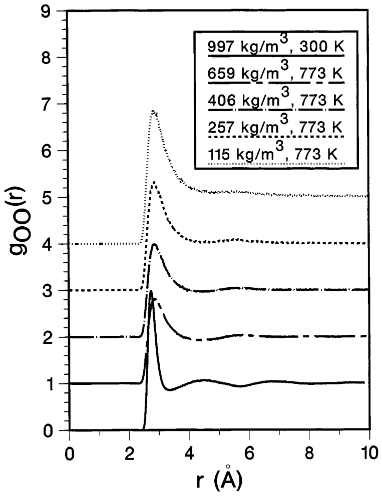


Figure 2. Oxygen−oxygen pair correlation functions of liquid and supercritical water. (Reprinted with permission from ref 28. Copyright 1994 American Chemical Society.)

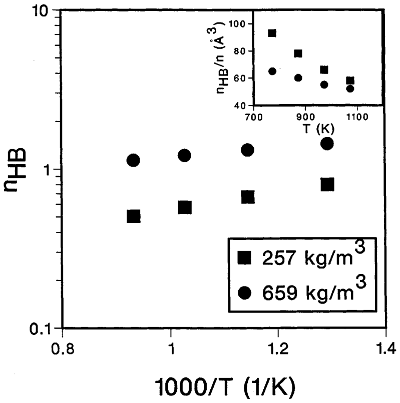


Figure 3. Number of hydrogen bonds per water molecule. (Reprinted with permission from ref 30. Copyright 1996 American Chemical Society.)

Molecular simulations have shown that although most water molecules belong to clusters of five members or less at the supercritical conditions of 773−1073 K and 0.12−0.66 g/cm^3, a small number of clusters that are as large as 20+ molecules might also exist.[24,29,30] These studies demonstrate that although HTW is much less ordered than ambient liquid water, it still retains some liquid water-like structure on a microscopic level.

The changes in the extent of hydrogen bonding are accompanied by corresponding changes in the static dielectric constant of water,[28,47,53,54] as shown in Figure 4c. Uematsu and Franck proposed the following empirical equation to correlate the experimentally measured dielectric constant (ϵ) for water with temperature and density

$$\epsilon = 1 + \left(\frac{A_1}{T}\right)\rho + \left(\frac{A_2}{T} + A_3 + A_4T\right)\rho^2 + \left(\frac{A_5}{T} + A_6T + A_7T^2\right)\rho^3 + \left(\frac{A_8}{T^2} + \frac{A_9}{T} + A_{10}\right)\rho^4 \quad (1)$$

where T is a normalized temperature, ρ is a normalized density, and A_i are fitting parameters.[54] With increasing temperature and decreasing density, the static dielectric constant of water decreases. For example, the dielectric constant is 21 at 300 °C and 0.75 g/cm^3 and 4.1 at 500 °C and 0.30 g/cm^3, compared to 78 for ambient liquid water.[54] With such a low dielectric constant, HTW behaves more like polar organic solvents rather than ambient liquid water under certain conditions. Consequently, small organic compounds are highly soluble in HTW and completely miscible in supercritical water (SCW),[12,13] whereas ions generally exist as contact pairs, resulting in reduced solubility for inorganic salts.[55] Section IV.B discusses the solvation behavior of various compounds in HTW in much more detail.

The structural changes of water also affect the dynamics of water molecules. The breaking of the hydrogen-bond network reduces the barrier for translational and rotational motions. This effect contributes to the increase in the self-diffusivity of water with increasing temperature and decreasing density.[31,50−52,56] With the change in density from 1 to 0.1 g/cm^3, the diffusivity increases by roughly an order of magnitude. The diffusivity behavior at low densities ($\rho < \rho_c$) is qualitatively consistent with the kinetic theory of gases.[50] Similarly, the rotational relaxation time decreases with increasing temperature, but its variation with density shows a minimum near 0.2 g/cm^3 at 600 K.[50] These changes in transport properties can affect reactions that are influenced by nonequilibrium solvation effects (section IV.A.3) or reactions that are diffusion-controlled (section V.B).

Figure 4b shows that the ion product (K_w) is another important property of water that varies considerably with changes in temperature and density. Marshall and Franck proposed the following empirical equation to correlate the experimentally

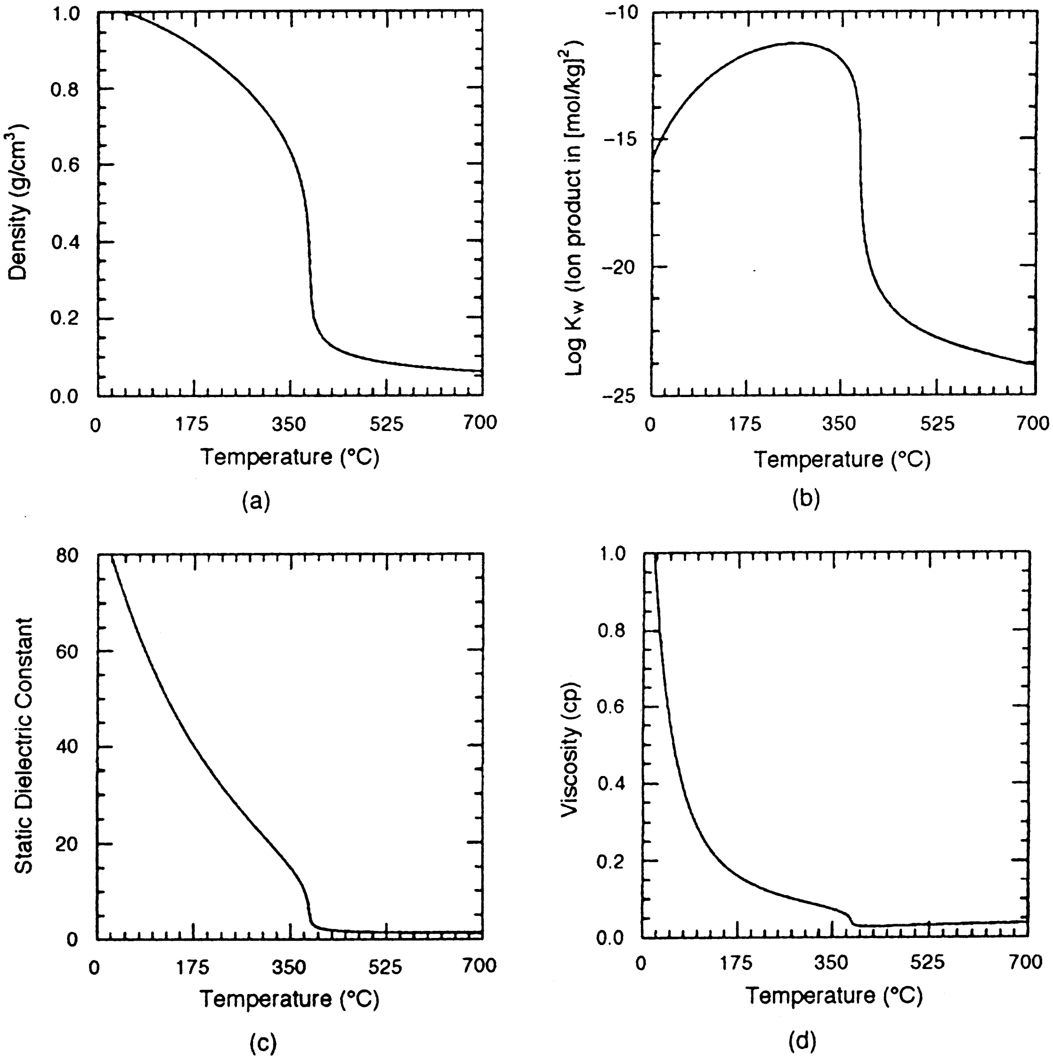


Figure 4. Properties of pure water at 250 bar as a function of temperature. (Reprinted with permission from ref 17. Copyright 1999 National Association of Corrosion Engineers.)

measured ion product of water [K_w in (mol/kg)^2] with temperature and density

$$\log K_\mathrm{w} = A + \frac{B}{T} + \frac{C}{T^2} + \frac{D}{T^3} + \left(E + \frac{F}{T} + \frac{G}{T^2}\right) \log \rho \tag{2}$$

where T is temperature in Kelvin, ρ is density in g/cm^3, and $A-G$ are fitting parameters.[57] The value of K_w for liquid water near the critical temperature is about 3 orders of magnitude higher than that of ambient liquid water. Consequently, HTW at these conditions enjoys concentrations of H^+ and OH^- ions that are naturally higher than in ambient liquid water. As such, dense HTW is an effective medium for acid- and base-catalyzed reactions (section III.B.1). On the other hand, K_w for SCW at gaslike densities (<0.1 g/cm^3) can be tens of orders of magnitude lower than for ambient liquid water. Accordingly, free-radical chemistry dominates at these high-temperature, low-density conditions. Antal et al. proposed that ionic mechanisms are favored when $K_w > 10^{-14}$ and free-radical mechanisms are favored when $K_w \ll 10^{-14}$.[58] Westacott et al.[59,60] also explored how the competition between radical and ionic mechanisms changes as the water density changes. Their computational results for *tert*-butyl chloride dissociation in SCW showed that the ionic heterolytic dissociation is favored over free-radical homolytic dissociation at densities greater than 0.03 g/cm^3.

III. Roles of Water in Chemistry

A. Water as a Reactant/Product

Individual water molecules may participate in elementary reaction steps as reactants or products. Examples reported in the literature include hydrolysis, hydration, hydrogen exchange, and free-radical oxidation chemistry. Siskin and Katritzky[2,10,11] and An et al.[9] provide overviews of primarily their own previous work on reactions of organic compounds with water in HTW.

1. Water in Hydrolysis and Hydration

Hydrolysis is a chemical reaction in which a bond cleavage is effected by water or by acid or base produced from a reaction of water with salts. Hydrolysis of organic compounds in HTW has been pursued for different purposes, with one being destruction of organic wastes. In some cases, hydrolysis occurs as a side reaction during supercritical water oxidation (SCWO), which is the oxidative destruction of organic compounds in SCW. Hydrolysis of complex polymeric materials in HTW is a potential means for recovering valuable chemical resources. It could provide a route to chemical recycling of waste plastics. Hydrolysis of biomass in HTW could provide an alternative source of chemical feedstocks.

There are numerous studies on the hydrolysis of model compounds in HTW. These simpler compounds mimic important moieties in more complex materials (e.g., coal, lignin, energetic materials). Understanding the reactivity of these model compounds in HTW should provide insights into the hydrothermal processing of the more complex materials. Table 1 summarizes the published experimental studies of hydrolysis in HTW.

Table 1. Experimental Studies of Hydrolysis in HTW

reactant	ref
ethers	61,63,64,73,74,75,76,78,135,137,195,279
esters	62,67,68,77
amides	71,72,86,280
nitriles[a]	1,70,71,72,86,138
amines	1,61,62,76,98,281,282,283,284
nitroalkane	69
alkyl halide	104,206,207
nylon	275
poly(ethylene terephthalate)	273,285
polycarbonate	81
phenolic resin	82
epoxy resin	286
cellulose	133,276,274,278,287,288
chitin	278
cellobiose	80
glucose	100,289,290
fructose	79,290
vegetable oils	291,292

[a] Nitriles are first hydrated to form amides, which are then hydrolyzed.

The experimental studies in Table 1 demonstrated that many organic compounds, both small and polymeric, are hydrolyzed to various degrees in HTW, depending on their reactivity. Fully hydrocarbon compounds are generally resistant to hydrolysis in "pure" HTW or HTW without added catalysts. Compounds that are particularly susceptible to hydrolysis in HTW are those containing a saturated carbon atom attached to a heteroatom-containing functional group.[61,62] Table 2 summarizes the expected products for the hydrolysis of ethers, esters, amides, amines, nitroalkanes, and alkyl halides. Diaryl ethers are generally very stable, although there are conflicting reports regarding the reactivity of diphenyl ether in pure HTW (ref 63 vs refs 61 and 64). Hydrolysis of nitriles is a two-step process. An amide, formed by the addition of water to the cyano group in a nitrile, is what actually undergoes hydrolysis. Carboxylic acids undergo decarboxylation and thermal degradation in pure HTW but not hydrolysis, although these reactions are sometimes mislabeled as hydrolysis.[65,66] A more appropriate term for the reaction of carboxylic acid in pure HTW would be hydrothermolysis or hydrous pyrolysis.

Table 2. Expected Products from Hydrolysis in HTW[a]

reactant	reaction
ethers	$ROR' + H_2O = ROH + R'OH$
esters	$RCOOR' + H_2O = RCOOH + R'OH$
amides	$RCONH_2 + H_2O = RCOOH + NH_3$
1° amines	$RNH_2 + H_2O = ROH + NH_3$
2° amines	$RNHR' + H_2O = ROH + R'NH_2$
3° amines	$RR'NR'' + 2H_2O = ROH + R'OH + R''NH_2$
1° nitroalkanes	$RCNO_2 + H_2O = RCHO + HNO_3$
2° nitroalkanes	$RCNO_2R' + H_2O = RCR'O + HNO_3$
alkyl halides	$RX + H_2O = ROH + HX$
1° *gem*-dihalides	$RCX_2H + H_2O = RCHO + 2HX$
2° *gem*-dihalides	$RCX_2R' + H_2O = RCR'O + 2HX$

[a] RCHO − aldehydes, RCR′O − ketones.

The reactivity of some organic compounds in HTW can be reinforced by autocatalysis from some water-soluble hydrolysis products. Specifically, carboxylic acids produced by the hydrolysis of esters, aldehydes, and amines, and mineral acids (HX, HNO_3) produced by the hydrolysis of halogen- and nitrogen-containing compounds can act as an acid catalyst. Similarly, ammonia produced by the hydrolysis of amines, amides, and nitriles can act as a base catalyst. Autocatalysis for hydrolysis in pure HTW has been demonstrated for esters[67,68] and nitriles (amides).[69−72] Penninger et al. proposed an autocatalytic mechanism for diphenyl ether hydrolysis in pure HTW with phenol as the acid autocatalyst.[63] The acid/base behavior of these water-soluble hydrolysis products in HTW is important, since it affects the extent of autocatalysis in the overall reaction kinetics (see section IV.A.1).

For the decomposition of thermally labile heteroatom-containing reactants that undergo neat pyrolysis in the absence of water, both the hydrolysis and pyrolysis pathways are accessible in HTW. The competition of these two pathways results in a product spectrum that is different from that for the neat pyrolysis. The selectivity toward hydrolysis is sensitive to the reaction conditions, as shown in Figures 5 and 6. Increasing water density favors the hydrolysis pathway, whereas increasing temperature favors the pyrolysis pathway.[61,63,68,70,73−80] Figure 5 shows the methanol yield from guaiacol hydrolysis in SCW. Higher water densities clearly produce higher methanol (hydrolysis product) yields. Increasing the salt concentration also accelerates hydrolysis, as long as the reaction mixture remains homogeneous.[75,76,78,81−83] Figure 6 provides an example. Temperature, water density, and salt concentration affect the hydrolysis kinetics by modifying the ability of HTW to solvate polar and ionic species. The solvation effects on reaction kinetics are discussed further in section IV.A.1.

Besides the hydration of the cyano group in nitriles, very few examples for the hydration of organic compounds in HTW are reported in the literature. The hydration of alkenes and alkynes in HTW is limited by the chemical equilibrium, and low yields of the corresponding alcohols or ketones have been reported for the hydration of carvone, 1-phenylprop-1-yne, and 1-heptyne,[9] phenylacetylene,[9,84] and 1-hexyne and 2-butyne.[85] The hydration of the carbon−carbon double bond of an unsaturated nitrile or acid

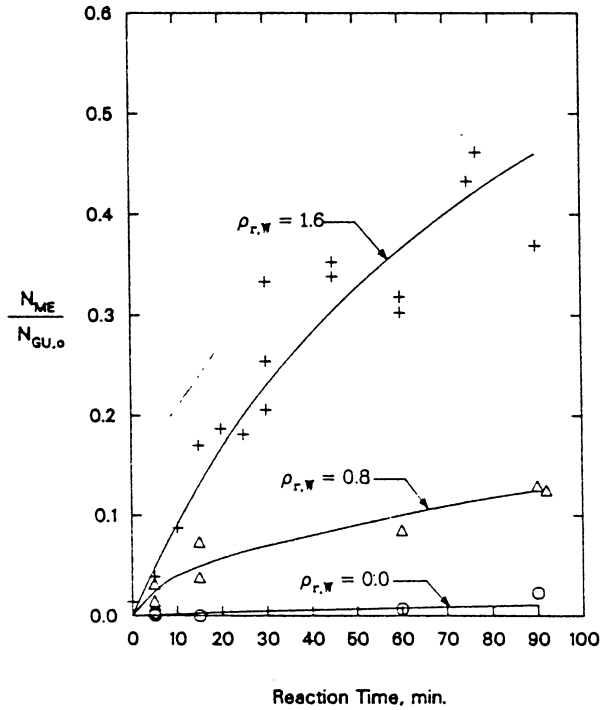


Figure 5. Influence of water density on the temporal variations of methanol yield from pyrolysis of guaiacol at 383 °C. (Reprinted with permission from ref 74. Copyright 1985 American Chemical Society.)

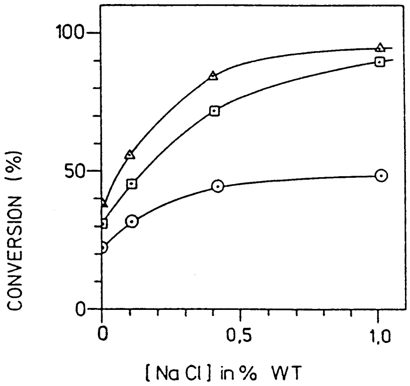


Figure 6. Conversion of methoxynaphthalene in supercritical aqueous NaCl at 0.25 g/cm^3 (circles), 0.35 g/cm^3 (squares), and 0.45 g/cm^3 (triangles). (Reprinted with permission from ref 78. Copyright 1989 American Chemical Society.)

(e.g., acrylonitrile, acrylic acid) is facile, however, because of the presence of an electron-withdrawing substituent.[86] The reaction of unsaturated nitriles in HTW can have a complex pathway, because the reactant has two functional groups that react with water, as shown in Figure 7 for acrylonitrile.[86] Acrylonitrile can undergo a typical nitrile hydrolysis pathway that forms acrylic acid and ammonia via an acrylamide intermediate. Acrylonitrile, acrylamide, and acrylic acid react with water at the carbon–carbon double bond and form 3-hydroxypropionitrile, 3-hydroxypropionamide, and 3-hydroxypropionic acid, respectively. The saturated nitrile and amide undergo further hydrolysis reactions. The carbon–carbon double bond in acrylonitrile can also react with ammonia produced by amide hydrolysis to form 3-aminopropionitrile.

2. Water as a Hydrogen Source

Experimental data suggest that water can supply hydrogen atoms that participate in reactions in HTW. Judging from the product spectra for isoquinoline and quinoline pyrolysis in SCW, Ogunsola speculated that hydrogen was generated from water.[87] Hydrogen–deuterium exchange data also provide evidence for hydrogen supply by water. Deuterium can be incorporated into the products of hydrocarbon pyrolyses in supercritical D_2O.[88,89] Kruse and Ebert[88] proposed that the H–D exchange occurs with radical intermediates. The H–D exchange also occurs readily between deuterium oxide and acidic protons on various organic compounds, such as at the α and α′ positions of ketones (2,5-hexanedione, pinacolone, acetone, cyclopentanone, 1,4-cyclohexanedione, acetophenone, and deoxybenzoin),[90,91] at the C9 position of fluorene and 9-phenylfluorene,[90] and at the $-CH_2-$ position of 4-ethylphenol.[92]

Because of its hydrogen-donating ability, water can have a great influence on the product distribution from pyrolysis. Added hydrogen participates in chain-terminating reactions in free-radical chemistry. Thus, it can shift the selectivity of pyrolysis away from the formation of high molecular weight species, which can form in significant quantities for the neat pyrolysis of hydrocarbons and polymers. Water suppresses the formation of char and polycondensates during the pyrolysis of guaiacol,[73] di-*n*-butylphthalate,[77] 1-nitrobutane,[69] and polyethylene.[93−95] Water reduces the frequency of intra- and interpolymer hydrogen transfers during polystyrene pyrolysis and suppresses polymer cross-linking.[96] Note, however, that the reduced yields of char and polycondensates from pyrolysis in HTW can also be explained in terms of dilution by the solvent and cage effects, which hinder recombination reactions (see section V.B).

Several mechanisms by which water generates hydrogen have been proposed. Moriya et al. noted that hydrocracking of polyethylene in HTW produced alcohols and ketones but very little char compared to the neat pyrolysis. They suggested that hydrogen is liberated when the alcohols, which are formed during the reactions between hydrocarbons and water, are converted to the corresponding ketones.[95] On the basis of the hydrogen balance of the products and the oxygen content in the char formed from isoquinoline pyrolysis, Houser et al. proposed that water liberates hydrogen by oxidizing the carbon component.[97] Similarly, Houser et al. proposed that water serves as a source of hydrogen by oxidizing the benzylic carbon of benzylamine.[98] Hydrogen is produced when the resulting benzoic acid undergoes decarboxylation to form benzene. The overall stoichiometry for these reactions is

$$C_6H_5CH_2NH_2 + 2H_2O \rightarrow C_6H_6 + CO_2 + NH_3 + 2H_2$$

Hydrolysis has also been invoked as a mechanism by which HTW provides hydrogen.[73]

In the presence of carbon monoxide, water can generate hydrogen molecules via the water–gas shift

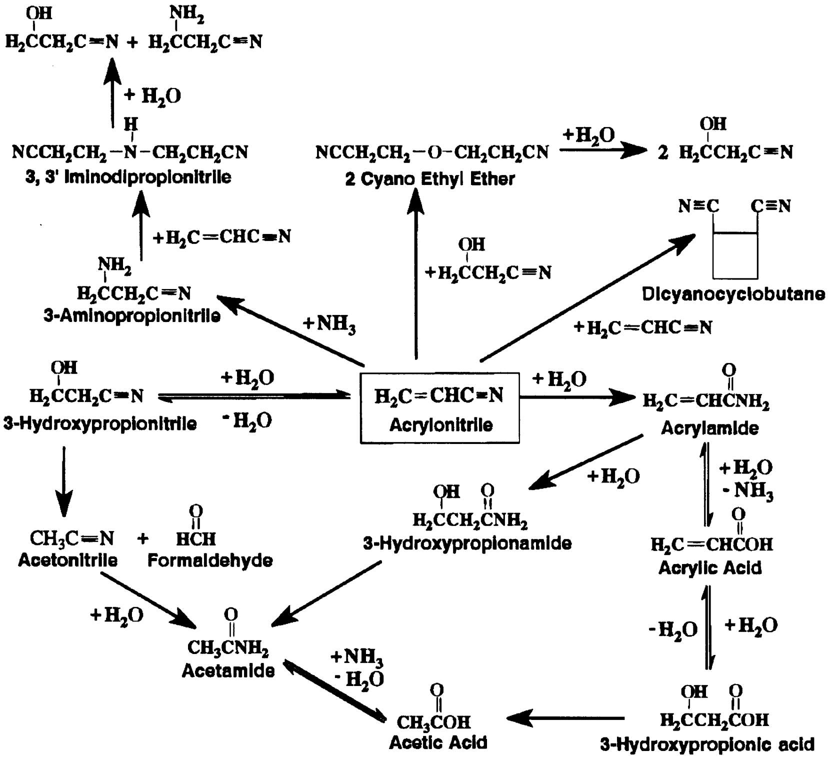


Figure 7. Global hydrothermal reaction network for acrylonitrile. (Reprinted with permission from ref 86. Copyright 1999 American Chemical Society.)

reaction ($CO + H_2O \rightleftharpoons CO_2 + H_2$), which is a significant side reaction for the steam reforming or oxidation of organic compounds in HTW. The water–gas shift reaction in HTW has been observed during the steam reforming of glucose[99,100] and biomass,[101,102] the pyrolysis of alkyldiammonium dinitrate,[103] and the oxidation of methylene chloride,[104] lactic acid,[66] and carbon monoxide.[105–107] Adschiri, Arai, and coworkers performed the hydrogenation of dibenzothiophene[108] and heavy oils[109] in HTW. They produced the hydrogen in situ by partially oxidizing the organic compounds to generate carbon monoxide, which then undergoes the water–gas shift reaction. The authors proposed that the reactive intermediate generated by the water–gas shift reaction is the actual hydrogenation agent, not the hydrogen molecule itself. In a similar spirit, Matsumura et al. performed the co-liquefaction of coal and cellulose by taking advantage of the hydrogen generated in situ by the water–gas shift reaction during cellulose reforming.[110]

3. Water in Free-Radical Chemistry

Water participates as a reactant in several of the elementary reaction steps that occur during SCWO. The govering mechanism for SCWO is free radical, and it is analogous to that for gas-phase oxidation at the same temperatures. The reactions in which water participates often involve the formation or destruction of highly reactive free-radical intermediates. Consequently, these steps can play an important role in the overall kinetics. Examples of such reactions appear in detailed chemical kinetics models for SCWO of carbon monoxide,[105,106,111] hydrogen,[111–113] methane,[113,114] methanol,[113,115,116] phenol,[117] benzene,[118] and ethanol[119]

$$H_2O + M \rightleftharpoons OH + H + M$$

$$H_2O + H \rightleftharpoons OH + H_2$$

$$H_2O + O \rightleftharpoons OH + OH$$

$$OH + HO_2 \rightleftharpoons H_2O + O_2$$

$$OH + HR \rightleftharpoons H_2O + R$$

$$H_2O + HO_2 \rightleftharpoons OH + H_2O_2$$

The species M in these reactions is a collision partner, which is primarily water for reactions in SCW. Section V.A discusses the role of water as a collision partner.

Reactions such as these have been invoked as at least a partial explanation for the experimentally observed water density (or pressure) effects on SCWO reaction rates.[111,112,120] Because the hydroxyl radical (OH) is the most effective oxidant present during SCWO, reactions that form this species make large contributions to the overall oxidation kinetics. In this sense, the last reaction is particularly important, because the resulting hydrogen peroxide subsequently dissociates and forms two additional OH radicals ($H_2O_2 = 2OH$), effectively generating three OH radicals from a single hydroperoxyl radical (HO_2), which is a less reactive oxidant.

Figure 8 shows kinetic decay constants calculated from experimental data and a detailed chemical kinetics model for CO oxidation in SCW at 570 °C. Both the experiments and the model show that the rate increases as the water concentration increases.

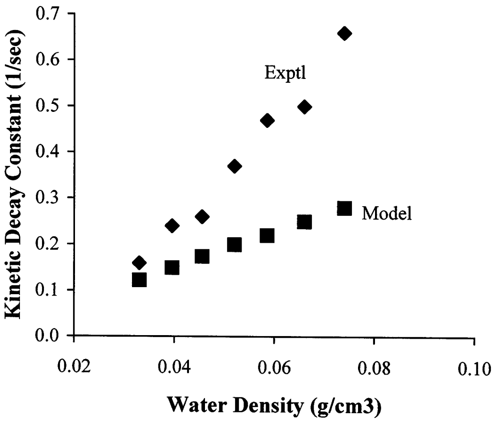


Figure 8. Predicted effects of operating pressure on kinetic decay constant for CO oxidation in water at 570 °C (data from reference 111).

The increase in the model is due entirely to water's role as a reactant, product, and collision partner in elementary reaction steps. Interestingly, the model is not capable of predicting the sharper increase in rate observed experimentally. This discrepancy suggests that water plays additional roles in influencing SCWO kinetics.

B. Water as a Catalyst

Individual water molecules can participate in elementary reaction steps as catalysts. Examples include water as a source of an acid or base catalyst and as a catalyst that modifies and stabilizes the transition states.

1. Water as Acid/Base Catalyst Precursor

The high natural concentrations of the H^+ and OH^- ions resulting from the high K_w of liquid HTW (see section II) facilitate acid- or base-catalyzed reactions in HTW. Many acid- or base-catalyzed reactions proceed rapidly in HTW in the presence of acid or base in quantities that are significantly lower than what would be required at ambient conditions. The higher thermal energy in HTW apparently compensates for the lower H^+ and OH^- concentrations. Nevertheless, the H^+ and OH^- ions from self-ionization of HTW are sufficiently abundant that some reactions that require a strong mineral acid or base at ambient conditions proceed readily in HTW even in the absence of added catalysts. In such cases, water participates not only as a source of an acid or base catalyst but also as a conjugate base or acid, respectively. The temperature and density dependence of the dissociation constant for water and for added acid/base catalysts, which determines the availability of the H^+ and OH^- ions in HTW, contributes to the experimentally observed temperature and density dependence of the kinetics for these reactions in HTW. Acid catalysis dominates the examples reported in the literature. In this section, we discuss the role of water as a source of an acid or base catalyst in alcohol dehydration, hydrolysis, addition of water to double bonds, rearrangements, Friedel–Crafts alkylation/acylation, aldol condensation, and Cannizaro reaction.

The dehydration reactivity of alcohols in HTW depends on the structure of the alcohol. Although alcohol dehydration is nominally acid- or base-catalyzed, the acid catalysis path appears to dominate in HTW. Significant contributions in the field of alcohol dehydration in HTW were made by Antal and co-workers. They reported that ethanol, 1-propanol, 2-propanol, glycol, glycerol, and xylose dehydrate in the presence of dilute acid,[58,121–125] whereas *tert*-butyl alcohol dehydrates readily in pure HTW.[126,127] The *tert*-butyl alcohol dehydration rate increases with the addition of acid but decreases with the addition of base, which indicates that the reaction proceeds by an acid-catalyzed mechanism.[127] Xu and Antal reported an excellent correlation between the yields of *tert*-butyl alcohol and the H^+ concentration.[126] Figure 9 shows proposed mechanisms for propanol dehydration in HTW. Water plays a role as the source of H^+ and also as a reactant/product in several steps. Cyclohexanol also dehydrates readily in pure HTW.[90,128] Akiya and Savage predicted the effect of the water density on the product yields for cyclohexanol dehydration in SCW using a kinetics model that accounted for the density dependence of the native H^+ concentration.[128] Increasing water density favors the dehydration of lactic acid to acrylic acid[129] and the isomerization of 1- to 2-butanols and of 1-butene to isobutene in pure HTW.[77] These transformations can be rationalized in terms of acid catalyis by water-derived H^+ ions, and the observed water density effects can be attributed to the increas-

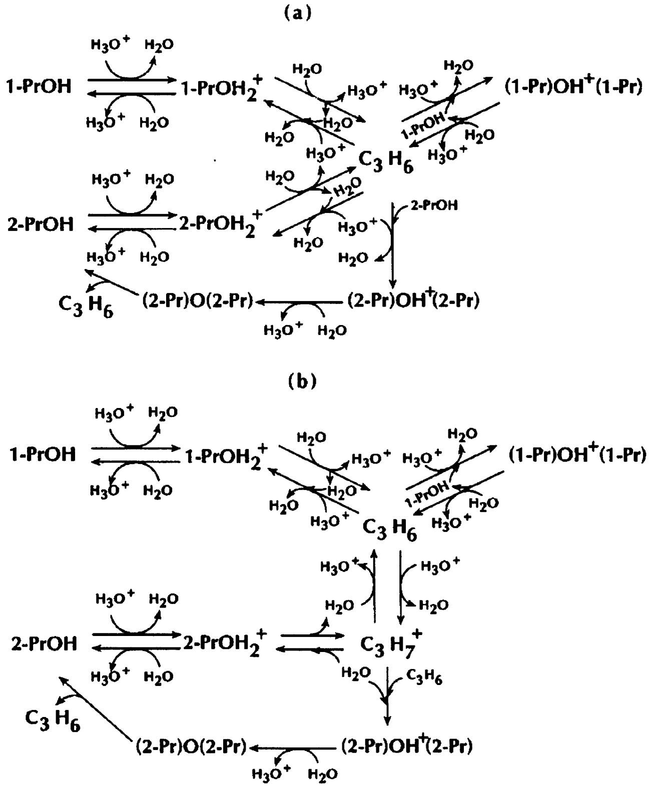


Figure 9. Acid-catalyzed reactions of 1-propanol and 2-propanol in hot liquid water: (a) $E2/Ad_E3;E2/Ad_E3$/Uni mechanism, (b) $E2/Ad_E3;E1/Ad_E3$/Uni mechanism. (Reprinted with permission from ref 125. Copyright 1998 American Chemical Society.)

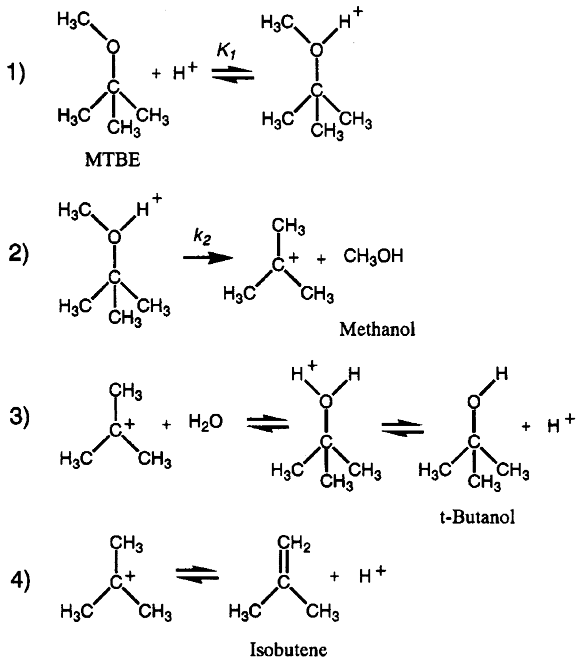


Figure 10. Acid-catalyzed mechanism for the decomposition of MTBE. (Reprinted with permission from ref 137. Copyright 2001 American Chemical Society.)

ing H^+ concentration. Because alcohols dehydrate so readily in HTW, they can be used as alkene synthons for organic synthesis in HTW.[130-132]

Hydrolysis is nominally catalyzed by either acid or base in the presence of added catalysts. For hydrolysis in pure HTW, however, experimental data suggest that the dominant mechanism is acid catalysis by H^+ ions from the self-ionization of water. Some compounds that hydrolyze at ambient conditions only in the presence of mineral acids (e.g., H_2SO_4, HCl) hydrolyze rapidly in HTW even in the absence of added acids.[90,133] Penninger et al. proposed an acid-catalyzed S_N1 mechanism in which H^+ ions are provided by water for the hydrolysis of diphenyl ether.[63] They showed that the kinetics model based on this mechanism is consistent with the experimental data. The hydrolysis rate for diaryl ethers (including diphenyl ether) in HTW decreases upon the addition of salts (NaCl, LiCl, KBr, Na_2SO_4).[134,135] These additives behave as the salts of strong bases and weak acids in HTW and, thereby, reduce the activity of H^+ ions from water. For the hydrolysis of substituted benzoates in pure HTW, Lesutis et al. proposed the acid-catalyzed $A_{Ac}2$ mechanism in which H^+ ions are supplied by water and used the global rate equation based on this mechanism to obtain the rate constants from experimental data.[67] These rate constants exhibit no substituent effects, further supporting the proposed mechanism.[136] Similarly, Krammer and Vogel proposed the $A_{Ac}2$ mechanism for the hydrolysis of ethyl acetate in nearcritical liquid water, although they suggested that the dominant mechanism in SCW is the uncatalyzed direct attack of water.[68]

Another example of acid catalysis in pure HTW is the decomposition of methyl *tert*-butyl ether (MTBE). This reaction likely occurs via the 4-step mechanism in Figure 10. The MTBE is first protonated and then eliminates methanol to form *tert*-butyl carbocation. This intermediate can then undergo hydrolysis to form *tert*-butyl alcohol or eliminate H^+ to form isobutene. The pseudo-first-order rate constant for MTBE disappearance in HTW at 250 bar exhibited a peculiar temperature dependence (see Figure 11) with a sharp discontinuity in the Arrhenius plot near the critical temperature.[137] This non-Arrhenius behavior is an artifact from excluding the H^+ concentration (from water) in the rate law. The H^+ concentration varies widely over this temperature range, and including it in the kinetics analysis led to rate constants that showed the expected Arrhenius behavior. The same authors observed a similar temperature dependence for the pseudo-first-order rate constant for methylene chloride hydrolysis in HTW but rationalized it in terms of the changes in the dielectric constant of water, as discussed in section IV.A.1.

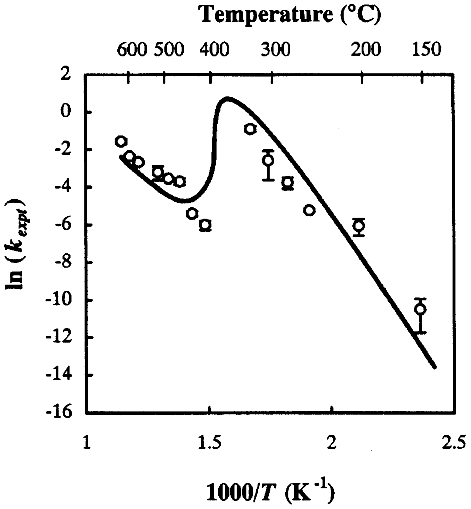


Figure 11. Experimental rate constant for MTBE hydrolysis in HTW. (Reprinted with permission from ref 137. Copyright 2001 American Chemical Society.)

Both the 1,4-nucleophilic addition of water to the carbon–carbon double bond of unsaturated nitriles and the 1,2-nucleophilic addition of water to the cyano group of both saturated and unsaturated nitriles proceed upon addition of acid or base catalysts. The same reactions in pure HTW appear to proceed predominantly by an acid-catalyzed mechanism. In this case, the catalyst is H^+ ions from water and water itself acts as a nucleophile. Klein and coworkers performed kinetics experiments for the addition of water to various nitriles in pure HTW and deuterated HTW and calculated the ratio of the experimental rate constants in the two reaction media (k_{H_2O}/k_{D_2O}).[138,139] Their results are consistent with water, and not OH^-, being the dominant nucleophile for the hydration of the cyano group[138] and the hydration of the alkene moiety[139] in HTW. This finding supports the hypothesis that the operating mechanism for the nitrile hydration in pure HTW is acid catalysis.[69,70,86,72,1] Alkyne hydration in HTW also appears to be acid-catalyzed, although alkynes are not very reactive in HTW in the absence of added catalysts.[9,85]

Several types of catalyzed rearrangements proceed in HTW in the absence of added catalysts. The rearrangements of pinacol, 1,1′-dihydroxy-1,1′-dicylopentyl, and 1,1′-dihydroxy-1,1′-dicylohexyl to the corresponding ketones occur rapidly in HTW.[90] The H−D exchange data for the pinacol rearrangement to pinacolone in D_2O support both acid- and base-catalyzed mechanisms for this reaction, with D_2O as the source of the catalyst.[91] Ikushima and co-workers reported that the Beckman rearrangement of cyclohexanone oxime to ϵ-caprolactam and the pinacol rearrangement to pinacolone proceed readily in HTW and proposed that these reactions are catalyzed by H^+ ions from water.[140,141]

The Friedel−Crafts reactions are another type of acid-catalyzed reaction that proceed in HTW in the absence of added catalyst, but the equilibrium yields are generally low. The Friedel−Crafts alkylation of phenol and alkyl-substituted phenols with alcohols (as alkene synthons via alcohol dehydration) proceeds in HTW.[131,132] The equilibrium yields were approximately 20%. Alkylation by 1-propanol resulted in an isopropyl substituent, because of the skeletal rearrangement of the propyl cation.[131] The Friedel−Crafts acylation of phenol and of resorcinol with acetic acid also occurs in HTW in the absence of added catalyst.[142] The same reactions in neat acetic acid, however, proceeded with a 10-fold increase in rate.[142] Self-acylation of benzoylbenzoic acid to form anthraquinone in HTW required addition of mineral acids.[131]

Aldol condensation or its reverse reaction is nominally catalyzed by either an acid or a base. Experimental data suggest, however, that aldol condensation in pure HTW is base-catalyzed. The aldol condensation of acetaldehyde proceeds readily in HTW without added catalysts but is suppressed upon the addition of H_2SO_4.[121] In pure HTW, 2,5-dimethylpyrrole reacts with water to form 3-methylcyclopent-2-en-1-one. This compound then undergoes ring opening to form ammonia and hexanedione, followed by the intramolecular aldol condensation of hexanedione.[143] The ammonia produced in the second step of the reaction makes the aqueous medium weakly basic. Additionally, the intramolecular aldol condensation of hexane-2,5-dione in HTW is greatly facilitated by dilute NaOH.[144]

The Cannizzaro reaction is also base-catalyzed and proceeds readily in HTW. This class of reaction proceeds at ambient conditions only in the presence of a strong base such as NaOH. The Cannizzaro reaction of formaldehyde that forms methanol and formic acid has been demonstrated in HTW in the absence of added catalysts.[145] Yamasaki et al. reported that the hydrolysis of dichloromethane in HTW is followed by the Cannizzaro reaction, which produces methanol and formate.[146] The authors showed that H−D exchange occurs extensively at all positions during these reactions in D_2O. This result is in constrast to the lack of H−D exchange at the α position for the Cannizaro reaction in ambient liquid water, which suggests that water does not function as the hydrogen source at ambient conditions.[147]

2. Water as Catalyst in the Transition State

Water molecules can catalyze a reaction by directly participating in the transition state and reducing its energy. This form of catalysis is important for reactions involving some type of intramolecular hydrogen transfer. In general, water molecules make the geometry of the transition-state species less strained and more suited for the reaction to proceed. Water molecules act as a proton relay, thereby facilitating the formation and cleavage of bonds that lead to the products. Klein, Brill, and co-workers proposed this type of water catalysis for the intramolecular hydrogen-transfer step during the conversion of nitroaniline to benzofurozan[148] and the decarboxylation of acetic acid derivatives[149] in HTW.

The role of water in the hydrogen transfer has been elucidated by computational quantum chemistry. Water facilitates the isomerization by intramolecular proton transfer for formic acid,[150] dihydroxycarbene,[151] nitromethane,[152] and formamidine.[153,235] Specifically, quantum chemical calculations demonstrated that the inclusion of one water molecule in the isomerization transition state reduces the activation barrier by 27 kcal/mol for nitromethane[152] and by a factor of 2 for formamidine,[153] compared to the activation barriers for the neat isomerization. Water also facilitates formamide hydrolysis, which involves a hydrogen transfer from the added water to the amine group,[154] and aldol condensation, which involves a hydrogen transfer between the two reactants.[155]

Quantum chemical calculations further revealed the role of water in formic acid decomposition. Formic acid decomposes through two pathways, dehydration and decomposition, both of which require intramolecular hydrogen transfer. Experiments show that the rate of decomposition is orders of magnitude higher in HTW than in the gas phase at the same temperature and that selectivity is markedly different in the two reaction media.[156,145] In their pioneering work, Melius et al.[157] first demonstrated that water molecules promote formic acid decomposition by acting as a proton relay in the transition state. Akiya and Savage[158] followed that work and correctly reproduced the experimental trends. Later, Wang et al. obtained very similar results[159,160] but were apparently unaware of the earlier studies. These calculations predict that the activation energy in HTW should be approximately 20−30 kcal/mol lower than the gas-phase value. Figure 12 displays sketches of the energy diagrams and the structures of the different transition states.

IV. Roles of Intermolecular Interactions in HTW

There are many examples of solute−solvent and solvent−solvent interactions having some effects on the kinetics of reactions in HTW. These effects can be pronounced in SCW because of its high isothermal compressibility. Consequently, many studies that are cited in this section focus on supercritical systems. Kajimoto's recent review of the solvation effects on reactions in supercritical fluids emphasizes carbon dioxide and other nonaqueous systems.[161] The present

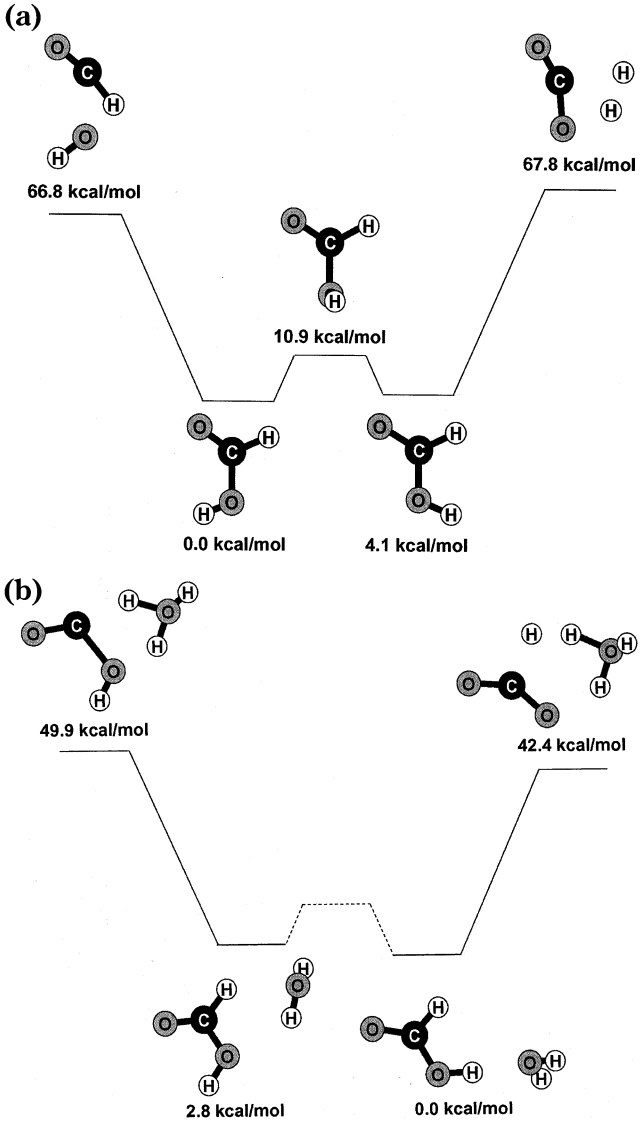


Figure 12. Energy diagram for formic acid decomposition (a) in the absence of water and (b) assisted by one water molecule.

review is complementary because we focus on various types of physical effects that arise from intermolecular interactions involving water.

A. Solvation Effects

According to conventional transition-state theory, the rate constant for a reaction at temperature T and density ρ is

$$k = \kappa \frac{k_B T}{h} \rho^{(1-n)} \exp\left(-\frac{\Delta G^{\ddagger}}{RT}\right) \tag{3}$$

where κ is the tranmission coefficient, n is the sum of the reactants' stoichiometric coefficients, and $\Delta G^{\ddagger}$ is the free energy of activation. For a reaction in a solvent, the solute–solvent interactions influence the rate constant by modifying the free energy of activation and the transmission coefficient. The solvent-induced changes to the free energy of activation are typically called the equilibrium solvation effects, whereas the solvent-induced changes to the transmission coefficient are called the nonequilibrium solvation effects.

Nonequilibrium solvation effects are important when the solvent molecules cannot adjust to the change in the reacting system rapidly enough to maintain equilibrium solvation.[162] The nonequilibrium solvation effects result in solvent-induced barrier recrossing, so they are manifested in the transmission coefficient being less than unity. These effects are particularly important for reactions involving substantial changes in the electronic structure of the reactant(s). Although the nonequilibrium solvation effects are generally observed for systems with strong solute–solvent coupling, the deciding factor is the difference in the time scales for the reaction and the solvent reorganization.[163] The solvent essentially becomes a part of the reaction coordinate, and the solvent dynamics play a crucial role in the reaction kinetics. The solvent's response to the changes in the reacting system is greatly influenced by the nature of the solute–solvent interactions.

When the solvent molecules adjust rapidly enough to the changes in the reacting system that the equilibrium solvent structure is constantly maintained, the equilibrium solvation effects on the rate constant are dominant. In this case, the total free energy of activation can be separated into the activation barrier for the reaction in the gas phase and the change in the activation due to the presence of the solvent

$$\Delta G^{\ddagger} = \Delta E_{\text{gas}}^{\ \ddagger} + \Delta G_{\text{sol}}^{\ \ddagger} \tag{4}$$

Assuming that the reaction mechanism is identical in the gas phase and in HTW, we can express the rate constant in HTW in terms of the corresponding gas-phase rate constant

$$\frac{k_{\text{HTW}}}{k_{\text{gas}}} = \exp\left(-\frac{\Delta G_{\text{sol}}^{\ \ddagger}}{RT}\right) \tag{5}$$

The solvent contribution $\Delta G^{\ddagger}_{\text{sol}}$ is essentially the difference between the free energies of solvation for the reactant(s) and for the transition state.

The pressure and density dependence of reaction rate constants can be understood in terms of the equilibrium solvation effects. From eq 3, one can derive the following relationships

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = (1-n)\kappa_T - \frac{\Delta \bar{v}^{\ddagger}}{RT} \tag{6}$$

$$\left(\frac{\partial \ln k}{\partial \rho}\right)_T = \frac{1-n}{\rho} - \frac{1}{\rho \kappa_T}\left(\frac{\Delta \bar{v}^{\ddagger}}{RT}\right) \tag{7}$$

where κ_T is the solvent isothermal compressibility and $\Delta \bar{v}^{\ddagger}$ is the activation volume. In compressible systems, both κ_T and $\Delta \bar{v}^{\ddagger}$ are themselves functions of pressure (density). The activation volume is the difference between the partial molar volumes of the transition state and the reactant(s), and its value depends, in part, on the solute–solvent interactions.

If the nonequilibrium solvation effects cannot be neglected, then one must also account for the effect of pressure (density) on the transmission coefficient (not shown in eqs 6 and 7).

1. Effects of Preferential Solvation

The preferential solvation of the reactants or transition-state species in water at different temperatures and pressures/densities will influence the kinetics of reactions in HTW,[164] as indicated by eqs 5−7. Differences in the solvation behavior for different solutes are magnified by the compressibility effects at nearcritical conditions.[164] The magnitude of the activation volume for reactions in HTW can be significant, especially at supercritical conditions. For example, values on the order of 10^2-10^3 cm^3/mol have been reported for hydrolysis[68,70,72,78,165] and the water−gas shift reaction[166] in HTW. Klein and coworkers decomposed the overall activation volume into different components (e.g., electrostatic, hydrostatic, diffusion, phase behavior) to obtain insights into the relative importance of different solvent properties and to interpret the observed pressure effects on reaction kinetics in HTW.[70,167]

The effects of preferential solvation in HTW are most pronounced for reactions that involve charge localization or delocalization (i.e., ionic or polar nonionic reactions). The solute−solvent interactions for such systems are dominated by the electrostatic interactions, and consequently, the dielectric constant of the medium is an important indicator for the ability of water to solvate the reactants and transition states. The experimentally observed temperature and density effects on the rates of various ionic and polar reactions in HTW have often been rationalized in terms of changes in the dielectric constant with temperature and density. Hydrogen bonding with water provides additional stabilization of ionic and polar species, however, and its contribution to preferential solvation in HTW should not be overlooked. Reactions involving a transition state that is more (or less) polar than the individual reactant(s) are facilitated by increasing (or decreasing) dielectric constant and/or extent of hydrogen bonding. Therefore, the rates of ionic and polar reactions in HTW generally increase with increasing density.

There are two general classes of ionic reactions: ionogenic and iso-Coulombic. The rate of an ionogenic reaction, which involves the dissociation of a neutral molecule into charged species, increases with increasing dielectric constant and hydrogen bonding because the medium better stabilizes the ions produced. Thus, at constant temperature, the rate constant of an ionogenic reaction in HTW increases with increasing water density or pressure, as shown in Figure 13 for ammonia-assisted deprotonation of β-naphthol.[168] This mechanism has also been invoked to rationalize the increase in the rate of hydrogen exchange reactions of methanol and ethanol in SCW with increasing pressure.[92] Similar trends have been observed for equilibrium constants of ionogenic reactions, including β-naphthol dissociation,[169] the reaction of β-naphthoic acid with ammonia,[170] and nitric acid dissociation[171] in HTW.

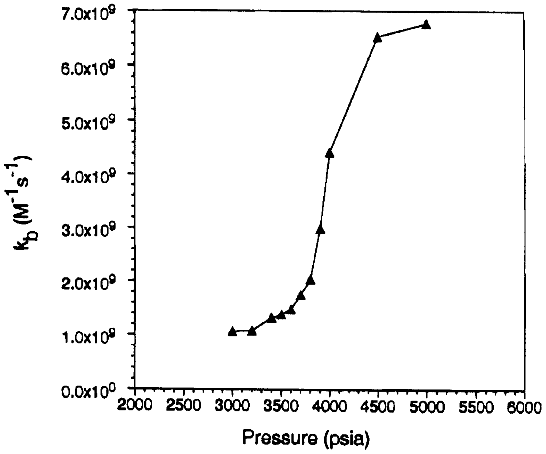


Figure 13. Pressure dependence of the rate constant of ammonia-assisted deprotonation in water at 400 °C. (Reprinted with permission from ref 168. Copyright 1996 American Chemical Society.)

For an iso-Coulombic reaction, for which the number of charges is preserved, the effect of water density on the kinetics and equilibrium is generally small.[172,173] The effect can be significant, however, if the ions formed and consumed during the reaction are substantially different in size. With decreasing solvent dielectric constant, the formation of ions with smaller charge-to-volume ratio is increasingly favored, because their solvation is more energetically favorable at these conditions. This size dependence has been observed for the acid-catalyzed dehydration of 1-propanol,[165] the reaction of β-naphthol with OH^-, acetate, and borate,[168,169] the reaction between boric acid and OH^-,[174] and the protonation of organic compounds[175,176] in HTW.

There are numerous theoretical investigations of solvation effects on the S_N2 reaction of methyl chloride and a chloride ion ($CH_3Cl + Cl^-$). This reaction has received attention as a prototype for an ionic reaction with identical reactants and products. The solvation effects observed arise from the change in the polarity of the reactants as they traverse the reaction coordinate. Gas-phase quantum chemical calculations show that the reactants first form an asymmetrical ion−dipole complex $[Cl\cdots CH_3Cl]^-$ which then turns into a symmetrical transition state $[Cl\cdots CH_3\cdots Cl]^-$.[177,178] As shown in Figure 14, the gas-phase reaction energy profile has an energy minimum corresponding to the ion−dipole complex because of the attractive ion−dipole interactions. In ambient liquid water, however, there is a dramatic change in the reaction energy profile due to solvation effects.[177−180] The energy minimum at the ion−dipole complex disappears because the energy reduction from the ion−dipole attraction is offset by the energy penalty for desolvating the chloride ion that is required to form the complex. Furthermore, the activation barrier in ambient liquid water is about twice as high as the gas-phase value, because the solvation of the transition state, with delocalized charge distribution, is less favorable than that of the ion−dipole complex. In SCW, the shape of the reaction energy profile is very similar to that in ambient liquid water, but the barrier height is lower by a few kcal/mol in SCW.[181−183] This difference in the activa-

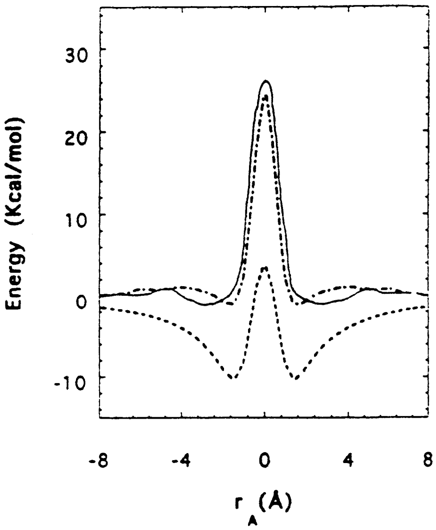


Figure 14. Calculated internal energes in the gas phase (- - -) and the potential of mean force in aqueous solution under ambient (—) and supercritical (- • -) conditions, as a function of the reaction coordinate. (Reprinted with permission from ref 181. Copyright 1994 American Chemical Society.)

tion barrier is much smaller than expected from the difference in the dielectric constant or hydrogen bonding (see sections IV.B.1 and IV.B.4). The activation barrier is insensitive to changes in water density (at $\rho_r = 0.5-1.5$) but decreases with increasing temperature (hence decreasing dielectric constant and hydrogen bonding).[184]

Westacott et al. recently investigated hydrolysis of *tert*-butyl chloride in SCW using molecular dynamics simulations to examine the water density effects on this model S_N1 reaction.[59,60] This reaction is sensitive to changes in water density, because the first step is the dissociation of *tert*-butyl chloride. Westacott et al. computed the potentials of mean force corresponding to heterolytic dissociation and to homolytic dissociation at different densities. They found that the transition from ionic to free-radical mechanism occurs at a very low density, 0.03 g/cm^3, which is considerably lower than what would be expected if local density enhancement (see section B) were ignored.

The acid–base behavior of molecules dissolved in HTW is an important part of their reactivity. Since acid–base reactions typically involve charge separation and association, their reaction kinetics and equilibrium are affected by the dielectric constant and hydrogen bonding of water. At constant temperature, increasing the water density favors an increasing degree of charge separation. Generally, charge separation is not favored in SCW, and cation–anion pairs in SCW exist primarily as contact-ion pairs (see section IV.B.1).[173,185–188] The temperature effect on the dissociation equilibrium constant is more complex, since it arises from the competition between the energy required for dissociation and the energy required to solvate the ions formed by the reaction. The temperature and density dependence of reaction kinetics for some ionic reactions has been attributed to the change in the acid–base behavior of the reactant or catalyst.[63,68] In fact, the acidity and basicity of some species in HTW show dramatic temperature and density dependence, possibly because the dielectric constant of water varies widely under the conditions examined.

Molecules generally exhibit less ionization in HTW than in ambient liquid water. For example, the pK_a of benzoic acid and acetic acid in HTW increases from 4.20 and 4.75 at ambient to 6.21 and 6.01 in HTW, respectively, whereas the pK_a of ammonia decreases from 9.25 at ambient to around 5 in HTW.[71] Figure 15 shows that the dissociation constant for HCl, for instance, decreases by 13 orders of magnitude from 298 K to the critical temperature of water, thereby significantly reducing its acidity in HTW.[189] The excited-state deprotonation of β-naphthol in water is suppressed at temperatures above 100 °C, and the conjugate anion completely disappears at temperatures above 200 °C.[190] The fluorescence decay rate constant for this reaction increases with density, and the extrapolation of the Arrhenius plot constructed from the ambient-temperature data did not correctly predict the high-temperature data. The cause of this discrepancy is that as temperature increases, water loses its tetrahedral structure, which is integral to water's ability to accept a proton.

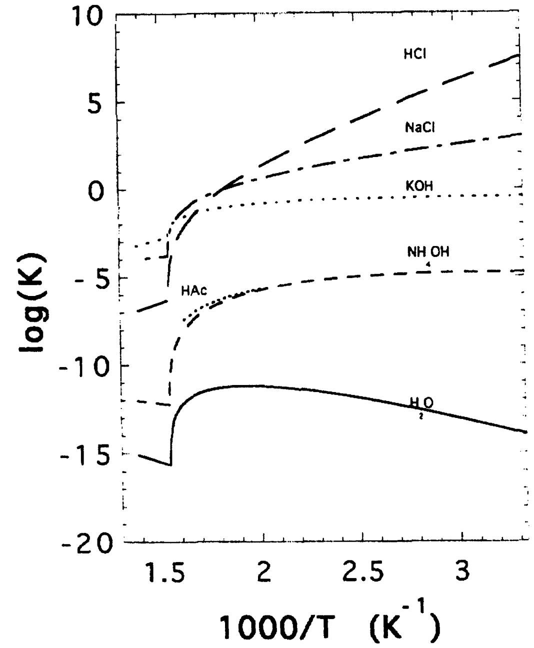


Figure 15. $\log_{10} K$ versus 1000/T along the saturation curve for water and in SCW at the critical density. (Reprinted with permission from ref 189. Copyright 1998 PRA Press.)

The observed loss of the Brønsted acidity of these species in water with increasing temperature and decreasing density originates from the diminishing ability of water to solvate the ionic species, thereby inhibiting charge separation. In addition, with a less extensive hydrogen-bond network, HTW is less capable of accepting the ejected proton than is ambient liquid water. Since the free proton has nowhere to go, it quickly recombines with its conjugate base. These results are in agreement with thermodynamic studies showing dramatic decreases in the acid dissociation constant for a wide variety of weak acids in aqueous solution above 300 °C.[172]

Interestingly, the acid and base catalysts appear to be more effective in HTW than in ambient liquid water in some cases, despite the reduced ionization of molecules dissolved in HTW. Evilia and co-workers showed that HCl in SCW is more reactive than at ambient temperature and that it can protonate hexane.[176] They also showed that organic compounds, the acidity or basicity of which at room temperature is negligibly small, react with base or acid, respectively, in SCW at sufficiently rapid rates that H$-$D exchange with water is observed in a time scale of minutes.[176,191-193] For example, C$-$H bonds with pK_a as high as 50 underwent H$-$D exchange by acid$-$base reaction in D_2O at 400 °C.[191] The increased reactivity of acids and bases in HTW is attributed to the reduced solvation of these ionic species at these conditions, as discussed above. Also, the addition of H^+ ions to the organic compounds may be favored because protonated hexane has a much lower charge-to-volume ratio than H^+.[175,176] The efficacy of water itself as a source of an acid catalyst, on the other hand, improves in HTW through a different mechanism. To rationalize their experimental data on the Beckmann and pinacol rearrangements in HTW, Ikushima, Sato, and co-workers[140,141] proposed that the reactivity of the protons generated from the self-ionization of water is caused by the concomitant increase in K_w and decrease in the ability of water to accept ejected protons at nearcritical conditions.

The response of a nonionic reaction to the changes in the dielectric constant and hydrogen bonding of water depends on the difference in the polarity between the reactant and the transition state. If the transition state is more polar than the reactant(s), a nonionic reaction behaves just like an ionogenic reaction. That is, the rate increases with increasing water density. The water$-$gas shift reaction proceeds via a formic acid or formate intermediate, so it provides an example in which the transition state is more polar than the reactants (CO, H_2O). The rate constant for the water$-$gas shift reaction in HTW increases with increasing water density, as shown in Figure 16, and the activation volume for this reaction is about -1100 cm^3/mol.[157,166] Water can also alter the reaction pathway for multistep reactions by providing different degrees of stabilization for different reaction intermediates. This effect was observed for the decomposition of nitromethane in HTW.[152]

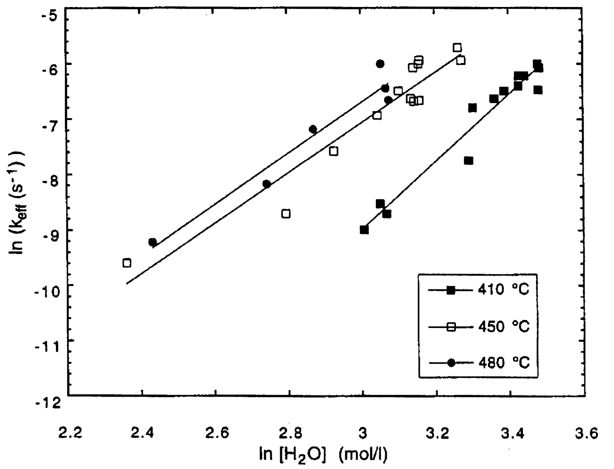


Figure 16. Apparent first-order rate constant for water$-$gas shift reaction in SCW. (Reprinted with permission from ref 166. Copyright 1998 American Chemical Society.)

As expected from the foregoing discussion, the effect of preferential solvation by water on the kinetics of hydrolysis in HTW depends on the reaction mechanism.[194] Neutral hydrolysis, with water as the nucleophile, proceeds through a transition state that is more polar than the isolated reactants, so its rate constant increases with the increasing dielectric constant and hydrogen bonding of water. On the other hand, basic hydrolysis, with OH^- as the nucleophile, proceeds through a transition state that is less polar than the isolated reactants, so its rate constant increases with the decreasing dielectric constant and hydrogen bonding. The experimentally observed acceleration of hydrolysis in HTW with decreasing temperature, increasing pressure, and increasing salt concentration supports the neutral hydrolysis mechanism (see section III.A.1). For example, hydrolysis rate constants correlate well with the dielectric constant of water.[61] The apparent second-order rate constant for guaiacol hydrolysis itself increases with water density, and it increases further upon the addition of salts.[75] The Hammett reaction constant for the hydrolysis of substituted anisoles is 1.8, which indicates that the reaction involves the formation of a negative charge in the transition state that would be stabilized by electron-withdrawing substituents.[195] These data all support hydrolysis in pure HTW proceeding by the S_N2 attack of water as the nucleophile.

The literature suggests that the solvation effects are not negligible for free-radical reactions, even though the electrostatic interactions are much less significant for these reactions than for ionic or polar reactions. Kinetics models for SCWO based on gas-phase combustion mechanisms fail at high water densities, even when the rate constants are corrected for high pressures,[105,111,114,196,197] in part because the models do not account for the solvation effects. Experiments show that the rate constant for hydrogen peroxide dissociation in SCW is higher than the gas-phase, high-pressure limit rate constant and changes with water density.[198] Molecular dynamics simulations provided the density-dependent rate constant and equilibrium constant and the solvent contribution to the free energy of activation for H_2O_2 dissociation in SCW.[199,200] These results for the rate constant, displayed in Figure 17, were consistent with and accounted for the experimental observations. They showed that the rate constant increases with increasing density at $\rho_r < 1$, because the solute$-$water interactions become increasingly attractive as H_2O_2 dissociates. At $\rho_r > 1$, however, the rate constant decreases with increasing density because of the diminishing isothermal compressibility of water.

Additional insights into the solvation effects on polar reactions in HTW are provided by theoretical studies that treat the solvent as a dielectric con-

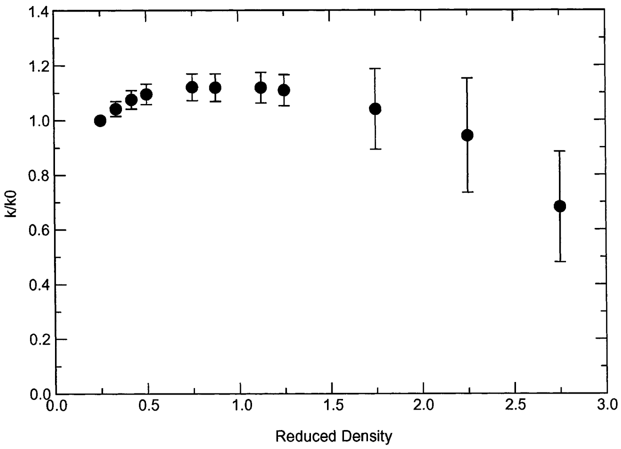


Figure 17. Relative rate constant for H_2O_2 dissociation in SCW at $T_r = 1.15$.

tinuum. Quantum chemical calculations have been performed with various electrostatic continuum solvation models to directly compute the solvent contribution to the free energy of activation for the S_N2 reaction of CH_3Cl and Cl^- [183,201,202] and anisole hydrolysis[203,204] in HTW. These studies also revealed that solvent compressibility plays an important role in the solvation effects on reaction kinetics, as discussed in section IV.B.4.

The Kirkwood analysis quantifies the effect of solvent polarity on the rate constant for reactions wherein there is a changing dipole moment.[205] For the reaction between neutral molecules A and B in a dielectric continuum, the gas-phase free energy of activation is corrected with the free energy change accompanying the transfer of a dipole from a medium with the dielectric constant of 1 to ϵ. The resulting rate constant is

$$\ln k_{\mathrm{sol}} = \ln k_{\mathrm{gas}} + \frac{N_{\mathrm{A}}}{RT}\left(\frac{\epsilon - 1}{2\epsilon + 1}\right)\left[\frac{\mu_{\ddagger}^2}{r_{\ddagger}^3} + \frac{\mu_{\mathrm{A}}^2}{r_{\mathrm{A}}^3} + \frac{\mu_{\mathrm{B}}^2}{r_{\mathrm{B}}^3}\right] \tag{8}$$

where k_{gas} is the gas-phase rate constant and μ_i and r_i are the dipole moment and molecular radius of species i, respectively. Tester and co-workers[206,207] reported that the extent of hydrolysis of methylene chloride in HTW is significant under subcritical temperatures, whereas relatively little hydrolysis occurs under supercritical conditions. They applied the Kirkwood analysis, modified to use liquid water instead of the $\epsilon = 1$ medium as the reference, and obtained an excellent correlation of the experimental rate constant, as shown in Figure 18. The consistency between eq 8 and the experimental data provided further support for the S_N2 mechanism for hydrolysis in HTW.

An alternative method of assessing the solvation behavior of various solutes in HTW is the use of the Hildebrand solubility parameter, which reflects the strength of van der Waals forces acting on a given substance. Generally, materials with similar solubility parameters have a high affinity for each other. The Herbrandson and Neufeld analysis combines transition-state theory and regular solution theory[208] and correlates the rate constant with the solubility parameters (δ) and molar volumes (v) of all species involved in the reaction[209]

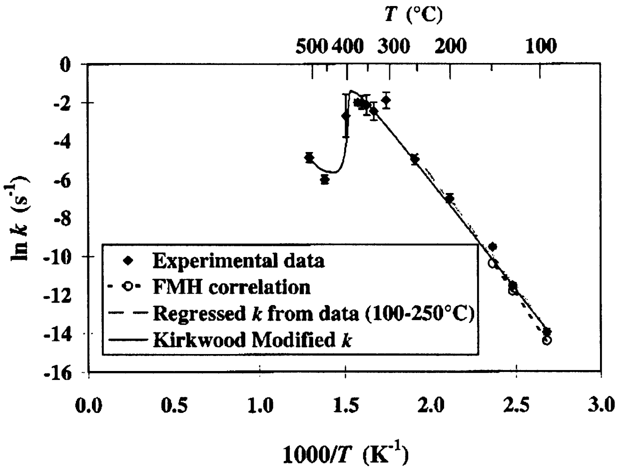


Figure 18. Apparent first-order rate constant for methylene chloride hydrolysis in HTW. (Reprinted with permission from ref 207. Copyright 1999 American Chemical Society.)

$$RT \ln k = 2B\bar{\delta} - v_{\ddagger}\delta_{\ddagger}^2 + \sum_{\text{reactants}} v_i \delta_i^{\,2} + C \tag{9}$$

$$B = v_{\ddagger}\delta_{\ddagger} - \sum_{\text{reactants}} v_{\mathrm{i}}\delta_{\mathrm{i}} \tag{10}$$

where $\bar{\delta}$ is the mixture solubility parameter. The parameter B is a measure of the difference in polarity between the reactant(s) and the transition state, and C is a constant. Because the solubility parameter is higher for a more polar substance, B is positive if the transition state is more polar than the reactants. Huppert et al. applied this analysis to the hydrolysis of guaiacol in HTW.[75] They used a density-dependent mixing rule to calculate $\bar{\delta}$ in eq 9 and obtained a correlation that is explicitly density dependent

$$RT \ln k \left(\frac{\rho_{\mathrm{W}}}{M_{\mathrm{W}}} + \frac{\rho_{\mathrm{G}}}{M_{\mathrm{G}}}\right) = \left(\frac{2B\delta_{\mathrm{W}}^0}{\rho_{\mathrm{W}}^0}\right)\rho_{\mathrm{W}} + C' \tag{11}$$

where the subscripts W and G stand for water and guaiacol and the superscript 0 denotes the liquid-phase reference state. The parameters B (same as eq 10) and C' were adjusted to fit eq 11 to experimental data. The positive value of B obtained for guaiacol hydrolysis in HTW provided yet another piece of evidence for the S_N2 mechanism for hydrolysis in HTW.[75]

2. Effects of Hydrophobicity

A different type of equilibrium solvation effect is the hydrophobic effect, which is the strong tendency of organic solutes to aggregate to minimize the water–organic interface.[210] The origin of this effect has been attributed in large part to the high cohesive energy of ambient liquid water due to its hydrogen-bond network, such that the water–water interactions are much stronger and more attractive than the interactions between water and organic solutes. The hydrophobic effect accelerates the kinetics of condensation-type organic reactions in water by bringing the reactants close together. The hydrophobic effect also modifies the selectivity of these reactions by favoring the product that is more compact (i.e., smaller water–organic interface). Generally, conditions and additives that decrease the hydrocarbon solubility in water favor the aggregation of nonpolar species and promote the hydrophobic effect, whereas those that increase the hydrocarbon solubility diminish the hydrophobic effect. The hydrophobic effect on the rate of organic reactions was first noted in the pioneering work by Breslow and co-workers on Diels–Alder reactions in ambient liquid water[211] and has subsequently been described in detail.[15,16,212–214]

Some notable examples of the hydrophobic effect are described below. The Diels–Alder reaction of cyclopentadiene with butenone in water is 730 times faster than in isooctane and 60 times faster than in methanol.[211] This reaction has an endo/exo ratio of 25.0 in water, in contrast to only 3.85 in excess cyclopentadiene and 8.5 in ethanol.[215] The Claisen rearrangement of allyl vinyl ether in water is 106 times faster than in benzene[216] and 214 times faster than in cyclohexane.[217] The Mukaiyama reaction of the trimethylsilyl enol ether of cyclohexanone and benzaldehyde proceeds readily in water in the absence of catalysts, whereas a Lewis acid catalyst or extremely high pressure is required to drive the same reaction in methylene chloride.[218] The syn/anti selectivity for this reaction is 85:15 in water, compared to 75:25 in methylene chloride. Numerous other examples can be found in the review articles cited above.

As discussed in the previous section, water can facilitate polar reactions by stabilizing the transition state via electrostatic interactions. Water, however, can also act as a diluent that hinders bimolecular reactions (see section V.B). Because the hydrophobic effect brings the organic reactants in water closer to each other, water can reduce the activation barrier for polar bimolecular reactions without reducing their rate by dilution.[212] Thus, stabilization by electrostatic interactions with water can be important even for some reactions that are dominated by the hydrophobic effect.[217,219,220–226]

With a lower dielectric constant and fewer hydrogen bonds (section II), HTW exhibits a higher solubility for organic compounds than does ambient liquid water. Consequently, the hydrophobic effect is less pronounced in HTW. This reduction in the extent of the hydrophobic effect was demonstrated by the weaker potential of mean force for a benzene dimer in SCW than in ambient liquid water,[227] as shown in Figure 19. It is also evident in the loss of stereoselectivity for the Diels–Alder reactions of cyclopentadiene with various dienophiles in SCW compared to the same reactions at ambient conditions.[228] Because the selectivity for Diels–Alder reactions arises from the difference in the hydrophobicity of the products, the observed loss of selectivity is consistent with the diminishing hydrophobic effect in SCW compared to that in ambient liquid water.[229] The rate of a Diels–Alder reaction is faster in SCW than in ambient liquid water, but the origin of this rate acceleration is thermal activation and not the hydrophobic effect.[230]

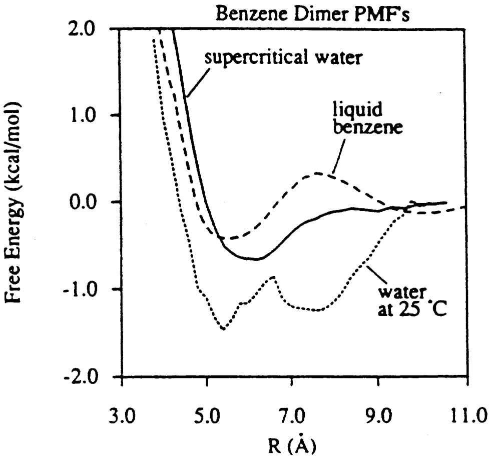


Figure 19. Computed potential of mean force for the benzene dimer in SCW at 400 °C and 350 atm, ambient water at 25 °C and 1 atm, and liquid benzene. (Reprinted with permission from ref 227. Copyright 1993 American Chemical Society.)

3. Effects of Solvent Dynamics

For reactions involving a substantial change in the electronic structure of the reactant(s), the dynamical response of the solvent can play a crucial role in the kinetics. When the solvent cannot adjust to the changes in the reacting system rapidly enough to maintain the equilibrium solvation, it can induce barrier recrossings during the reaction. One way to obtain evidence for such nonequilibrium solvation effects is to compute the transmission coefficient by molecular dynamics simulation. Reactions involving a change in the charge distribution of the reactant(s) are often chosen as model systems, because of the strong solute–solvent coupling that is expected to enhance the nonequilibrium solvation effects in water. For the prototypical S_N2 reaction of CH_3Cl and Cl^- in liquid water, the transmission coefficient is reported to be 0.55[178,231] or 0.47 if the solvent is assumed to be frozen.[231] The rate of change of the atomic charge distribution along the reaction coordinate for this reaction has a major effect on the solvent dynamics.[231,232] Similarly, the transmission coefficient for a model S_N1 reaction of *tert*-butyl chloride in ambient liquid water is 0.53.[233] The bromination of ethylene in water, which involves charge separation, has a transmission coefficient of 0.44.[234] In other words, only about one-half of the trajectories across the activation barrier are reactive for these reactions in liquid water. On the other hand, water-assisted intramolecular proton transfer of formamidine, which involves a negligible change in the reactant charge distribution, does not induce any solvent reorganization.[235] This type of data is currently not available in the literature for reactions in HTW.

Computer simulations that determine the time scales for the reaction and solvent dynamics provide valuable insights into the nonequilibrium solvation effects. Tuñon et al. studied the dynamics for proton transfer between a water molecule and a hydroxide ion in ambient liquid water.[236] The reaction is fast, occurring in 20−30 fs, whereas the solvent response to the charge distribution change after the proton transfer is delayed by 50 fs, which suggests that the nonequilibrium solvation effects are not negligible in this case. Re and Laria studied the dielectric response of SCW ($T = 645$ K, $\rho = 0.3-1.0$ g/cm^3) following an instantaneous charge jump of an initially neutral Lennard−Jones solute.[237] Figure 20 shows that, compared to solvation in ambient liquid water, the overall solvation process in SCW at liquidlike densities is an order of magnitude faster, but it becomes slower as the density decreases. The dynamic responses of the solvent show a bimodal behavior, characterized by a fast inertial regime lasting a few femtoseconds followed by a much slower diffusional regime that dominates the long-time behavior. The latter regime becomes increasingly dominant with decreasing water density. Balbuena et al. examined the reorientation dynamics of water molecules in the first solvation shell of monovalent ions in SCW.[238] The reorientation time in SCW was generally an order of magnitude smaller than in ambient liquid water. On the basis of these limited data, one might expect that, at least for reactions involving a change in the charge distribution, the nonequilibrium solvation effects in SCW are less pronounced than in ambient liquid water.

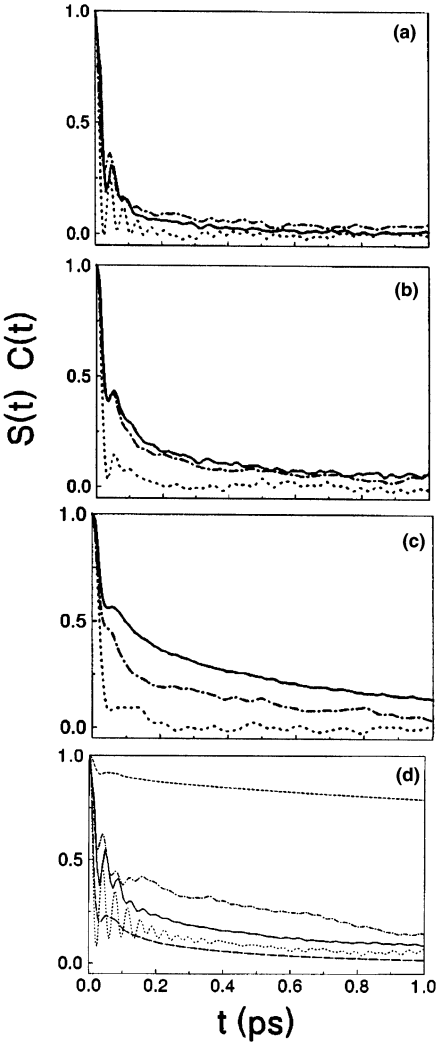


Figure 20. Dielectric response $S(t)$ (—) for supercritical SPC water at $T = 645$ K at different densities: (a) 1 g/cm^3, (b) 0.65 g/cm^3, (c) 0.3 g/cm^3, and (d) for ambient liquid water. Corresponding equilibrium time correlation functions $C(t)$ for charged (- • -) and neutral (• • •) solutes. (Reprinted with permission from ref 237. Copyright 1997 American Chemical Society.)

B. Density Inhomogeneity Effects

Introducing a solute molecule into a solvent creates a local density perturbation due to the differences in solute−solvent and solvent−solvent interactions. Such solute-induced effects on the local solvent microstructure are accentuated at nearcritical conditions, where the high solvent compressibility allows solvent molecules to move into energetically favorable locations with relative ease.[239−241] Therefore, in a solvent near its critical point, the local solvent density around solute molecules can differ from the bulk density. Consequently, the local environment experienced by solute molecules can be quite different than that expected on the basis of the bulk solvent properties. For example, Figure 21 summarizes results from spectroscopic measurements that show that the local water density around benzophenone at supercritical conditions (380 °C) is approximately 20−50% higher than the bulk water density.[239] The density enhancement occurs when water molecules are attracted to solutes that are polarizable, polar, or ionic. The extent of this effect is reduced if the solute−water interactions are weak.

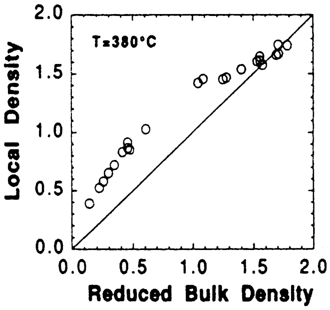


Figure 21. Local density (relative to ρ_c of pure water) estimated from the $\pi-\pi^*$ ν(max) of benzophenone in water at 380 °C. (Reprinted with permission from ref 239. Copyright 1994 American Chemical Society.)

Because the solvent density inhomogeneities determine the reaction environment experienced by solute molecules in compressible fluids, they can have an impact on the solvation effects described in the previous sections for reactions in SCW. Tucker has written excellent reviews of the experimental, theoretical, and computational studies that elucidate the solvent density inhomogeneities found at supercritical conditions.[240,241] These reviews contain several examples for SCW solutions that focus mostly on ionic systems. In this section, we extend Tucker's treatment of SCW solutions by discussing additional examples of the solvation characteristics of ions, radicals, organic compounds, and gases in SCW.

The origin of the local density inhomogeneity is different from that of the divergence in partial molar volumes, which is sometimes (incorrectly) attributed to the formation of stable solvent "clusters" around the solute, as Levelt Sengers,[242,243] Tucker,[240,241] and Chialvo[164,244] have pointed out. The local density inhomogeneity is the direct consequence of solute−solvent interactions. Although the solute−solvent interactions determine the sign of partial molar volume divergence, the divergence itself arises from the divergence of solvent−solvent correlation, which controls the extent of solvent density enhancement and therefore is a true critical phenomenon. Because it is the solute's local environment, rather than its extended surroundings, that determines solvation, the divergence of partial molar volumes near the critical point does not signify any *anomalous* solvent effects on chemical reactions.[240,245]

Solvent-sensitive solute properties (e.g., solvatochromic shifts, intensities, solvation free energies) exhibit a characteristic nonlinear bulk density dependence at nearcritical temperatures.[240,241] Three characteristic density regions are typically observed: a strong density dependence at low densities ($\rho_r < \sim 0.5$), a weaker density dependence at high densities ($\rho_r > \sim 1.5$), and very little density dependence at nearcritical densities ($\sim 0.5 < \rho_r < \sim 1.5$). This "three-regime" behavior has been observed for acetone and benzophenone in SCW.[239] This phenomenon arises from the differences in the bulk-density dependence of the local density in these three regimes.[246,247] In the low-density regime, increasing the bulk density results in the addition of solvent molecules to the first solvation shell, thereby altering the local environment around the solute. In the near-critical density regime, the solvation shell is saturated, due to the high solvent compressibility, and further increases in the bulk density do not change the local density. In the high-density regime, the increasing bulk density increases the local density by the compression of the local solvent sphere. Such bulk density dependence of the local environment can contribute to the experimentally observed density dependence of the reaction kinetics.

Statistical mechanical theories augmented with computer simulations provide insights into the solvation behavior in supercritical fluids. In particular, the local density inhomogeneities around infinitely dilute solute molecules are described by the Kirkwood−Buff fluctuation theory,[248] extended by Tucker,[240,241] Chialvo,[244,249] and Debenedetti.[250,251] Debenedetti developed a scheme for classifying mixtures based on the nature of the solute−solvent interactions. This classification is based on the sign of the partial molar volume ($\bar{v}_i^\infty$) and of the solute−solvent fluctuation integral

$$G_{ij} = \int_0^\infty [g_{ij}(r) - 1] 4\pi r^2 \, dr \qquad (12)$$

where $g_{ij}(r)$ is a solute−solvent pair correlation function. Mixtures are either attractive ($\bar{v}_i^\infty < 0$, $G_{ij} > 0$), repulsive ($\bar{v}_i^\infty > 0$, $G_{ij} < 0$), or weakly attractive ($\bar{v}_i^\infty > 0$, $G_{ij} > 0$). A weakly attractive mixture is one for which the solute−solvent interactions are attractive but weaker than the solvent−solvent interactions. Computer simulations that have been performed to calculate these properties provide additional insights into the nature of a given supercritical mixture, as discussed below.

1. Ions

Solvation of ions in water is important for reactions involving a change in charge distribution, and it has been studied extensively using molecular simulations. Sodium and chloride ions have been the most popular ions to investigate.[33,34,182,185−187,252−255] These studies show that the ion−water interactions are very strong even at supercritical conditions and that the ion-SCW mixtures are strongly attractive, according to Debenedetti's definitions. As shown in Figure 22, the water density in the first solvation shell is about an order of magnitude higher than the bulk density and is similar to that observed for ion solutions at ambient conditions, which suggests that the local environment around these ions in SCW resembles that in the ambient liquid water. Figure 23 shows similar results for the local and bulk water

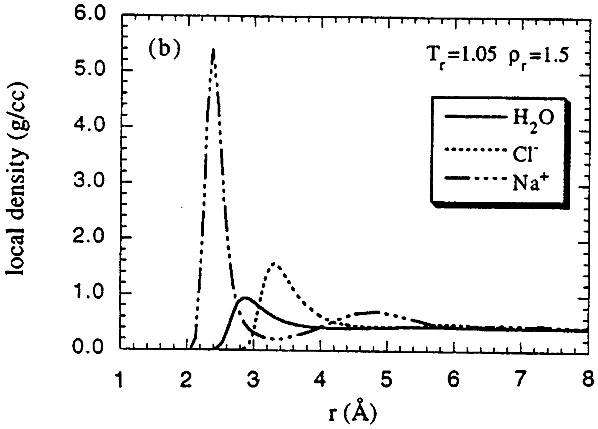


Figure 22. Comparison of local density profiles around species in solution for an infinitely dilute NaCl aqueous solution at T_r = 1.05 and ρ_r = 1.5. (Reprinted with permission from ref 254. Copyright 1999 American Institute of Physics.)

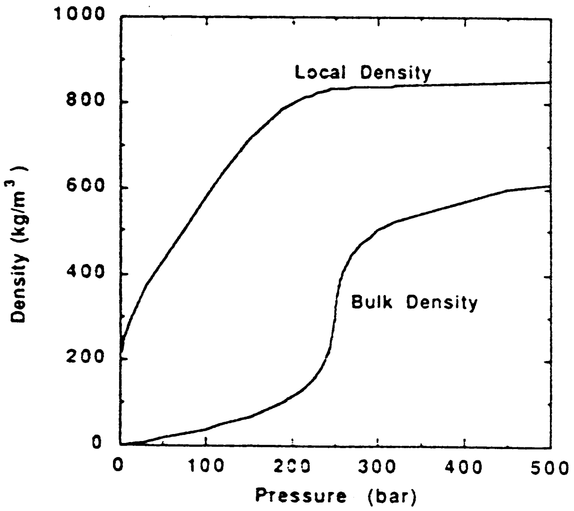


Figure 23. Comparison of bulk density with the local density 2.2 Å from the center of a monovalent ion in water at 385 °C. (Reprinted with permission from ref 257. Copyright 1989 American Chemical Society.)

densities around a monovalent ion. Additional work with mono- and divalent cations (Li^+, K^+, Rb^+, Be^{2+}, Mg^{2+}, Ca^{2+}, and Sr^{2+}) and anions (F^-, I^-, OH^-) in SCW provided results that agree qualitatively with the results for Na^+ and Cl^-.[173,185,256] The correct ion solvation number can be computed by analogy with adsorption using a Langmuir-type model, which assumes strong adsorbent–adsorbate (i.e., ion–water) interactions and weak adsorbate–adsorbate (i.e., water–water) interactions.[256] These results are consistent with the strong ion–water interactions as revealed by experimental measurements of the redox potential for the I_2/I^- reaction in SCW.[257]

On the basis of X-ray absorption fine structure measurements and molecular simulations, however, Wallen et al. demonstrated that pronounced dehydration occurs around a Br^- ion in SCW.[258] For example, a change in state from ambient liquid water to SCW at 425 °C and 0.42 g/cm^3 causes the hydration number around Br^- to decrease from 7.1 to 2.8. The quantitative difference between this study and others is perhaps due to the higher temperature and lower density at which these measurements were made, compared to the conditions used in the other simulation studies cited herein.

Ion–water interactions in SCW are stronger than water–water interactions, with ions disrupting the hydrogen-bonding structure of water. Whereas the cation–water interactions are dominated by electrostatic interactions, the anion–water interactions are primarily ion–water hydrogen bonding.[185] The ion–ion interactions are stronger than ion–water interactions in SCW, because of the lower dielectric constant of water at these conditions. For example, the potential of mean force for the Na^+Cl^- pair in water at 400 °C and 350 atm shows that the minimum energy is 26 kcal/mol lower than at 25 °C and 1 atm and that there is no solvent-separated minimum.[222] Consequently, cations and anions in SCW often exist as contact ion pairs rather than as dissociated ions.[186–188,222] The ion association also increases the net entropy in nearcritical water, because the entropy loss due to the electrostriction by water molecules is smaller for ion pairs than for free ions. As a result, inorganic salts have low solubilities in SCW.

2. Organic Compounds

The interactions of organic molecules with the surrounding water molecules depend largely on their functional groups. Near the critical point ($T_r = 1.05$, $\rho_r = 1.0$), methanol and benzonitrile in SCW experience higher-than-bulk local water density whereas benzene and toluene in SCW experience lower-than-bulk local water density.[34,253] Thus, at this condition, methanol and benzonitrile are weakly attractive whereas benzene and toluene are repulsive. At a higher density ($T_r = 1.0$, $\rho_r = 1.5$), however, methanol and benzonitrile encounter lower-than-bulk local water density, suggesting that the nature of these weak organics–water interactions can change with the bulk water density. These organic solutes being repulsive or weakly attractive is consistent with the large, positive partial molar volume of ethylene in water (~10^3 cm^3/mol), measured near the critical temperature of water.[259] Matubayashi and Nakahara found that the free energy penalty for inserting a nonpolar solute such as methane in HTW at high densities ($\rho > \sim 0.6$ g/cm^3) is higher than that in ambient liquid water, which indicates that methane–water interactions are more repulsive in HTW than in ambient liquid water.[260] The authors attribute the high solubility of the nonpolar solutes in HTW despite the unfavorable solute–water interactions to the elevated temperature, which is a nonspecific driving force for mixing any materials.

3. Noble Gases and Radicals

The interactions of noble gases with water are generally weak and repulsive. Cummings, Cochran, Chialvo, and co-workers investigated the solvation of argon and xenon atoms in SCW. Computer simulations have shown that the argon atom is surrounded by a local water density that is lower than the bulk, whereas the xenon atom is surrounded by a local water density that is only slightly higher than the bulk.[33,34,253] Both species, however, experience a local water density that is lower than the local density surrounding another water molecule. These simulation results suggest that the interactions between water and these noble-gas atoms are generally less attractive than the water–water interactions but that the extent of repulsion can vary with the identity of the noble gas. These results are consistent with the large, positive partial molar volumes for argon and xenon atoms in water measured near the critical temperature of water.[259]

The solvation of free-radical species in HTW has received little attention so far. Molecular simulations showed that a hydroxyl radical (OH) and H_2O_2 form repulsive mixtures in SCW.[199] Simulations also revealed that the fugacity coefficients for a hydroperoxyl radical (HO_2) in SCW deviate substantially from unity.[261] This result is significant in the context of SCWO, for which HO_2 is an important reactive intermediate. A standard simplification for the detailed chemical kinetics modeling for SCWO has been to take fugacity coefficients to be unity when calculating chemical equilibrium constants. The simulation-based fugacity coefficient for HO_2 in SCW, shown in Figure 24, clearly showed that this simplification is not necessarily an accurate one. An alternative approach to the ideal gas assumption is to use an equation of state to estimate the fugacity coefficients. This approach is troublesome because the critical properties required are not available for free radicals. The esimated critical properties for HO_2 in CHEMKIN Real Gas,[262] an independent extension of the popular CHEMKIN kinetics modeling package, led to fugacity coefficients from the Peng–Robinson equation of state that were markedly different than those obtained from molecular simulations.

4. Role of Density Inhomogeneity in Solvation Effects

The augmentation or depletion of water density around the solute molecules causes the dielectric constant of water in the immediate vicinity of these solutes to be higher or lower, respectively, than that

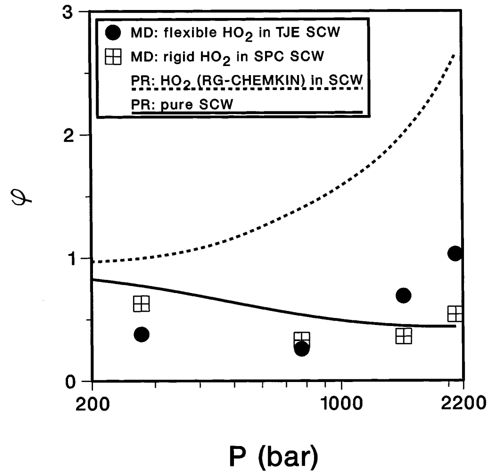


Figure 24. Fugacity coefficients for 0.004 mole fraction of solute at 773 K. (Reprinted with permission from ref 261. Copyright 1997 American Institute of Chemical Engineers.)

of the bulk water. If the reaction involves a substantial change in the charge distribution of the reactant(s), the local water density changes along the reaction path because of the solute−solvent interactions. Such a variation in the local density would cause the local dielectric constant to also change along the reaction path. The solvent contribution to the free energy of activation is thus affected by the compressible nature of HTW. For example, the barrier height for the S_N2 reaction of CH_3Cl and Cl^- in SCW is only a few kcal/mol lower in SCW than ambient liquid water.[181−183] This difference in the activation barrier is much smaller than expected from the difference in the dielectric constant or hydrogen bonding, which suggests that density augmentation around the ionic species (see section IV.B.1) causes the local reaction environment in SCW to closely resemble ambient liquid water.[181]

The solvent density inhomogeneity must be properly accounted for to describe accurately the effects of preferential solvation on reactions in compressible HTW. Quantum chemical calculations performed with the solvent modeled as a dielectric continuum demonstrated that the solvent density inhomogeneity needs to be included in the model to obtain accurate activation barriers for the S_N2 reaction of CH_3Cl and Cl^- [183,201,202] and anisole hydrolysis[203,204] in SCW. Flarsheim and co-workers showed that the classical Born model and a Born model modified to include the effects of solvent compressibility produce substantially different predictions for the partial molar volumes of and the free energy required to charge I^- in SCW.[257]

The local density inhomogeneity also affects acid-catalyzed reactions in HTW by causing the value of K_w in the immediate vicinity of the solutes to be different than that of the bulk water. Ikushima and co-workers reported that the temperature and pressure dependence of the kinetics for the Beckmann and pinacol rearrangements in pure HTW, both of which are catalyzed by H^+ ions from water, are inconsistent with the temperature and pressure dependence of K_w alone.[140,141] On the basis of this observation, they suggested that the local density inhomogeneity is a possible origin for the observed rate enhancement. That is, a local enhancement in the water density around the solutes might cause the local K_w to be higher than in the bulk solvent, resulting in the H^+ concentration near the reactants that is higher than predicted from the bulk K_w value.

For reactions in compressible HTW, the augmentation or depletion of water density around the solute molecules must vary along the reaction coordinate to maintain the equilibrium solvation, in response to the changes in the reacting solutes. If such response does not occur rapidly enough, the reaction is hindered and barrier recrossing occurs. Because the number of water molecules involved in the density augmentation or depletion can be quite large near the critical point, one might expect that the solvent reorganization along the reaction coordinate is very slow, causing unusually marked nonequilibrium solvation effects.[240] Luo and Tucker refuted this hypothesis on the basis of their computer simulation of ions in SCW.[202] They demonstrated that for systems in which electrostatic interactions are dominant, solvent compression in just the first two solvation shells is sufficient to gain the bulk of the compression-induced enhancement to the ion solvation energies. This result suggests that the magnitude of nonequilibrium solvation effects in SCW should be no greater than in liquid water.

V. Roles of Water as a Medium

Unlike the effects described in section IV, there are physical solvent effects that arise even in the absence of solute−solvent interactions. In these cases, the mere presence of a solvent can influence the reaction. Nominally unimolecular reactions in a gaslike environment are activated by collisions with surrounding molecules, and the kinetics can be influenced by collision frequencies. Thus, the rate depends on the concentrations of “third bodies” that can participate in these energy-transfer collisions. In a liquidlike environment, however, reaction kinetics are often governed by the diffusion process that controls the encounter of reactants and separation of products. The rate of diffusion-controlled reactions depends on the solvent viscosity. Both the collision and diffusion processes can play a significant role in the kinetics for reactions in SCW, which can be gaslike or liquidlike depending on the temperature and pressure. Furthermore, dissolution of solid materials as they react in HTW leads to chemistry that is very different from that encountered during neat reaction. The dissolution behavior can be sensitive to the temperature and pressure.

A. Effects on Energy Transfer

In SCWO, water participates as a collision partner in intermolecular energy-transfer steps, which are required for nominally unimolecular reactions to take place.[17] Water is a very effective energy-transfer agent, but this role does not account for the entire effect of SCW on SCWO reaction rates.[105] Many elementary reaction steps that involve collsion partners generate or consume key reactive intermediate species (e.g., OH, HO_2, H_2O_2). At gaslike densities, an increasing water density should thus promote these reactions and thereby influence the overall oxidation kinetics. Examples of such reactions are found in detailed chemical kinetics models for SCWO (section III.A.3).

$$H_2O + M \rightleftharpoons H + OH + M$$

$$H + O_2 + M \rightleftharpoons HO_2 + M$$

$$O + H + M \rightleftharpoons OH + M$$

$$H_2O_2 + M \rightleftharpoons OH + OH + M$$

$$HOCO + M \rightleftharpoons OH + CO + M$$

where *M* is the collision partner. Water's role as a collision partner in these and other reactions is often invoked to explain the experimentally observed water density (hence concentration of *M*) dependence of the global SCWO rates.[107,111,197]

B. Effects of Diffusion and Solvent Cages

A solvent can act as a physical barrier that retards the progress of a chemical reaction. A complete reaction in a solvent involves three steps: (1) diffusion of the reactant molecules to each other, (2) the chemical transformation, and (3) diffusion of the products away from each other.[205,263] The rate of diffusion of solutes in a given solvent depends on the solvent viscosity. If diffusion of reactive species in HTW is slower than the chemical transformation, then HTW slows down the overall rate of reaction. If a reaction is strongly diffusion-limited, then the other types of solvent effects, as discussed in previous sections, are not likely to play a role in the apparent reaction kinetics.

Brennecke and co-workers conducted a laser flash photolysis study of triplet−triplet annihilation of anthracene in SCW.[264] This reaction, which is known to be diffusion-controlled in liquid solvents, occurs in SCW as expected for such reactions. Figure 25 displays their results. The effect of the water density on the rate of this reaction in SCW can be predicted from the bulk solvent viscosity using the Stokes−Einstein−Smoluchowski (SES) formalism. This result is consistent with other spectroscopically examined diffusion-controlled reactions in various nonaqueous supercritical fluid media.[265−270] Deviations of the measured rate constants from the SES prediction near the critical point have been attributed to local density inhomogeneities.

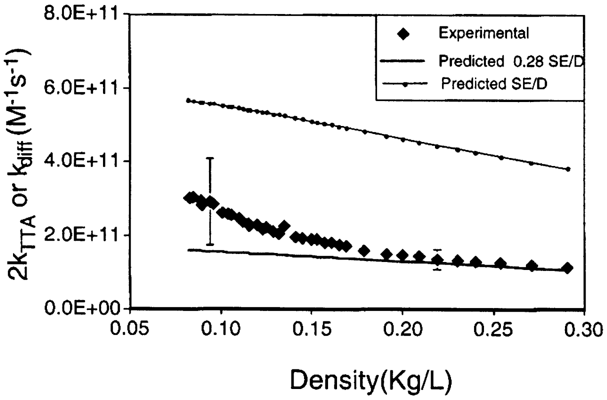


Figure 25. Experimental bimolecular rate constant ($2k_{TTA}$) and diffusion-controlled rate constant (k_{diff}) predicted by the Stokes−Einstein-based Debye (SE/D) equation with the spin statistical factor of 0.28 for triplet−triplet annihilation of anthracene in water at 420 °C. (Reprinted with permission from ref 264. Copyright 1999 American Chemical Society.)

Diffusion of solutes is hindered by the formation of a solvent cage around the solute molecules. Such solvent "cage effects" have been invoked for reactions in HTW to rationalize the change in the reaction pathways with the change in the solvent or with increasing water density. Cage effects hinder fission-type reactions (initiation, decomposition) in HTW by detaining the nascent products within the cage.[271] If the products cannot escape the cage, they are more likely to recombine and regenerate the reactant. A solvent cage can also reduce the rate of reaction by isolating the reactant molecules (slowing Step 1), thereby preventing solute−solute reactions, such as char and polycondensate formation,[63,73,78,95] but promoting solute−solvent reactions, such as hydrolysis[61,73,80] and water−gas shift reaction.[105,107] These effects become more pronounced with increasing water density. Cage effects can influence the density dependence of the decomposition kinetics for a reactant undergoing parallel fission-controlled pyrolysis and bimolecular hydrolysis pathways. The pyrolysis rate constant typically decreases with increasing water density due to cage effects, as just described. On the other hand, the hydrolysis rate increases with increasing water density due to increased water concentration. The competing effects of water density on the two reaction pathways can result in an extremum in the reactant conversion with increasing water density.[73]

C. Effects of Phase Behavior

Recent research on the use of HTW as a medium for decomposing complex (solid) materials for waste treatment or resource recovery has underscored the importance of phase behavior in the decomposition kinetics for heterogeneous systems.[272] Complete or partial dissolution of these materials and their decomposition products in HTW leads to chemistry that is different from that encountered during neat decomposition. Dissolution takes place presumably because HTW, especially SCW, is a suitable medium for breaking up the solid materials into smaller components that are more water soluble. Major contributions have been made by Smith, Arai, Adschiri, and co-workers in elucidating these phase behavior effects.

The dissolution of condensation polymers in HTW greatly facilitates monomer recovery by hydrolysis.[273−275] For example, the Arrhenius plot of the pseudo-first-order rate constant for cellulose decomposition in Figure 26 shows a discontinuity near 350 °C.[274,276] Above this temperature, the rate constant increases more rapidly with temperature than at *T* < 350 °C. No such discontinuity appeared, however,

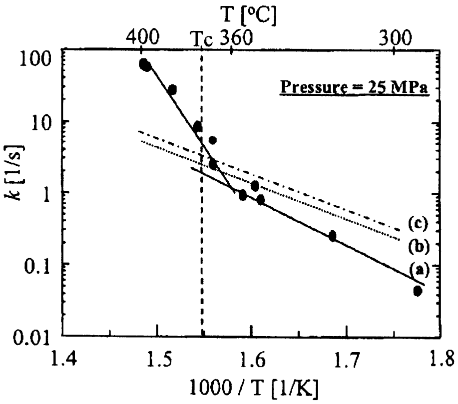


Figure 26. Decomposition rate constants of cellulose and related cellulosic compounds in HTW: (a) cellulose, (b) cellobiose, and (c) glucose. (Reprinted with permission from ref 274. Copyright 2000 American Chemical Society.)

for the rate constants for the decomposition of cellulose-derived compounds (cellobiose, glucose) that are water soluble.[80,277] This non-Arrhenius temperature dependence arises from a change in phase behavior. There is complete dissolution of cellulose in HTW above 350 °C, which eliminates mass-transfer limitations and permits the decomposition reaction to proceed at a faster rate.[274]

The dissolution behavior of these polymers depends on the reaction conditions such as the heating rate and duration, maximum temperature, polymer/water ratio, and pressure.[273,275] For example, if the heating rate is slow relative to the rate of heat transfer through the polymer, the polymer becomes completely miscible in water near its melting point, as shown for poly(ethylene terephthalate).[273] Otherwise, the polymer remains solid while the simultaneous dissolution and hydrolysis occur at the solid–fluid interface. At 272 °C, nylon 6,6 samples dissolved completely in HTW at pressures below 500 MPa but remained solid at higher pressures.[275] Interestingly, the rate of nylon hydrolysis in HTW increased monotonically with pressure under these conditions. In addition to the reaction conditions, polymer properties such as particle size and porosity also influence the dissolution behavior.[278]

Polymer–water phase behavior affects the product distribution for pyrolysis of addition polymers in HTW. Pyrolysis in HTW results in higher oil yields and significantly lower yields of coke and condensation products than neat pyrolysis for polyethylene[95] and polystyrene.[96] Neat pyrolysis of these polymers occurs in a molten polymer phase, whereas HTW promotes polymer decomposition by partial dissolution of this molten phase.[93,94] The resulting dilution of the polyethylene phase suppresses coke formation and shifts the pyrolysis selectivity from bimolecular hydrogen abstraction and addition to unimolecular β scission, thereby increasing the yield of α-olefins and low molecular weight products that subsequently react with water to form oxygenated compounds.[93,95,96] This trend is enhanced by increasing water density.

VI. Concluding Remarks

HTW is a unique medium for organic chemical reactions. The boundaries we have placed on the definition of HTW in this review are from liquid water at about 200 °C to supercritical water up to about 600 °C. Within these limits, its properties vary, in some cases considerably, with pressure and temperature. At the two boundaries we consider, water exists as a hot, expanded liquid and as a nearly ideal, high-temperature gas. Therefore, some of the roles for water for reactions in HTW are the same roles that any other liquid or gas can play in a liquid-phase or gas-phase reaction, respectively. Moreover, the limits encompass conditions near the critical point of water ($T_c = 374$ °C, $P_c = 218$ atm), so effects that are important in other supercritical fluids can also be important for HTW near its critical point. This applicability of concepts from gas-phase,[263] condensed-phase,[205] and supercritical-fluid-phase[7] kinetics is one of the unique features of chemical reaction kinetics

Table 3. Summary of Effects of Water for Organic Chemical Reactions in HTW

role of water	applicable conditions	affected reactions
reactant/product	any, but importance increases at higher water densities	reaction in which water is a reactant (e.g., hydrolysis, hydration, hydrogen abstration)
catalyst	any	proton-transfer reactions in which water interacts with reactant(s), typically via hydrogen bonding
acid/base catalyst precursor	more important at higher temperatures and liquidlike densities	acid/base-catalyzed reactions
preferential solvation/ desolvation of transition state	any, but probably less important at gaslike densities	reactions with change in solute–solvent interactions (e.g., electrostatic, hydrogen bonding, etc.) between reactant(s) and transition state; examples include reactions with a change in polarity along the reaction coordinate
hydrophobic effect	more important at near-ambient conditions than in HTW	condensation reactions with immiscible organic reactants
solvent dynamics	more important at liquidlike densities	very fast reactions (faster than solvent reorganization)
density inhomogeneities	supercritical conditions	any reaction can be affected by the local composition differing from the bulk composition
energy transfer	more important at gaslike densities; at liquidlike densities, energy transfer is not likely to be rate limiting	nominally unimolecular elementary reactions
cage effects	more important at liquidlike densities	bimolecular reactions (in either forward or reverse direction)

in HTW. Other unique features arise from the nature of water itself. That is, it can participate in hydrogen-bonding interactions, which can allow formation of alternate, lower-energy transition states or stabilize existing transition states, and it can dissociate to form H^+ and OH^-, which can accelerate acid- and base-catalyzed reactions.

Table 3 summarizes the roles of water that have been highlighted throughout this review. We have attempted to provide this information in such a form that readers can identify the roles and effects of water that are likely to be important for a particular chemistry at a particular set of reaction conditions.

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