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Effect of Water Density on Methanol Oxidation Kinetics in Supercritical Water

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We oxidized methanol in supercritical water at 500 °C to explore the influence of the water concentration (or density) on the kinetics. The rate increased as the water concentration increased from 1.8 to 5.7 mol/L. This effect of water density on the kinetics observed experimentally was quantitatively reproduced by a previously validated mechanism-based, detailed chemical kinetics model. In this model, reactions of OH radicals with methanol were the fastest methanol removal steps. The rates of these removal steps increased with water density at 500 °C because the OH radical concentration increased. The OH radical concentration increased with density because the rates of the steps $H + H_2O = OH + H_2$ and $CH_3 + H_2O = OH + CH_4$, which produce OH radicals, increased. Thus, the main role of water in accelerating methanol oxidation kinetics at 500 °C is as a hydrogen donor to a radical (R) in steps such as $R + H_2O = OH + RH$. This system provides a striking example of SCW being involved on the molecular level in the free-radical oxidation as a reactant in elementary steps.

Introduction

Water at temperatures and pressures that exceed the thermodynamic critical values ($T_c = 374$ °C, $P_c = 218$ atm) is an important reaction medium in both natural and engineered systems. In the environment, supercritical water conditions exist near ocean-floor hydrothermal vents. In the nuclear power, waste treatment, materials synthesis, and chemical processing industries, such conditions are used or being considered in many different applications. Given the importance of both organic and inorganic chemistry in supercritical water, there is interest in understanding relevant reaction mechanisms in detail and their responses to changes in reaction variables. In this article we focus on oxidation chemistry in supercritical water, which is important for both chemical synthesis[1] and waste destruction.[2]

Supercritical water oxidation (SCWO) is an organic waste destruction technology that competes with wet air oxidation and incineration. The oxidation reaction takes place at 400−600 °C and 220−300 bar. At these conditions small organic compounds, oxygen, and water are completely miscible and exist in a single fluid phase. This absence of phase boundaries and the higher temperature lead to faster reaction rates and essentially complete mineralization of organic carbon in a single processing step as compared with wet air oxidation. SCWO also represents a more controlled reaction and operates at a lower temperature than incineration. The technology is most attractive for organic waste streams with a high water content (e.g., sludges) and for high-risk wastes such as stockpiled propellants, explosives, chemical weapons, and energetic materials.

Previous SCWO research[3−6] has demonstrated that the oxidation rate can be sensitive to the water density (or concentration), with all other process variables held constant. For example, the phenol oxidation rate in SCW at 420 °C is inhibited by increasing water density at low densities but accelerated by water at high densities.[4,5] Phenol oxidation chemistry was too complex to allow definitive identification of the fundamental chemical or physical processes responsible for this behavior. Therefore, we initiated a study of methanol oxidation in SCW. The oxidation mechanism for this compound is established, and detailed mechanism-based models have been validated for SCWO. Indeed, methanol has been the subject of much previous SCWO research (e.g., refs 7−9). The independent variables that have received the most attention for this system are temperature, reaction time, and reactant concentration. The influence of water density on methanol SCWO has been explored only once previously.[10] The data showed that the disappearance rate for methanol decreased as the water density increased between 8.9 and 28.9 mol/L at 400 °C. The authors speculated that H^+ and OH^- ions, which are more abundant at higher densities, interacted with methanol to stabilize it and make it less reactive. In the present work, we focus on oxidation at 500 °C where the density is much lower. The ion product of water is also much lower and ionic effects are not expected to be important in this study.

Aside from this one previous low-temperature study, the effect of water density and the role of water during methanol SCWO are largely unexplored. Gaining information about the influence of this variable is important for both engineering purposes (perhaps finding a new way to accelerate SCWO rates) and fundamental understanding. The purpose of the work presented herein was to determine how water density affects methanol SCWO kinetics and then to provide physical or chemical explanations for any observed effect. Note that we will use the terms water density and water concentration interchangeably in this article. The terms differ only in that density is typically thought of in terms of mass and concentration in terms of moles.

Experimental Section

Methanol SCWO experiments were performed at 500 °C and different pressures in nominally isothermal, isobaric tubular flow reactors. At these conditions, the water density varied from 1.8 to 5.7 M. Two tubular reactors, which differed only in their volumes (17.2 and 67.7 cm^3), were used to explore a range of residence times and gather data over a range of methanol

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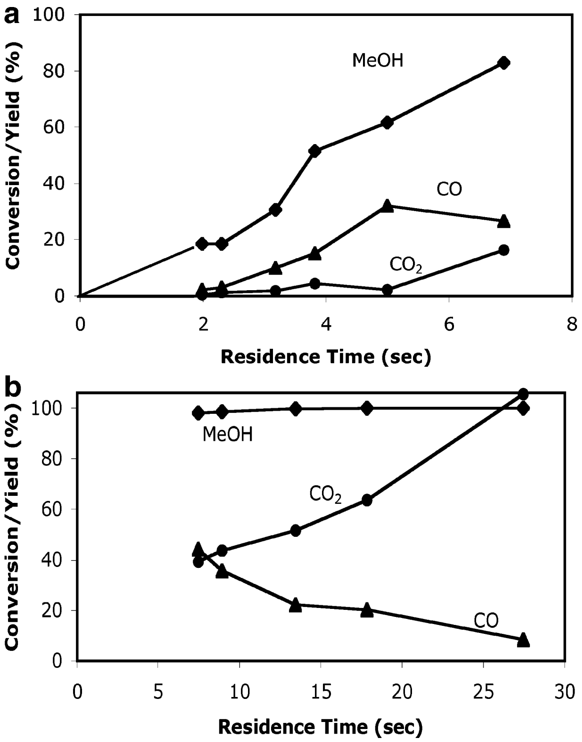

Figure 1. Experimental results for methanol SCWO at 500 °C: (a) $[H_2O] = 1.8$ mol/L; (b) $[H_2O] = 5.7$ mol/L.

conversions (X) at each temperature. Each methanol conversion profile (X vs residence time (τ)) was collected using approximately the same reactant feed concentrations (i.e., $[\mathrm{MeOH}]_o = 1.0$ mmol/L; $[O_2]_o = 7.0$ mmol/L) as determined at reaction conditions. Since over 99.5% of the molar mass in the reactor was water during these experiments, we assumed that the system physical properties could be taken to be those of pure water. The experimental apparatus, procedure, and gas chromatographic method for gas analysis are discussed fully in a previous article on phenol SCWO.[3]

We used a gas chromatograph with flame ionization detection to determine the methanol concentration in the reactor effluent. The injection port and oven temperatures were set at 165 and 125 °C, respectively. Helium at 30 mL/min carried the constituents in the 1 μL sample through the 8 ft × $^1/_8$ in. o.d. stainless steel Supelco Hayesep T 100/120 packed column. The total run time for each sample was 11 min. The detector was set at 175 °C with hydrogen and air flow rates of 35 and 350 mL/min. Standard solutions with known amounts of methanol were analyzed to create an independent calibration curve.

The experiments provided the molar yields of CO and CO_2 (moles of product formed per mole of methanol fed to the reactor) and molar conversion (moles of reactant consumed per mole of methanol fed to the reactor) of methanol as a function of the reactor residence time for a fixed set of reaction conditions (temperature, pressure, feed concentrations). Formaldehyde is also known[11,12] to be a product of methanol SCWO, but we could not determine its yield with our chromatographic analyses. Varying the pressure from run to run while holding the temperature constant provided isothermal variation of the water density (concentration), which is the variable of chief interest in this study.

Experimental Results

Figure 1 shows CO and CO_2 product yields and methanol conversion as a function of the reactor residence time for the highest and lowest water concentrations investigated. At the lowest water density (Figure 1a), the methanol conversion increases steadily and reaches a value of 83% at 6.9 s. The yield of CO was always higher than the yield of CO_2. At the highest water density, the conversion is 98% at 7.5 s, the shortest time attainable at these conditions in our reactor system. The CO and CO_2 yields were nearly equal at this time. Comparing these results to assess the effect of the water density involves uncertainty because identical residence times could not be explored in the experiments. Nevertheless, comparing the data at a residence time of around 7 s suggests that the oxidation reaction was more rapid at the higher density as evidenced by the higher methanol conversion and higher gas yields.

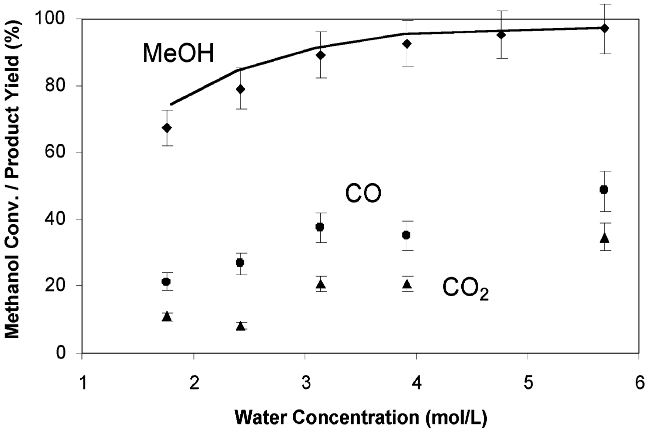

Figure 2. Effect of water density on methanol SCWO at 500 °C and $\tau = 5.5$ s.

To better assess the effect of the water concentration on the oxidation kinetics, we determined the methanol conversions and CO_x yields at $\tau = 5.5$ s for each of the six different water densities explored experimentally. Figure 2 displays these experimental results along with results for methanol calculated from a detailed chemical kinetics model that will be discussed later. Most points on Figure 2 were obtained by linear interpolation between two experimental measurements that spanned $\tau = 5.5$ s. The data points at water densities of 4.8 and 5.7 mol/L, however, were obtained by extrapolating 0.9 and 2 s, respectively, below the shortest experimental residence times. Since the two extrapolated points are at methanol conversions near 100%, this extrapolation should provide a good estimate of the conversion. The error bars in Figure 2 are based on Brock's analysis[11] that revealed a relative uncertainty of 8% and 12% for methanol and gas yields, respectively. Figure 2 shows that as the water concentration increases but all other parameters remain fixed, the methanol conversion increases. Likewise, the carbon oxide yields also increase with density at 500 °C.

The effects of water density apparent in Figure 2 are attributable to the underlying chemistry and are not artifacts from interfering phenomena. In previous work[3] with this same experimental apparatus we showed that parasitic effects potentially caused by things such as deviations from plug flow or phase behavior did not affect the SCWO results.

We desired to verify that the present kinetic results were consistent with those from previous studies of methanol oxidation in supercritical water. Vogel et al.,[7] in their critical review, recommend $\log A\ (\mathrm{s}^{-1}) = 13.2$ and $E_a = 199$ kJ/mol as the best estimates of the Arrhenius parameters in a pseudo-first-order rate law for methanol SCWO at low concentrations in a tubular flow reactor. Using these recommended values for post-induction-period kinetics leads to a calculated rate constant

TABLE 1: Revised Kinetics Data in Methanol SCWO DCKM[a]

reactn no.[b]	reactn	$k = AT^n \exp(-E/RT)$			ref
		A[c]	n	E[d]	
13	$CH_3O \rightarrow CH_3 + O$				20
24	$CH_3 + O_2\ (+M) \rightarrow CH_3O_2\ (+M)$				
	collisions with H_2O enhanced by	15.4			21
46	$CH_3OH + OH = H_2O + CH_2OH$	1.43×10^{14}	0.0	3177	22
52	$CH_3OH\ (+M) \rightarrow CH_2OH + H\ (+M)$				
	collisions with H_2O enhanced by	18.5			21
53	$CH_3OH\ (+M) \rightarrow CH_3 + OH\ (+M)$				
	collisions with H_2O enhanced by	18.5			21
58	$CO + OH + H \rightarrow CH_2 + O_2$				20
60	$CO_2 + H + H \rightarrow CH_2 + O_2$				20
64	$CO + H + H \rightarrow CH_2 + O$				20
96	$CH_3 \rightarrow CH + H_2$				20
109	$CO + HO_2 = OH + CO_2$	2.08×10^{12}	0.5	22853	23
113	$CO + H\ (+M) \rightarrow HCO\ (+M)$				
	collisions with H_2O enhanced by	15.4			21
132	$H + O_2 \rightarrow OH + O$	2.07×10^{14}	-0.097	15023	24
132	$OH + O \rightarrow H + O_2$	$K_c = 288T^{-0.367} \exp(-8390/T)$			20
134	$H_2 + O_2 = H + HO_2$	7.40×10^5	2.4328	53507	25
140	$H + O_2\ (+M) \rightarrow HO_2\ (+M)$	$k = 5.72 \times 10^{13}(T/300)^{0.44}$			26
	low-pressure limit (N_2)	$k = 1.96 \times 10^{16}(T/300)^{-1.4}$			
	TROE centering	$F_c = 0.78$			
	collisions with H_2O enhanced by	15.4			21
146	$HO_2 + HO_2 = O_2 + H_2O_2$	1.03×10^{14}	0.0	11041	19
	second exponential	1.94×10^{11}	0.0	-1409	
147	$H_2O_2\ (+M) \rightarrow OH + OH\ (+M)$				
	low-pressure limit (Ar)	2.29×10^{16}	0.0	43643	19
	collisions with H_2O enhanced by	18.5			21
151	$OH + H_2O_2 = HO_2 + H_2O$	1.70×10^{18}	0.0	29411	19
	second exponential	2.00×10^{12}	0.0	427	

[a] Reference 11. [b] Reference 10. [c] Units: mole-cm-s-K. [d] Units: cal/mol.

of 0.58 s^{-1} at 500 °C, which is about 60% higher than the mean rate constant obtained experimentally (0.37 s^{-1}). Recognizing that the Vogel et al. kinetics do not account for the influence of oxygen or water density on the rate and that there is modest lab-to-lab variation in SCWO kinetics reported in the literature, we take this level of agreement to indicate adequate consistency with previous results.

In the present experiments, where the reaction medium was 99.5% water by moles, it was not possible to vary the water concentration and the system pressure independently. Separating the influence of these two variables is possible, however, by adding a second component to the reaction medium. Adding helium, for example, allows one to maintain the pressure used in an experiment with pure water but obtain a different (lower) water concentration by dilution. Time limitations prevented us from performing such experiments for methanol SCWO. However, previous work with phenol SCWO[3−6] in water−He mixtures showed conclusively that it is the water concentration and not the system pressure that has the major influence on the SCWO rates. Thus, we expect that it is the water concentration that plays a role in methanol SCWO and not the total system pressure or total system density. This expectation will be tested and verified in the following section.

Detailed Chemical Kinetics Model

The experimental results showed that methanol SCWO rates are sensitive to the water density at 500 °C. We desired to discover the reason(s) for this sensitivity. A validated mechanism-based detailed chemical kinetics model (DCKM) is one tool that can be used to this end. A DCKM is a set of elementary reaction steps, associated kinetics, and thermochemical data. Such a model explicitly includes effects on kinetics due to water's role as a reactant, product, and collision partner in elementary reactions and energy transfer steps. A validated DCKM is one that has been shown to give faithful predictions of experimental observations for the system of interest.

Several DCKMs have been proposed for methanol SCWO (e.g., refs 8, 12−15), with predictive abilities generally being good at high temperatures ($T \geq 500$ °C). The models' predictive abilities tend to deteriorate at temperatures approaching water's critical point because of thermodynamic nonidealities, near-critical phenomena, and perhaps changes in the underlying chemistry not included in the models. We used Brock's DCKM,[11] which was validated for methanol SCWO, as the foundation for the model in this work. We used Chemkin III to solve the ordinary differential equations implied by the DCKM for methanol SCWO in a plug flow reactor. Note that this validated DCKM is a predictive, not correlative, tool. That is, it uses the underlying chemistry and physics to predict the outcome of experiments. Our use of the validated methanol DCKM is driven by the desire to learn what it predicts for the density dependence of methanol disappearance kinetics at 500 °C.

We modified Brock's model so it included more recent kinetics and thermochemical data for some steps and species as noted in Tables 1 and 2. In addition, we also tuned a preexponential factor and a rate constant to bring the model results for methanol into quantitative accord with the present experimental results at 500 °C. Specifically, we decreased the preexponential factor for k_∞ for H_2O_2 dissociation from the value recommended by Baulch et al.[16] for gas-phase oxidation to $10^{13.78}$ s^{-1}, which is close to the experimental value of $10^{13.4}$ s^{-1} reported by Croiset et al.[17] for this reaction in SCW. Second, we increased the rate constant for $OH + H_2O_2 = HO_2 + H_2O$ at 500 °C from the value of $10^{12.18}$ recommended by Kappel et al.[18] to $10^{13.48}$ L/mol-s. Holgate and Tester[19] noted, as we did in this work, that the kinetics for this step need to be faster in SCW than the published gas-phase values to reproduce experi-

TABLE 2: Revised Thermochemical Data in the Methanol SCWO DCKM[a]

species	$\Delta H_f(298)$[b]	$S(298)$[c]	$C_p(300)$[c]	$C_p(400)$[c]	$C_p(500)$[c]	$C_p(600)$[c]	$C_p(800)$[c]	$C_p(1000)$[c]	$C_p(1500)$[c]	ref
HO_2	3.00	54.73	8.34	8.95	9.49	9.97	10.78	11.39	12.45	27
OH	8.85	43.88	7.15	7.10	7.07	7.06	7.13	7.33	7.81	28, 29

[a] Reference 11. [b] Units: kcal/mol. [c] Units: cal/(mol K).

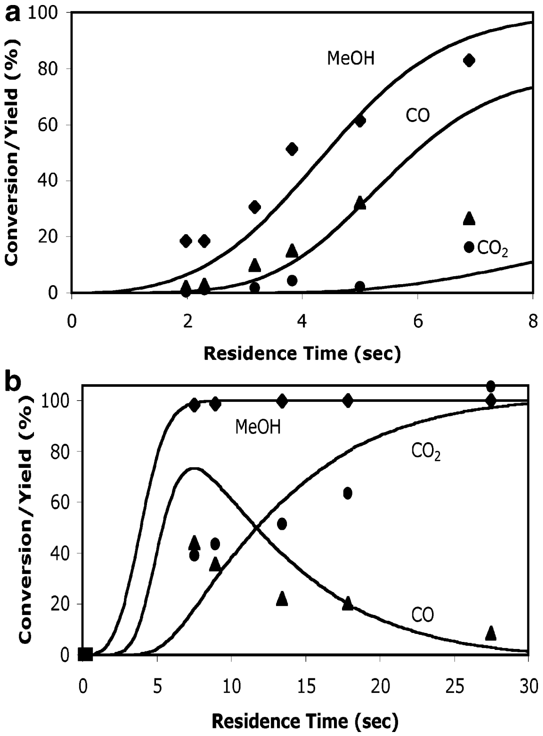

Figure 3. Model and experimental results for methanol SCWO at 500 °C: (a) $[H_2O] = 1.8$ mol/L; (b) $[H_2O] = 5.7$ mol/L.

mental SCWO data using a DCKM. Note that the simulation was conducted both with and without these adjusted values, and the adjustment did not affect the trend predicted by the model for the effect of water concentration on the kinetics of methanol SCWO.

Figure 3 compares the model results to experimental findings at 500 °C and two different water densities. The model reproduces experimental methanol conversions quite well at 500 °C. The carbon oxide yields predicted show the same trends as the data, but the conversion of CO to CO_2 appears to be faster in the experiments than in the model.

Knowing that the detailed chemical kinetics model matches the experimental results for methanol at 500 °C allows us to compare and contrast the experimental and predicted effect of water density on methanol SCWO. Figure 2 shows that the model does a good job of predicting the effect of water density on the conversion of methanol at 500 °C and the reactant concentrations used experimentally. Given that the model matches experimental trends for methanol so closely in Figure 2, it is reasonable to conclude that water's main effect on methanol SCWO at 500 °C is caused by water participating in the elementary chemical reactions as a reactant, product, or collision partner. These are the only roles of water explicitly included in the DCKM.

Mechanistic Insight

Having shown that the DCKM can predict the effect of water density observed experimentally at 500 °C, we next sought to discover the step(s) and chemical species responsible for this effect. That is, we desired to use the DCKM to obtain molecular-level insight into the cause of the density-dependent global oxidation rate. Net rate analysis, wherein one calculates the net rate for a specific chemical entity for each of the contributing elementary steps, is the tool we used to this end. The DCKM runs used in this analysis were conducted at 500 °C with feed concentrations of $[MeOH]_o = 1.0$ mmol/L and $[O_2]_o = 7.0$ mmol/L.

Previous work[12] on methanol SCWO showed that the main routes for methanol removal involve OH and HO_2 radical attack. Table 3 confirms that this is the case for different water densities at 500 °C and 70% conversion by showing that 99.8% of the methanol is removed by three key elementary reactions. Table 3 also shows that the rate of methanol removal increases by 45% between the lowest and highest water densities shown. Given that the rate constants for the three reactions remain fixed (since the temperature is fixed at 500 °C and the rate constants are not pressure dependent), the increased methanol disappearance rate with increasing water density must be caused by changes in the concentrations of the species participating in the three elementary reactions. The methanol concentration is the same in each run (all results shown are for 70% conversion), so it must be density-induced changes in the concentrations of OH and HO_2 that cause changes in the methanol disappearance rate. These changes in species' concentrations are caused by water's effect as a reactant, product, or collision partner in elementary steps.

Table 3 shows that both the hydroxyl and hydroperoxyl radical concentrations increase with water density, but the hydroxyl radical concentration experiences a greater percent increase. The rate of step 51, the fastest step for methanol removal, increases in direct proportion to the increase in the hydroxyl radical concentration. This correspondence indicates that the increase in methanol conversion seen experimentally at 500 °C can be attributed largely to a density-induced increase in the OH radical concentration.

We next sought an explanation for the increase in the OH radical concentration. One possibility is water's role as a collision partner in unimolecular reactions that remain in the falloff region even at these high pressures. Previous work[12] has shown that the OH radicals are formed primarily from the decomposition of H_2O_2 (R147 in Brock's[11] DCKM). We confirmed that this is also the case under the present reaction conditions. This H_2O_2 decomposition step has density-dependent kinetics, and its effective rate constant increases with increasing density. For example, in the DCKM we used, the forward rate constant at 500 °C for $H_2O_2\ (+M) = 2\ OH\ (+M)$ is 1.08, 1.10, 1.11, and 1.12 s^{-1} at water densities of 1.8, 2.4, 3.9, and 5.7 mol/L, respectively. Note that M is an arbitrary collision partner. The higher densities facilitate collisional energy transfer, so the reaction rate constant increases closer to its high-pressure limit, which is 1.18 s^{-1} at 500 °C. Thus, we conclude that one, albeit minor, way that water accelerates the rate of methanol SCWO at 500 °C is through its role as a collision partner in this elementary step with density-dependent kinetics. The rate constant increases by only about 4%, however, whereas the OH radical concentration increases by nearly 45% over the same density region. Thus, it appears that the very modest increase

TABLE 3: Effect of Water Density on Methanol Removal Rates at 500 °C and 70% Conversion

ρ_{H_2O} (mol/L)	τ (s)	reactn no.	elementary reactn	% of total rate	rate (mol cm^{-3} s)	concn (mol/L)	
						[OH]	[HO_2]
1.81	5.4	51	$CH_3OH + OH = H_2O + CH_2OH$	83.1	-1.68×10^{-7}	3.03×10^{-11}	6.27×10^{-7}
		52	$CH_3OH + OH = H_2O + CH_3O$	14.1	-2.84×10^{-8}		
		53	$CH_3OH + HO_2 = H_2O_2 + CH_2OH$	2.6	-5.22×10^{-9}		
2.41	4.8	51	$CH_3OH + OH = H_2O + CH_2OH$	83.5	-1.87×10^{-7}	3.27×10^{-11}	6.62×10^{-7}
		52	$CH_3OH + OH = H_2O + CH_3O$	13.8	-3.08×10^{-8}		
		53	$CH_3OH + HO_2 = H_2O_2 + CH_2OH$	2.5	-5.64×10^{-9}		
3.90	3.7	51	$CH_3OH + OH = H_2O + CH_2OH$	84.5	-2.20×10^{-7}	3.80×10^{-11}	7.10×10^{-7}
		52	$CH_3OH + OH = H_2O + CH_3O$	13.2	-3.44×10^{-8}		
		53	$CH_3OH + HO_2 = H_2O_2 + CH_2OH$	2.4	-6.15×10^{-9}		
5.69	3.05	51	$CH_3OH + OH = H_2O + CH_2OH$	85.2	-2.50×10^{-7}	4.39×10^{-11}	7.55×10^{-7}
		52	$CH_3OH + OH = H_2O + CH_3O$	12.5	-3.66×10^{-8}		
		53	$CH_3OH + HO_2 = H_2O_2 + CH_2OH$	2.2	-6.37×10^{-9}		

in this rate constant cannot account for the 10-fold greater increase in the OH radical concentration.

To determine whether some other elementary reaction with density-dependent kinetics (e.g., unimolecular or collisionally activated steps) might be contributing to the higher OH radical concentrations at the higher water densities, we exercised the DCKM at the lowest and highest water densities examined experimentally but used the same rate constant for a given reaction at both densities. These simulations provided results that were nearly indistinguishable from the results obtained by using the true density-dependent kinetics for these reactions. Obtaining the same results from the model regardless of whether it contained density-dependent kinetics for unimolecular reactions indicates that the energy transfer processes that cause density-dependent kinetics for these reactions cannot possibly be responsible for the effects observed. Thus, this result is entirely consistent with our expectation that the system pressure is not the root cause of the effects observed. Rather, it is the water concentration that is the key. Having molecules available as collision partners for energy transfer is not adequate to cause the density dependence observed. The molecules must be water. This result means that the role of water as a collision partner, though occurring, is not responsible for the increased disappearance of methanol at higher water densities. Rather, the key must exist within water's role as a reactant or product in some elementary step(s).

Having narrowed the cause of the density-dependent kinetics to water's role as a reactant or product, we next examined all of the steps in the mechanism that included water molecules as reactant or product. At the reaction conditions we examined, the two steps below account for 99.8% of the total water consumption rate. Coincidentally, both of these steps produce OH radicals.

$$CH_3 + H_2O = CH_4 + OH \tag{R4}$$

$$H + H_2O = H_2 + OH \tag{R148}$$

Net rate analysis revealed that these reactions proceed in the direction written above and that the rates of these two steps increase 2.6- and 4.2-fold as the water density increases from 1.81 to 5.69 mol/L. These two steps are in quasi-equilibrium at the conditions examined. Increasing the water concentration, then, causes a concurrent increase in the OH radical concentration by LaChatelier's principle.

The rate of OH production in these steps is low ($\sim 10^{-10}$ mol cm^{-3} s^{-1}) compared to the rate of OH radical production from H_2O_2 dissociation ($\sim 10^{-7}$ mol cm^{-3} s^{-1}), but it is not low when compared to the net rate for OH ($\sim 10^{-11}$ mol cm^{-3} s^{-1}). The net rate (production rate minus consumption rate) is orders of magnitude lower than both the OH production and consumption rates because OH is a very reactive, short-lived radical intermediate. Indeed, the net rate being very much less than the production or consumption rates for a reactive intermediate is the very basis for the quasi-stationary-state approximation in chemical kinetics. The nearly perfect balance in the quasi-stationary-state between the fast rate of OH production from H_2O_2 and the fast rate of OH disappearance as it attacks methanol leads to a very much smaller net rate. This balance, then, allows water-concentration-driven changes in the rate of comparatively slow steps for OH production (e.g., R4, R148) to become important and cause the water-concentration-induced rate acceleration observed at 500 °C. Thus, we conclude that water accelerates the rate of methanol SCWO at 500 °C and low concentrations primarily through its role as a reactant in elementary steps that produce OH radicals. In these steps, water serves as a hydrogen donor to a free radical.

Conclusions

At 500 °C, methanol SCWO rates are sensitive to the water concentration. The methanol conversion and carbon oxide yields both increase as the water density increases. A previously validated detailed chemical kinetics model for methanol SCWO was quantitatively consistent with the experimental results at 500 °C. The model predicted that the system pressure had only a very minor effect on the kinetics. The water concentration, on the other hand, had a much larger effect. Net rate analysis revealed that the water concentration influenced the global SCWO rate by increasing the generation rate of highly reactive OH radicals. The important steps were ones wherein a free radical abstracted an H atom from water to form OH plus a molecular product. These steps were quasi-equilibrated, so increasing the water concentration increased the concentration of OH radicals in the quasi-stationary-state.

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References and Notes

(1) Dunn, J. B.; Savage, P. E. *Environ. Sci. Technol.* **2005**, *39*, 5427.

(2) Savage, P. E. *Chem. Rev.* **1999**, *99*, 603.

(3) Henrikson, J. T.; Savage, P. E. *AIChE J.* **2003**, *49*, 718.

(4) Henrikson, J. T.; Chen, Z.; Savage, P. E. *Ind. Eng. Chem. Res.* **2003**, *42*, 6303.

(5) Henrikson, J. T.; Savage, P. E. *Ind. Eng. Chem. Res*. **2004**, *43*, 4841.

(6) Koo, M.; Lee, W. K.; Lee, C. H. *Chem. Eng. Sci.* **1997**, *52*, 1201.

(7) Vogel, F.; DiNaro Blanchard, J. L.; Marrone, P. A.; Rice, S. F.; Webley, P. A.; Peters, W. A.; Smith, K. A.; Tester, J. W. *J. Supercrit. Fluids* **2005**, 34, 249.

(8) Watanabe, M.; Sato, T.; Inomata, H.; Smith, R. L.; Arai, K.; Kruse, A.; Dinjus, E. *Chem. Rev.* **2004**, *104*, 5803.

(9) Kruse, A.; Ederer, H. J.; Mas, C.; Schmieder, H. In *Supercritical Fluids: Fundamentals and Applications*; Kiran, E., Debendetti, P. G., Peters, C. J., Eds.; Kluwer Academic Publishers: Netherlands, 2000; pp 439.

(10) Watanabe, M.; Sue, K.; Adschiri, T.; Inomata, H.; Smith, R. L.; Arai, K. *Chem. Commun.* **2001**, 2270.

(11) Brock, E. E. Ph.D. Thesis, University of Michigan, Ann Arbor, MI, 1997.

(12) Brock, E. E.; Oshima, Y.; Savage, P. E.; Barker, J. R. *J. Phys. Chem.* **1996**, *100*, 15834.

(13) Brock, E. E.; Savage, P. E.; Barker, J. R. *Chem. Eng. Sci*. **1998**, *53*, 857.

(14) Dagaut, P.; Cathonnet, M.; Boettner, J. C. *J. Supercrit. Fluids* **1996**, *98*, 33.

(15) Oshima, Y.; Bijanto, B.; Koda, S. *J. Chem. Eng. Jpn.* **2000**, *33*, 507.

(16) Baulch, D. L.; Cobos C. J.; Cox R. A.; Esser C.; Frank, P.; Just, Th.; Kerr, J. A.; Pilling, M. J.; Troe, J.; Walker, R. W.; Warnatz, J. *J. Phys. Chem. Ref. Data* **1992**, *21*, 411.

(17) Croiset, E.; Rice, S. F.; Hanush, R. G. *AIChE J.* **1997**, *43*, 2343.

(18) Kappel, Ch.; Luther, K.; Troe, J. *Phys. Chem. Chem. Phys*. **2002**, *4*, 4392.

(19) Holgate, H. R.; Tester, J. W. *J. Phys. Chem.* **1994**, *98*, 810.

(20) Denotes a reverse reaction rate constant calculation incorporating the compressibility factor (Z).

(21) Hunter, T. B.; Wang, H.; Litzinger, T. A.; Frenklach, M. *Combust. Flame* **1994**, *97*, 201.

(22) Feng, J.; Aki, S. N. V. K.; Chateauneuf, J. E.; Brennecke, J. F. *J. Phys. Chem. A* **2003**, *107*, 11043.

(23) Volman, D. H. *Photochem. Photobiol*. **1996**, *100*, 1.

(24) Troe, J. *Z. Phys. Chem*. **2003**, *217*, 1303.

(25) Michael, J. V.; Sutherland, J. W.; Harding, L. B.; Wagner, A. F. *Proc. Combust. Inst.* **2000**, *28*, 1471.

(26) Troe, J. *Proc. Combust. Inst.* **2000**, *28*, 1463.

(27) DiNaro, J. L.; Howard, J. B.; Green, W. H.; Tester, J. W.; Bozzelli, J. W. *J. Phys. Chem. A* **2000**, *104*, 10576.

(28) Ruscic, B.; Wagner, A. F.; Harding, L. B.; Asher, R. L.; Feller, D.; Dixon, D. A.; Peterson, K. A.; Song, Y.; Qian, X.; Ng, C.; Liu, J.; Chen, W.; Schwenke, D. W. *J. Phys. Chem. A* **2002**, *106*, 2727.

(29) *Thermochemical Database, Chemkin 3.7*; 1997.