

# Inhibition and Acceleration of Phenol Oxidation by Supercritical Water

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We have performed phenol supercritical water oxidation experiments to elicit water's influence on the reaction kinetics. We report, for the first time, both an acceleration and an inhibition of phenol disappearance by water. More specifically, experiments at 380 and 420 °C with similar residence times and phenol and oxygen concentrations showed that as the water concentration increased from 1 to 7 M the phenol conversion decreased. As the water concentration increased further from 7 to 22 M, the phenol conversion reached a minimum and then increased as the water concentration increased. Power law rate equations, which have been used in the past, are not capable of modeling water's effect on phenol supercritical water oxidation kinetics. We provide a new rate equation with a different functional form that possesses this capability. Also, by using a detailed chemical kinetics model, we eliminated the possibility that the observed effects of water are due to its acting as a collision partner, reactant, or product in elementary reactions steps.

## Introduction

Supercritical water oxidation (SCWO) involves the oxidative destruction of organic compounds in water at temperatures above 374 °C ( $T_c$ ) and pressures above 221 bar ( $P_c$ ). In the supercritical region, water's dielectric constant is lowered and hydrogen bonding is greatly reduced. Oxygen and small organic compounds become completely miscible with the water, allowing intimate contact of the reactants and removing any interphase transport limitations. The technology typically competes with wet air oxidation and incineration. The variables that affect SCWO rates are the organic compound identity and concentration, oxidant identity and concentration, temperature, pressure, and water concentration. Of these variables, the influence of the water concentration is the least understood. Six past studies<sup>1–6</sup> have reported the effect of water on phenol SCWO rates.

Thornton and Savage<sup>1,4</sup> reported that phenol destruction rates increased as the water concentration/system pressure increased. Their investigation of phenol SCWO spanned temperatures and water concentrations ranging from 380 to 420 °C and from 6.0 to 28 M. The reaction order for water of 0.70, however, was elicited exclusively from data at 380 °C. Gopalan and Savage<sup>2</sup> later revisited the SCWO of phenol and extended the temperature range over which rate data are available. These new data came from experiments at temperatures and water concentrations ranging from 420 to 480 °C and from 5.3 to 7.3 M. Combining their data with those of Thornton and Savage, they obtained new parameters for a global power-law rate equation. The new water reaction order was 0.42. Because of the limited variation of water concentration in their own data, Gopalan and Savage relied largely on the previous data to determine the water reaction order in the phenol disappearance rate equation.

Another group to derive a positive water reaction order (1.38) from experimental data was Koo et al.<sup>6</sup> This work was unique in that it used a helium–water mixture as the reaction medium. The new solvent system allowed the system pressure and the water concentration to be varied independently. They explored temperatures and water concentrations ranging from 380 to 440 °C and from 4.9 to 13 M.

The only previous report of a negative water reaction order for phenol SCWO is that of Oshima et al.<sup>5</sup> Their water order of  $-0.45$  was determined from experiments done at temperatures and water concentrations ranging from 370 to 430 °C and from 11 to 28 M.

We very recently reported results from phenol SCWO experiments in which the system pressure was decoupled from the water concentration by introducing helium.<sup>3</sup> We investigated temperatures from 420 to 465 °C and water concentrations from 1.6 to 6.8 M. We observed an apparent negative reaction order for water but did not attempt to quantify this effect by fitting a global rate equation. As the water concentration decreased, phenol disappearance rates increased. This effect was the opposite of that observed by previous investigators in our laboratory.<sup>1,2,4</sup>

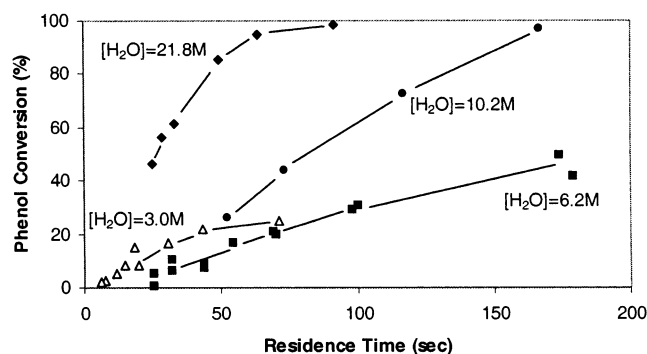
This review of the relevant literature shows that different researchers, both in different and in the same laboratories, have reported both negative and positive water reaction orders for phenol SCWO. This apparent conflict in the literature could be resolved, however, if water inhibits phenol SCWO in some regions of the parameter space and accelerates it in other regions. It is possible that all previous reports of water's effect on phenol SCWO can be integrated to provide a single cohesive picture. We initiated an experimental campaign to collect phenol SCWO data over a wide range of water densities, with water density as the sole independent variable to test this hypothesis.

## Experimental Section

We performed phenol SCWO experiments in an isothermal, isobaric tubular flow reactor at 380 and 420

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**Figure 1.** Effect of the water concentration on phenol conversion (380 °C,  $[\phi\text{OH}]_0 = 0.18$  mmol/L,  $[\text{O}_2]_0 = 6.1$  mmol/L).

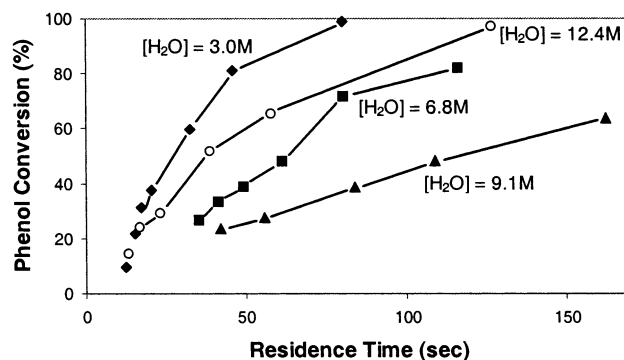
°C and pressures ranging from 124 to 310 bar. The water concentration was varied from 1.6 to 22 M. Two types of reaction media (pure water and  $1/3$  helium– $2/3$  water by moles) were employed at 420 °C, while only pure water was used as the reaction medium at 380 °C. From run to run, the phenol and oxygen concentrations at the reactor entrance at reaction conditions were generally kept constant at  $[\phi\text{OH}] = 0.19 \pm 0.04$  mmol/L and  $[\text{O}_2] = 6.6 \pm 1.1$  mmol/L so that the role of water in the phenol SCWO reaction could be observed more easily. The upper and lower bounds specified for the reactant concentrations are 1 standard deviation about the mean. The experiments employed a fluidized sand bath capable of controlling the temperature to within  $\pm 1$  °C and a back-pressure regulator capable of controlling the pressure to within  $\pm 30$  psi. The reactor effluent was analyzed chromatographically to determine the phenol conversion. An earlier paper<sup>3</sup> provides complete details regarding the experimental apparatus and analytical procedures.

## Experimental Results

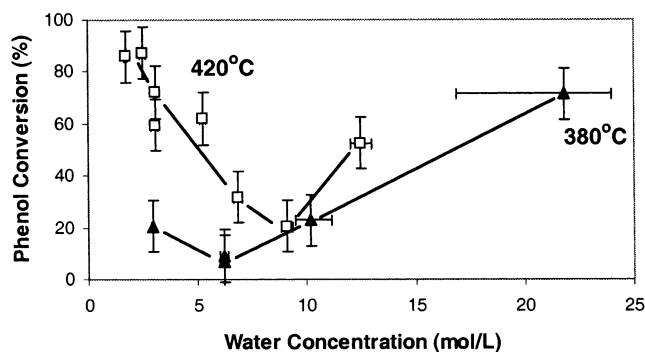
Figure 1 displays phenol conversion profiles at 380 °C for different water concentrations. As the water concentration increased from 6.2 to 22 M, the phenol conversion at a given residence time also increased. This result is consistent with the positive reaction order for water reported by Thornton and Savage<sup>4</sup> for the same range of water concentrations. As the water concentration decreased from 6.2 to 3.0 M, however, the phenol conversion increased. Because the phenol conversions at 6.2 and 3.0 M were comparable, we performed each experiment twice to verify that the difference was not simply a reflection of experimental uncertainty. As seen in Figure 1, the difference between the conversions at 6.2 and 3.0 M exceeds the difference between the duplicate experiments at the same water concentration.

Figure 2 shows the results from experiments at 420 °C where water concentration was an independent variable. As the water concentration increased from 3.0 to 9.1 M, the phenol conversion decreased. As the water concentration increased further from 9.1 to 12.4 M, however, the phenol conversion increased. These trends are the same as those observed in the experiments at 380 °C. Figures 1 and 2 show that water can either inhibit or accelerate phenol SCWO kinetics depending on the value of the water concentration.

Figure 3 further demonstrates the inhibiting and accelerating effects of SCW at 380 and 420 °C by showing the phenol conversion as a function of water concentration at a reactor residence time of 40 s and



**Figure 2.** Effect of the water concentration on phenol conversion (420 °C,  $[\phi\text{OH}]_0 = 0.16$  mmol/L,  $[\text{O}_2]_0 = 6.1$  mmol/L).



**Figure 3.** Inhibition and acceleration of phenol conversion at  $\tau = 40$  s by supercritical water at 380 °C ( $[\phi\text{OH}]_0 = 0.18$  mmol/L,  $[\text{O}_2]_0 = 6.2$  mmol/L) and 420 °C ( $[\phi\text{OH}]_0 = 0.19$  mmol/L,  $[\text{O}_2]_0 = 6.9$  mmol/L).

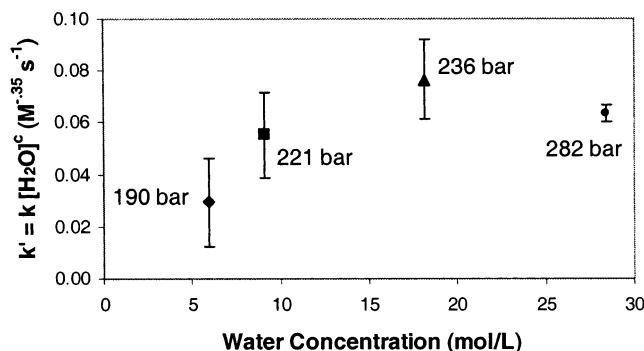
fixed reactant concentrations. The data used in Figure 3 are taken from Figures 1 and 2 and from the helium–water mixture results at 420 °C from our previous work.<sup>3</sup> If data did not exist at exactly  $\tau = 40$  s for a given experimental concentration profile, then linear interpolation was used to estimate the conversion. The horizontal error bars represent the variation in the nominal water concentrations we report herein, while the vertical error bars signify an experimental uncertainty of  $\pm 10\%$  associated with the phenol conversion.<sup>3</sup> Figure 3 shows that at both temperatures the phenol conversion goes through a minimum at a water concentration of around 6–9 M.

The data in Figures 1–3, which are a representative set of the 252 experimental data points listed in the Supporting Information, clearly show that SCW inhibits phenol SCWO at low water concentrations ( $< 5$  M) and that it accelerates the rate of phenol disappearance at high water concentrations ( $> 10$  M). More work is required to determine whether minima such as those in Figure 3 exist at other temperatures and for other organic compounds and whether the location of the minima is a function of temperature or other process variables.

The discovery of a minimum in the rate of disappearance of phenol during SCWO might offer an explanation for the apparent discrepancy in the literature regarding the effect of water on the reaction rate. The enhancing and inhibiting effects of water concentration on phenol SCWO, which are present at both 380 and 420 °C, suggest that previous phenol SCWO results may not be in conflict with each other but may simply be manifestations of sampling different regions of the same parameter space. Table 1 summarizes the experimental

**Table 1. Experimental Conditions Used To Determine the Effect of Water on Phenol SCWO Kinetics**

ref	reactor volume (cm <sup>3</sup> )	temp (°C)	pressure (bar)	res. time (s)	phenol concn (mmol/L)	oxygen concn (mmol/L)	water concn (mol/L)	phenol conv (%)	obsd water order
Gopalan and Savage <sup>2</sup>	7	380–480	253–282	3–98	0.030–0.53	1.6–9.4	5.3–28	7–99	0.42
Oshima et al. <sup>5</sup>	1	370–430	187–282	3–8	0.010–0.13	0.84–5.3	11–28	6–36	–0.45
Thornton and Savage <sup>1,4</sup>	7	380	190–282	1–111	0.17–2.1	6.5–56	6.0–29	1–99	0.70
Koo et al. <sup>6</sup>	27	380–440	193–274	12–140	1.2–8.7	53–180	4.9–13	11–99	1.38
Henrikson and Savage <sup>3</sup>	67	420–465	141–241	7–278	0.18	6.7	1.6–6.8	8–100	negative
this work	67, 17	380–465	124–310	4–304	0.19	6.6	1.6–22	4–100	variable

**Figure 4.** Effect of the water concentration on the global rate constant for phenol SCWO at 380 °C.

conditions used by different groups to determine the effects of water during phenol SCWO.

Three of the previous studies in Table 1 concluded that increasing the water concentration during phenol SCWO increases the phenol disappearance rate. All three groups used water concentrations of 4.9 M and above. As shown in Figure 3, this lower bound for the water concentration is near the location of the minimum. Hence, these three groups may have sampled primarily the high-concentration side of the curve.

Our previous paper<sup>3</sup> and that of Oshima et al.<sup>5</sup> are the only reports of SCW inhibiting the rate of phenol SCWO. Our work was done at water concentrations no higher than 6.9 M, so we may have sampled only the low-concentration side of the curve in Figure 3. The results of Oshima et al., however, are not as easily explained. Oshima et al. obtained a negative water reaction order even though they operated in a high water concentration regime (11–28 M). The only noticeable differences in their experimental conditions relative to those of others in Table 1 are that they explored only low phenol conversions and operated exclusively at higher ( $[H_2O] > 11$  M) water concentrations. One might be able to rationalize the Oshima et al.<sup>5</sup> result if there exists a region of the parameter space at these higher water densities where the rate is once again inhibited by water. We offer Figure 4, which shows the effect of the water density on the phenol SCWO kinetics at 380 °C as limited evidence to this end. The global rate constant,  $k'$ , on the  $y$  axis in Figure 4 was calculated from the Gopalan and Savage<sup>2</sup> rate equation for phenol SCWO using all of the data from Thornton and Savage<sup>1,7–9</sup> at 380 °C with at least 200% excess oxygen. It appears that there might be a region with a negative apparent water reaction order at water densities between 18 and 28 mol/L. Further investigation at water concentrations in this region is clearly warranted to discern more completely water's effect on phenol SCWO.

### Rate Equation for Phenol Disappearance

Several empirical rate equations have been proposed for the disappearance of phenol during SCWO.<sup>2,4–6,10–12</sup>

Typically, the five parameters that are used to fit data to a global power-law rate equation are the Arrhenius preexponential factor and activation energy and the reaction orders for phenol, oxygen, and water. Although these rate equations all describe the disappearance of phenol in excess oxygen, at reaction conditions where supercritical water constitutes at least 98 mol % of the fluid phase, the parameters in the rate equations are not identical. Part of the discrepancy no doubt stems from experimental error, from different approaches being used to fit the data, from exploring different regions of the parameter space, and from the data being collected from different laboratories around the world. The phenol reaction order is typically between 0.85 and 1.0, the activation energy ranges from 9.4 to 29.8 kcal/mol, and the reaction order for oxygen is between 0 and 0.5. Koo et al.<sup>6</sup> used a Langmuir-type oxygen dependence in the rate law, which led to an apparent oxygen order between 0.14 and 0.74. The water reaction order is the parameter with the greatest variability in these empirical rate equations. Reported water orders range from –0.45 to +1.38.

After examination of Figure 3, it becomes clear that a power-law treatment for water, though used extensively in the past for phenol SCWO, is not sufficient to describe the effect of water on the SCWO kinetics of phenol over a wide range of water densities. Recall from Figure 3 that, at water concentrations below about 6 M, the apparent reaction order for water would have a negative value, whereas at water concentrations greater than about 9 M, the reaction order for water would have a positive value. A rate equation with a single, invariant water order cannot simultaneously meet these conflicting demands. Therefore, it was necessary to develop a more versatile rate equation for phenol SCWO.

We offer eq 1 as the form of an improved rate equation for the disappearance of phenol during SCWO. The

$$\text{rate} = A \exp\left(-\frac{E_a}{RT}\right) [\phi\text{OH}] \left( \frac{[O_2]}{1 + b[O_2]} \right) ([H_2O]^{c_1} + d[H_2O]^{c_2}) \quad (1)$$

reaction rate constant is expressed in Arrhenius form, where  $A$  is the preexponential factor and  $E_a$  is the activation energy. The parameters  $b$ ,  $c_1$ ,  $c_2$ , and  $d$  determine the influence of the oxygen and water concentrations on the rate.

The phenol order is assumed to be 1 because reported values for the phenol reaction order do not differ much from unity.<sup>2,4–6,10–12</sup> Koo et al.<sup>6</sup> concluded that the oxygen order is 0.5–1.0 at low concentrations but approaches zero as the amount of excess oxygen is increased. We accounted for the influence of the oxygen concentration on the rate by using a saturation kinetics term capable of varying the apparent oxygen order between 0 and 1. Literature values for the oxygen order



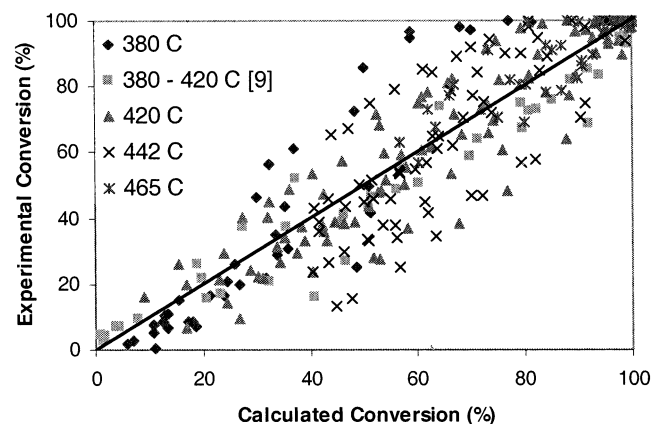


Figure 5. Parity plot for the new phenol SCWO rate equation.

fall in this range. This function provided a better fit of the data than a power law function for oxygen, and it did so without increasing the number of parameters. The most significant change in the rate equation is the function proposed to model the effect of water. This function is the sum of two components. The first term represents the inhibiting effect water has on phenol SCWO at low water densities ( $c_1 < 0$ ), and the second term represents the accelerating effect water has on phenol SCWO at high water densities ( $c_2 > 0$ ). The parameter  $d$  represents the relative importance of the two terms.

Combining the proposed rate equation with the design equation for an isothermal, isobaric plug-flow reactor and taking the oxygen concentration to be conversion invariant lead to eq 2 as the empirical model for phenol conversion ( $X$ ) during SCWO.  $\tau$  represents the reactor

$$X(\%) = \left\{ 1 - \exp \left[ -A \exp \left( -\frac{E_a}{RT} \right) \tau \left( \frac{[O_2]_0}{1 + b[O_2]_0} \right) \right. \right. \\ \left. \left. ([H_2O]_0^{c_1} + d[H_2O]_0^{c_2}) \right] \right\} \times 100 \quad (2)$$

residence time, and the concentration subscript o represents the reactor feed concentration. We used experimental data collected at temperatures and water concentrations ranging from 380 to 465 °C and from 1.6 to 22 M to determine the values of the parameters in eq 1. Because the vast majority of the data were collected at low water concentrations ( $[H_2O] < 7$  M), we also included all 52 data points from Li et al.<sup>9</sup> that were collected at temperatures between 380 and 420 °C with at least 180% excess oxygen. This set included many points at high water concentrations. We performed a nonlinear least-squares regression to fit the data to the model. The objective function was the sum of the squared difference between the experimental and calculated conversions for each experiment. We used the software package Scientist for the regression. Figure 5 displays a parity plot that compares the experimental phenol conversion with that calculated from eq 2 using the best-fit parameters that appear in Table 2. The apparent oxygen order obtained by using the saturation kinetics rate equation ranged from 0.72 to 0.87. If the model fit was perfect and there was no experimental error, then all of the points would fall on the diagonal line of Figure 5. The goodness of fit statistic ( $\chi^2$ ) in Table 2 is a measure of how well the model fits the experimental data. A value of this statistic near unity represents a moderately good fit.<sup>13</sup> The goodness of fit

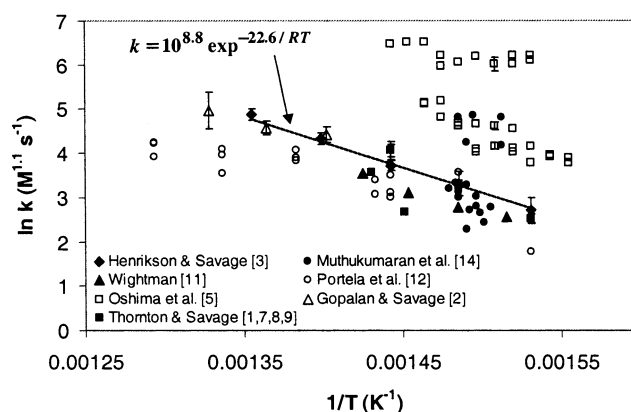


Figure 6. Comparison of previous phenol SCWO data with the new rate equation.

Table 2. Parameters in the Phenol SCWO Rate Equation

	parameter	value	95% CI
preexponential factor ( $M^{1.1} s^{-1}$ )	$\log A$	8.8	9.1
activation energy (kcal/mol)	$E_a$	22.6	2.8
oxygen parameter ( $M^{-1}$ )	$b$	36	22
water parameter	$c_1$	-2.1	0.4
water parameter	$c_2$	1.4	0.3
water parameter ( $M^{-3.5}$ )	$d$	0.0027	0.0015
$\chi^2$		1.45	

statistic was calculated as the minimized value of the objective function divided by the product of the square of the standard deviation in the conversion (estimated to be 10%) and the number of degrees of freedom in the regression analysis. The number of degrees of freedom is simply the number of data points minus the number of parameters in the model.

As a broader test of the validity of the new rate equation, we present Figure 6, which uses eq 2 with the parameters in Table 2 to calculate the global rate constant from previous experimental results for phenol SCWO. We used experimental results from plug-flow reactors and reactions with at least 200% excess oxygen. Figure 6 shows that the new rate equation does an adequate job of describing all of these published data with the exception of those from Oshima et al.<sup>5</sup> and a few data points from Muthukumaran et al.<sup>14</sup> Oshima's results are outside the concentration range we studied. Their phenol concentration was an order of magnitude lower than those used in our experiments, and the ratio of excess oxygen was 2.5 times higher on average. Oshima et al.<sup>5</sup> obtained a -0.45 water reaction order in their regression of data taken at water concentrations ranging from 11 to 28 M. The new rate law presented in eq 1 does not take the apparently inhibitive nature of water in this region of the parameter space into account. Because of this omission, we did not expect the new rate law to agree with Oshima et al.'s<sup>5</sup> results. Moreover, we have only limited experimental data in this high concentration region. A more comprehensive data set that spans a larger water concentration region in smaller experimental increments is required to make a more meaningful comparison and assessment of the Oshima et al. data. Work is underway to obtain this data set.

Not being fully satisfied with the scatter in Figure 5, we fit the data at each temperature to the new rate equation to learn whether the use of temperature-dependent parameters ( $b$ ,  $c_1$ ,  $c_2$ , and  $d$ ) would improve the agreement between the model and experiment. Table 3 provides the results of this parameter estima-

**Table 3. Parameters in the Phenol SCWO Rate Equation Determined at Individual Temperatures**

parameter	temperature			
	380 °C	420 °C	442 °C	465 °C
$k$ ( $M^{-1-c_1} s^{-1}$ )	12.9	27.4	63.8	74.6
$b$ ( $M^{-1}$ )	197	10.5	0	96.9
$c_1$	-2.7	-2.2	-1.8	-1.1
$c_2$	1.2	0.2	0	0
$d$ ( $M^{c_1-c_2}$ )	0.014	0.045	0	0
$\chi_v^2$	1.18	1.09	1.39	0.24
total $\chi_v^2$		1.04		

tion work. It is clear that the values of the parameters optimized from data at different temperatures take on different values. Thus, the use of temperature-dependent parameters would enhance the ability of the rate equation to fit the experimental data. We do not believe, however, that more detailed parameter estimation work is warranted until there is more complete experimental data. That is, it is clear that water can both inhibit and accelerate phenol SCWO, but the precise locations of these different regions and their quantitative contours have not yet been determined. For example, the minima in Figure 3 appear to occur at around 6.2 M for 380 °C and at around 9.1 M for 420 °C. This difference could reflect a temperature-dependent minimum, but there are presently insufficient data to make this claim. The rate equation may need additional modifications as a more complete picture of the water density dependence of phenol SCWO kinetics emerges.

### Why Does Water Both Inhibit and Accelerate Phenol SCWO?

Previous work<sup>3</sup> revealed that the different conversions observed at different water concentrations but otherwise identical reaction conditions cannot be attributed to parasitic effects such as interphase transport phenomena, pressure effects (e.g., extraordinarily large activation volumes), or departure from plug-flow behavior in the reactor. The presence of the minimum in Figure 3 suggests that water plays at least two different roles during phenol SCWO and that these roles have opposing effects on the kinetics. In this view, the minimum in conversion arises because different roles dominate in the low- and high-density regions. One possibility is that the density-dependent water properties favor different chemistries (free-radical vs ionic) in the low- and high-density regions. Another possibility is that the chemistry is the same throughout but that the water density influences the relative rates of competing or parallel steps. Akiya and Savage<sup>15</sup> reviewed the roles and effects that water has on reactions in high-temperature and supercritical water. They identified three main types of effects: chemical effects from the participation of water in elementary reaction steps, solvation effects arising from intermolecular interactions between water and reacting species, and physical effects such as collisional energy transfer, diffusion limitations, and solvent cage effects.

The density-dependent influence of several of these effects on the rates of individual elementary steps is easy to determine. For example, one would expect energy-transfer rates, reaction rates where water is a reactant, and the likelihood of cage effects and diffusion-controlled reactions to increase with increasing water density (concentration). How these qualitative effects on individual elementary steps would combine to influ-

**Table 4. Modifications of the Phenol SCWO Detailed Kinetics Model<sup>17</sup> at 442 °C and 238 atm<sup>a</sup>**

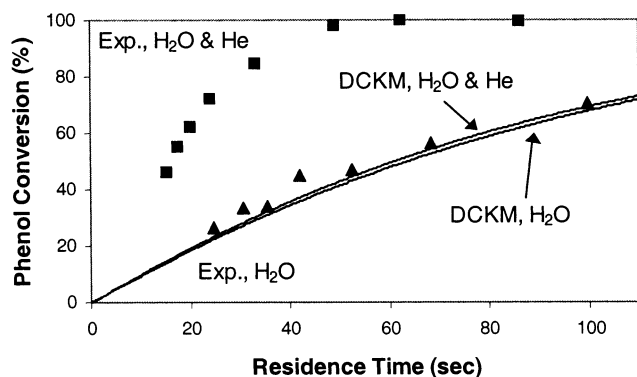
rxn no.	reaction	$k = AT^n \exp(-E/RT)$			ref
		$A$	$n$	$E$	
1	H <sub>2</sub> O <sub>2</sub> (+M) $\Rightarrow$ OH + OH (+M)				22
	low-pressure limit (Ar)	$1.81 \times 10^{16}$	0	42924	
	TROE centering	Fc = 0.5			
	collisions w/H <sub>2</sub> O enhanced by	$18.5^{23,24}$			
1a	OH + OH $\Rightarrow$ H <sub>2</sub> O <sub>2</sub>	$5.05 \times 10^{12}$	0	0	25
3	HO <sub>2</sub> + HO <sub>2</sub> = H <sub>2</sub> O + O <sub>2</sub>	$4.20 \times 10^{14}$	0	11983	26
	second exponential	$1.30 \times 10^{11}$	0	-1630	
4	H + O <sub>2</sub> (+M) = HO <sub>2</sub> (+M)	$8.81 \times 10^{10}$	1.0	445	27
5	OH + HO <sub>2</sub> = H <sub>2</sub> O + O <sub>2</sub>	$1.91 \times 10^{16}$	-1.0	0	28
6	H + HO <sub>2</sub> = OH + OH	$1.69 \times 10^{14}$	0	874	22
7	H + H (+M) $\Rightarrow$ H <sub>2</sub> (+M)	$2.24 \times 10^{13}$	0.5	0	29
	low-pressure limit (H <sub>2</sub> O)	$6.53 \times 10^{17}$	0	0	30
	collisions w/H <sub>2</sub> O enhanced by	$18.5^{23,24}$			
7a	H <sub>2</sub> $\Rightarrow$ H + H	$6.71 \times 10^{-18}$	0	0	25
8a	H <sub>2</sub> O $\Rightarrow$ H + OH	$1.12 \times 10^{-21}$	0	0	25
9	O + O (+M) $\Rightarrow$ O <sub>2</sub> (+M)	$7.63 \times 10^{12}$	0.5	0	29
	collisions w/ H <sub>2</sub> O enhanced by	$18.5^{23,24}$			
9a	O <sub>2</sub> $\Rightarrow$ O + O	$1.36 \times 10^{-22}$	0	0	25
15	H + O <sub>2</sub> = O + OH	$9.76 \times 10^{13}$	0	14844	30
16	O + H <sub>2</sub> = H + OH	$5.11 \times 10^4$	2.7	6280	30
18	H <sub>2</sub> + OH = H + H <sub>2</sub> O	$1.02 \times 10^8$	1.6	3299	30
19	O + H (+M) $\Rightarrow$ OH (+M)	$1.91 \times 10^{13}$	0.5	0	29
	collisions w/ H <sub>2</sub> O enhanced by	$6.0^{31}$			
19a	OH $\Rightarrow$ O + H	$2.09 \times 10^{-17}$	0	0	25
21	OH + OH $\Rightarrow$ O + H <sub>2</sub> O	$3.57 \times 10^4$	2.4	-2112	32
22	collisions w/ H <sub>2</sub> O enhanced by	$12.0^{31}$			
22a	CO <sub>2</sub> $\Rightarrow$ CO + O	$2.22 \times 10^{-25}$	0	0	25
23	CO + HO <sub>2</sub> = OH + CO <sub>2</sub>	$2.08 \times 10^{12}$	0.5	22853	33
26	C <sub>6</sub> H <sub>5</sub> OH + OH = C <sub>6</sub> H <sub>5</sub> O + H <sub>2</sub> O	$1.39 \times 10^8$	1.4	-962	34
27	C <sub>6</sub> H <sub>5</sub> O + OH = C <sub>6</sub> H <sub>5</sub> OOH	$1.00 \times 10^{12}$	0	0	18
121	HOCO + O <sub>2</sub> = CO <sub>2</sub> + HO <sub>2</sub>	$8.73 \times 10^{11}$	0	0	35

<sup>a</sup> A is in units of mol·cm<sup>3</sup>·s·K; E is in units of cal/mol.

ence the overall rate of phenol disappearance during SCWO, however, is much more difficult to ascertain. A model of the underlying reaction mechanism would be of great help in exploring such issues.

Gopalan and Savage proposed a reaction mechanism<sup>16</sup> and detailed chemical kinetics model (DCKM)<sup>17</sup> for phenol SCWO in the temperature range of interest. A mechanism-based model for benzene SCWO has also been developed,<sup>18</sup> and it includes phenol as one of the chemical species. We did not use this model in the present work because it was developed to model the chemistry at higher temperatures. Steps that are important at lower temperatures (such as phenoxy radical coupling) were not included. The Gopalan and Savage model<sup>17</sup> did not provide quantitative agreement with all of their experimental observations, but it did correctly predict several qualitative features of the reaction. In this section, we use that model to explore the influence of chemical effects (water as a reactant and product in elementary reaction steps) and a physical effect (water as a collision partner in energy-transfer steps) on phenol disappearance during SCWO. The objective of this exploration is to determine whether these roles for water can account for the inhibition and acceleration observed experimentally.

We used CHEMKIN III, a kinetics modeling software package, to exercise the DCKM for phenol SCWO. We updated the kinetic parameters where possible and manually calculated the reverse rate constants for many of the unimolecular reactions so as to include the compressibility factor ( $Z$ ) in the thermodynamic calculation. Table 4 lists the changes made to the parameters in the phenol SCWO DCKM. These changes reflect the inclusion of enhanced collision efficiencies for water, better treatment of falloff for hydrogen peroxide dissociation, and the inclusion of more recent recom-



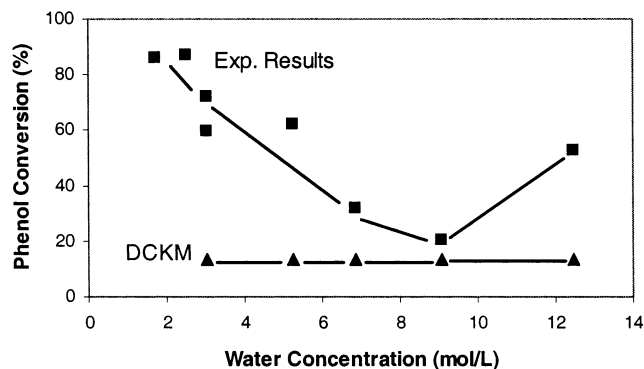
**Figure 7.** Comparison of DCKM prediction with experimental data for phenol SCWO at 442 °C and 241 atm, using pure H<sub>2</sub>O ([H<sub>2</sub>O]<sub>0</sub> = 6.0 mol/L, [ $\phi$ OH]<sub>0</sub> = 0.22 mmol/L, [O<sub>2</sub>]<sub>0</sub> = 7.4 mmol/L) and a H<sub>2</sub>O–helium mixture ([H<sub>2</sub>O]<sub>0</sub> = 2.9 mol/L, [ $\phi$ OH]<sub>0</sub> = 0.21 mmol/L, [O<sub>2</sub>]<sub>0</sub> = 7.8 mmol/L).

recommendations for some of the rate constants. The modeling approach, assumptions, and limitations are fully discussed elsewhere.<sup>19</sup>

Figure 7 presents results from the DCKM along with experimental data for phenol SCWO at 442 °C. This figure provides information about the effect of the reactor residence time and the water concentration on the phenol conversion. The experimental data show that diluting the reaction medium with helium increased the phenol conversion at a given residence time. The mechanism-based model showed the same effect, but it was very much smaller. The model does do a good job of predicting the conversion profile for the experiment done in pure water, but comparisons with data at other temperatures revealed that this quantitative agreement at 442 °C appears to be largely fortuitous.

A previous sensitivity analysis<sup>17</sup> showed that the predictions from the model were extremely sensitive to the kinetics used for the elementary step,  $\text{C}_6\text{H}_5\text{OH} + \text{O}_2 = \text{C}_6\text{H}_5\text{O} + \text{HO}_2$ . This step, though formally an initiation reaction in the forward direction, actually has a net rate in the reverse direction after the radical concentrations build up to their quasi-stationary-state levels. Because the net reaction rate for this step is in the reverse direction, this rate will be sensitive to the reverse rate constant, which we calculate from the forward rate constant and the equilibrium constant for this reaction. Therefore, sensitivity of the model results to the thermochemical data used for any of the species in this reaction would be anticipated. Sensitivity to the thermochemical data was indeed observed, and it was significant. Using sets of thermochemical data for phenol from two different sources<sup>20,21</sup> led to predicted conversions of 13.4% and 1.3%, respectively, for phenol SCWO at 40 s of residence time and the reaction conditions used in Figure 8. Although the heat capacity, standard enthalpy of formation, and standard entropy differed by less than 8%, they produced an order of magnitude difference in the predicted phenol conversion.

Clearly, a model that is so sensitive to seemingly small differences in thermochemical data will not afford a great deal of confidence in its quantitative predictions. Nevertheless, the qualitative predictions might remain useful. Therefore, we used the model to predict the effect of water density on phenol conversion at 420 °C. The results appear in Figure 8, along with the experimental results. The model predicts that the water density would have very little effect on the phenol conversion, whereas



**Figure 8.** Comparison of DCKM prediction with experimental data for phenol SCWO at 420 °C and  $\tau = 40$  s ([ $\phi$ OH]<sub>0</sub> = 0.19 mmol/L, [O<sub>2</sub>]<sub>0</sub> = 6.9 mmol/L).

the experiments showed a large and easily measurable effect. Therefore, if the model does indeed capture the important chemistry, we can conclude that the influence of water density on phenol SCWO kinetics cannot be attributed to the role of water as a reactant, product, or collision partner in elementary reaction steps.

## Summary

We have collected phenol SCWO data with the exclusive purpose of ascertaining the effect of water on the reaction rate. We have seen for the first time that water both inhibits and accelerates the oxidation of phenol at supercritical conditions depending upon the water concentration specified. It is unknown whether the observed minimum in the phenol destruction rate and the shape of the conversion vs water density curve are temperature-dependent. We have developed a new rate equation to account for both the inhibiting and accelerating effect of water on phenol SCWO. Further experimental work is required to determine water's effect at water concentrations greater than 15 M. On the basis of previous work, we ruled out interphase transport phenomena, pressure effects, and departure from plug-flow behavior as possible explanations of the inhibiting and accelerating effect of water on phenol SCWO. Furthermore, the present work with the most comprehensive and up to date DCKM available in the literature essentially rules out water's role as a reactant, product, and collision partner as explanations for water's effect.

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**Supporting Information Available:** Table with conditions used in and results from phenol SCWO experiments. This material is available free of charge via the Internet at <https://pubs.acs.org>.

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