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Abstraction of Hydrogen from Methanol by Hydroxyl Radical in Subcritical and Supercritical Water

Junbo Feng, Sudhir N. V. K. Aki, John E. Chateauneuf,*,† and Joan F. Brennecke*

Department of Chemical and Biomolecular Engineering, University of Notre Dame,
Notre Dame, Indiana 46556

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Reactions involving hydrogen abstraction by hydroxyl radical are an important class of reactions in subcritical and supercritical oxidation in water. However, the rates of individual hydrogen abstraction reactions are not available in the literature at the high temperatures and pressures necessary for near-critical or supercritical water oxidation. Here we present the measurements of the hydrogen abstraction from methanol by hydroxyl radical in water at temperatures from ambient to 390 °C and at 250 bar. •OH was generated by pulse radiolysis and the kinetics determined by monitoring the growth of the nitrohydroxycyclohexadienyl radical. The measured bimolecular rate constants show Arrhenius temperature dependence from ambient temperature through the supercritical region. The experimental rate constants for hydrogen abstraction from methanol by hydroxyl radical are significantly higher than the values used by a variety of researchers who have attempted to model oxidation of methanol in supercritical water using detailed chemical kinetics models.

Introduction

Supercritical water oxidation (SCWO) has been investigated extensively as a potential waste treatment technology.[1] Oxygen is totally miscible with water at supercritical conditions and the low temperatures (compared to incineration) suppress the formation of NO_x. Moreover, high destruction efficiencies have been achieved for a wide variety of compounds, including model organic compounds, typical organic wastes, chemical weapons, explosives, and propellants.[2−7]

There have been a number of attempts to model SCWO processes with elementary free radical reaction mechanisms.[8−21] A consistent result of the elementary reaction modeling of SCWO is that hydrogen abstraction by hydroxyl radical comprises a particularly important class of reactions.[8,9,11,13,22−27] These reactions are inevitably among the few rate-determining steps in SCWO.

A major question that remains is whether the rate constants for the important elementary reactions, taken from the combustion literature (gas-phase measurements) with some solvent corrections, really reflect the actual reaction rate constants under supercritical water (SCW) conditions. Therefore, our goal is to measure directly the bimolecular rate constant for hydrogen abstraction by hydroxyl radical from methanol, a well-studied model compound,[8,11,22,27−29] in water at conditions from ambient to supercritical. This will verify whether the rate constants used in the various detailed kinetics models for methanol destruction in SCW are correct.

Since direct measurement of hydroxyl radical concentration is difficult and the radicals formed by hydrogen abstraction from many compounds of interest in SCWO are difficult to detect, we have chosen to monitor the hydrogen abstraction from methanol by hydroxyl radical using competitive kinetics, where a hydroxyl radical addition reaction is the probe. We generate the hydroxyl radical by pulse radiolysis. Previously, we and others[30,31] have studied the addition reaction between nitrobenzene and hydroxyl radical in subcritical and supercritical water. Therefore, we have chosen to use nitrobenzene as the probe.

We present experimentally measured bimolecular rate constants of the hydrogen abstraction reaction of methanol by hydroxyl radical from ambient conditions to the supercritical region. The bimolecular rate constants follow simple Arrhenius behavior. In addition, we compare our measured values of the rate constants with those used for this reaction in the various elementary reaction models.[8,11,22,27,28]

Experimental Section

Materials. Nitrobenzene (Sigma−Aldrich, 99+%) was used as received. Methanol was used as received (Fisher Scientific, certified ACS). Water was filtered to 16 MΩ on a Millipore reagent water system at the Notre Dame Radiation Laboratory. All solutions were saturated with N_2O (Mittler, 99.0% minimum) before irradiation.

Experimental Apparatus and Procedures. The pulse radiolysis experiments were conducted using the Notre Dame Radiation Laboratory Titan Beta model TBS-8/16-1S electron linear accelerator. The details of this pulse radiolysis system and our modification of the system to accommodate the high-pressure, high-temperature optical cell have been described elsewhere.[31]

Experiments were performed with continuous flow of the single-phase aqueous solution (between 1 and 5 mL/min at ambient conditions) to prevent the buildup of unwanted byproducts. The high-pressure, high-temperature flow system has been described previously.[31] Since methanol is volatile, we were not able to degas the aqueous feed solution of methanol and nitrobenzene continuously with N_2O, as we had done previously with aqueous nitrobenzene solutions.[31] Instead, we thoroughly

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* Corresponding authors: for J.E.C., fax (269) 387-2909, e-mail chateauneuf@wmich.edu; for J.F.B., fax (574) 631-8366, e-mail jfb@nd.edu.

† Present address: Department of Chemistry, Western Michigan University, Kalamazoo, MI 49008.

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degassed an aqueous solution containing just nitrobenzene with N_2O. Then the necessary amount of an aqueous methanol solution was added to the degassed nitrobenzene/water solution and the feed container was sealed to prevent evaporation of the methanol and introduction of air. Sufficient stirring was used to dissolve the methanol solution in this feed solution, which was pumped continuously through the optical cell. Assuming that the aqueous methanol solution was fully saturated with air at ambient conditions,[32] the oxygen introduced with the methanol solution would only result in, at most, 20 μM oxygen in the final solutions used. This is because the methanol concentations needed for the quenching experiments were never greater than 3 mM. All the experimental data were obtained at a pressure of 250 bar, which ensured single-phase conditions at all temperatures investigated. This pressure is above the vapor pressure of water at subcritical temperatures, so at temperatures below 374 °C (the critical temperature of water) the experiments involved single-phase compressed liquids. Above the critical temperature, the solutions were single-phase supercritical fluids. The highest concentrations of nitrobenzene and methanol used were 7 and 3 mM, respectively, at ambient conditions. As a result, the physical properties of the aqueous solutions used were essentially those of pure water. Nitrobenzene and methanol are soluble in water at these low concentrations at both ambient and supercritical conditions.

The stability of nitrobenzene and methanol in subcritical and supercritical water was tested by flowing the aqueous feed solution through the reactor system, without radiolysis, and analyzing the effluent by gas chromatography. All conditions and procedures were identical to those used in the pulse radiolysis experiments. The decreases in the nitrobenzene and methanol concentrations were less than 3% and 4%, respectively, at all conditions studied (from room temperature to 390 °C and 250 bar). Thus, the rates of hydrolysis and thermal decomposition were sufficiently slow at temperatures below 390 °C that methanol and nitrobenzene can be considered stable for the short times (on the order of 1−2 min) that the solution is at elevated temperatures. This is consistent with our previous results for the stability of aqueous solutions of nitrobenzene alone.[31] Moreover, this is in agreement with previous reports of less than 5% conversion of nitrobenzene in water at 440 °C when the residence times are less than 3 min and there is no oxygen present[33] and less than 2% conversion of methanol in water at 300 °C when the residence times are 30 min and there is no oxygen present.[28]

Hydrogen Abstraction Reactions. Many saturated and unsaturated organic compounds react with hydroxyl radicals by hydrogen abstraction to form water and a carbon radical:[34]

$$RH + \bullet OH \rightarrow R\bullet + H_2O \tag{1}$$

In the present work, methanol has been chosen as the model compound to conduct the hydrogen abstraction reaction from ambient to supercritical conditions. There are two pathways for hydrogen abstraction from methanol by •OH:

$$CH_3OH + \bullet OH \xrightarrow{k_2} CH_3O\bullet + H_2O \tag{2}$$

$$CH_3OH + \bullet OH \xrightarrow{k_{bi}} CH_2\bullet OH + H_2O \tag{3}$$

Results from experiments where •OH is generated either by pulse radiolysis of water or by laser photolysis of hydrogen peroxide indicate that the proportion of α-carbon attack is almost 100% in methanol.[34] Therefore, reaction 3 is the dominant hydrogen abstraction pathway at ambient conditions. We assume that this is also the same at elevated temperatures, so the rate constant we measure for hydrogen abstraction of methanol by •OH is likely k_{bi}. However, this assumption is not vital since the detailed chemical kinetics models for SCWO of methanol assign the same or similar rate constants for both hydrogen abstraction reactions (2 and 3)[8,11,22] or only consider reaction 3.[27]

Analysis of Competition Kinetics. $CH_2\bullet OH$, the primary product from the hydrogen abstraction from methanol by hydroxyl radical, does not have accessible optical absorption at the ultraviolet−visible region. Technically, it is very difficult to monitor •OH at 250 nm because of its very low extinction coefficient, even at ambient conditions. It is even more challenging to monitor •OH at elevated temperatures, especially at supercritical conditions. Competitive kinetic techniques, i.e., kinetic probe techniques, are typically used to obviate this problem. The kinetic probe technique does not require knowledge of the reference solute bimolecular rate constant and has proven to be a powerful technique in both radiolytic and photolytic systems.[35] In fact, a rate constant of 8.3×10^8 M^{-1} s^{-1} [36] has been obtained for the reaction of $\bullet OH + CH_3OH$ (reaction 3) by monitoring the competitive growth kinetics of hydroxycyclohexadienyl radical ($C_6H_6\bullet OH$). Briefly, the kinetic probe technique requires that •OH react with a probe molecule, whose product can be detected easily and characterized. Here we choose nitrobenzene as the reference solute since we have studied hydroxyl radical addition to nitrobenzene (eq 4) in subcritical and supercritical water:[31]

$$C_6H_5NO_2 + \bullet OH \xrightarrow{k_4} \bullet OHC_6H_5NO_2 \tag{4}$$

In our previous work,[31] the bimolecular rate constants between nitrobenzene and •OH were measured from ambient conditions up to the supercritical region (390 °C, 250 bar). Details on the pulse radiolysis system and the generation of hydroxyl radical are also discussed in that paper.[31]

Although the bimolecular rate constants of the reaction between nitrobenzene and •OH are not necessary here to conduct the kinetic probe technique, it is very important to know that the product of reaction between nitrobenzene and •OH, nitrohydroxycyclohexadienyl radical, is detectable and has been characterized in the supercritical region. In the present study, varying amounts of methanol were added to the feed solution, while a particular probe concentration was maintained. The observed rate of disappearance of hydroxyl radical has three contributions: the desired reaction of •OH with methanol (eq 3), the reaction of •OH with the probe molecule (nitrobenzene) (eq 4), and any natural decay (k'):

$$\bullet OH \xrightarrow{k'} \text{solvent decay} \tag{5}$$

Thus, the rate of disappearance of •OH is shown in eq 6, and the pseudo-first-order rate constant (k_{obs}) for hydroxyl radical disappearance is shown in eq 7, where $k'' = k' + k_4[C_6H_5NO_2]$:

$$-\frac{d[\bullet OH]}{dt} = k'[\bullet OH] + k_4[C_6H_5NO_2][\bullet OH] + k_{bi}[CH_3OH][\bullet OH] \tag{6}$$

$$k_{obs} = k' + k_4[C_6H_5NO_2] + k_{bi}[CH_3OH] = k'' + k_{bi}[CH_3OH] \tag{7}$$

Using the growth in the absorbance of the product, $\bullet OHC_6H_5$-

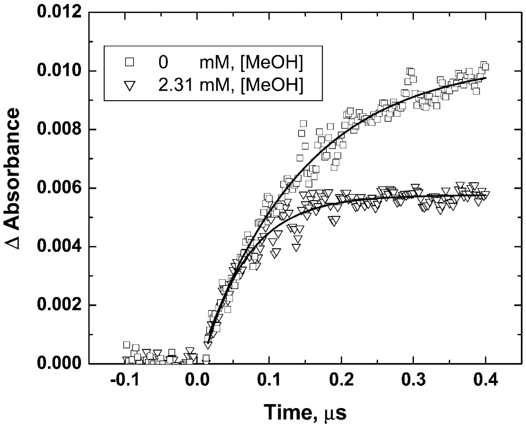

Figure 1. Typical growth profiles of nitrohydroxycyclohexadienyl radical at 405 nm at two different methanol concentrations at 200 °C and 250 bar; the solid lines indicate the best fits of the exponential growths.

NO_2, as a function of time, we are able to obtain the pseudo-first-order observed rate constants at each temperature and pressure using standard kinetic analysis.[37] Specifically, analysis of absorbance versus time traces was carried out with ORIGIN software (Version 6, Microcal Software Inc.) to fit the growth kinetics. Two typical growth profiles are shown in Figure 1 at two different methanol concentrations. The solid line shows the computer fit for the growth kinetics. The 95% confidence intervals on the growth rate constants were typically less than ±10%. As expected, the absorption of $\bullet OHC_6H_5NO_2$ reaches the maximum (equilibrium) value faster at the higher methanol concentration.

The desired bimolecular rate constant, k_{bi}, for this addition reaction at each state point was obtained from a linear plot of k_{obs} as a function of methanol concentration, as suggested by eq 7.

Results

Below we present the transient absorption spectra of nitrohydroxycyclohexadienyl radical from the reaction of nitrobenzene and •OH under the influence of the competitive hydrogen abstraction reaction of methanol by •OH. In addition, we will present the bimolecular rate constants obtained for the hydrogen abstraction reaction of methanol by •OH from ambient to 390 °C.

Transient Absorption Spectrum of Nitrohydroxycyclohexadienyl Radical, ($\bullet OHC_6H_5NO_2$). Previously, we found that the nitrohydroxycyclohexadienyl radical intermediate ($\bullet OHC_6H_5NO_2$) absorbs strongly at 410 nm at ambient conditions.[31] The absorption maximum shifted to shorter wavelengths (a blue shift) with increasing temperature, reaching 390 nm at supercritical conditions. Very similar trends were observed for nitrohydroxycyclohexadienyl radical in the methanol/water solutions used here. Typical normalized absorption spectra of $\bullet OHC_6H_5NO_2$ in a nitrobenzene/methanol/water solution are shown in Figure 2 at ambient conditions and at 300 °C. As shown in Figure 2, the absorption maximum shifts to shorter wavelengths with increasing temperature. These spectra are virtually identical to those obtained previously for nitrohydroxycyclohexadienyl radical in water from ambient to supercritical conditions.[31] The lack of any interference between nitrobenzene and methanol suggests that hydroxyl radical addition to nitrobenzene may be an appropriate probe for studying the hydrogen abstraction from methanol. All measurements were taken at the absorption maximum of nitrohydroxycyclohexadienyl radical for the temperature being investigated, to use the strongest signal available for the kinetics analysis.

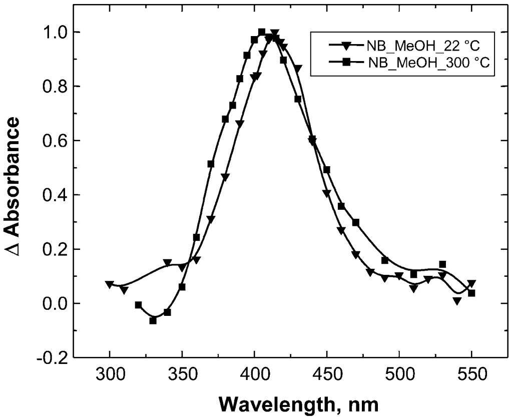

Figure 2. Transient absorption spectra of nitrohydroxycyclohexadienyl radical at 250 bar and $T = 22$ (▼) and 300 (■) °C in the nitrobenzene, methanol, and water mixture.

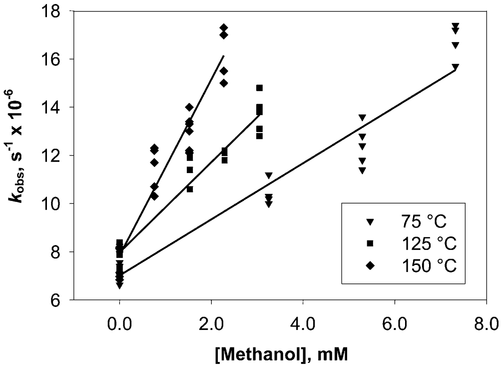

Figure 3. Effect of methanol concentration on the observed rate constant for the abstraction reaction of methanol by hydroxyl radical at 75, 125, and 150 °C.

Bimolecular Rate Constant. Measurements of the bimolecular rate constants for the hydrogen abstraction of methanol by •OH were conducted at 250 bar and temperatures from 22 to 390 °C. As mentioned above, the pressure of 250 bar was chosen to ensure that the bimolecular rate constants were measured at single-phase conditions throughout the entire temperature range. This resulted in a density decrease of pure water from 0.9971 g cm^{-3} at 25 °C and 1 bar to 0.2157 g cm^{-3} at 390 °C and 250 bar.[38] Mixture densities should be quite similar to these values since the highest nitrobenzene and methanol concentrations used were just 7 and 3 mM at ambient conditions, respectively. At the reaction conditions, the highest concentrations of nitrobenzene and methanol were even less since the solution density is lower at higher temperatures. Values of k_{bi} for the reaction of •OH with CH_3OH were obtained from the slopes of the k_{obs} versus CH_3OH concentration curves, according to eq 7. Examples are shown in Figure 3 for three representative temperatures. As seen in Figure 3, for a given temperature and pressure, multiple data were taken at each nitrobenzene concentration. The slopes, and therefore k_{bi}, increase with increasing temperature. All of these data were used to determine the k_{bi} values from the slopes of the quenching plots. The uncertainty in the experimental bimolecular rate constants was determined from the 95% confidence intervals on the slopes of the quenching plots. Thus, the uncertainty that we report results from the variability in the replicate experiments at a given concentration. The final results, the bimolecular rate constants, are shown in Figure 4, along with the uncertainty at

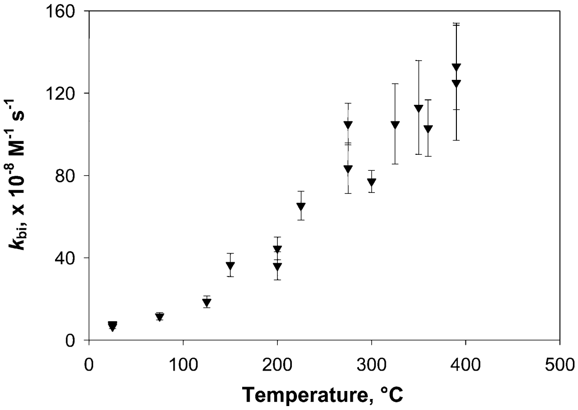

Figure 4. Effect of temperature on the bimolecular rate constant of the abstraction reaction of methanol by the hydroxyl radical from ambient conditions to 390 °C at a pressure of 250 bar.

each temperature indicated by error bars. It should be noted that at several temperatures (22, 200, 275, and 390 °C), we ran complete replicate sets of experiments with entirely different solutions and on entirely different days. As shown in Figure 4, the replicates are all entirely consistent within experimental uncertainty.

Bartels and co-workers[39] have recently suggested that in the radiolysis of water the yield of •H, which is generally considered to be negligible at ambient conditions in N_2O-saturated water,[34] might increase significantly with an increase in temperature at temperatures above 300 °C. If this is the case, there is the possibility that the bimolecular rate constants for hydrogen abstraction reaction from methanol by hydroxyl radical, determined as described above, could be in error. An increase in the yield of •H would have been unexpected since measurements and simulations at temperature up to 300 °C do not suggest this at all.[40] The production of •H is important because the adduct of •H with nitrobenzene absorbs at the same wavelength as the •OH adduct, which is the species being monitored. The additional reactions that would take place in the presence of •H are the reaction of $C_6H_5NO_2$ with •H to form $\bullet HC_6H_5NO_2$, the solvent decay of •H, and the hydrogen abstraction from CH_3OH by •H. However, detailed analysis of the rate equations shows that the presence of •H and $\bullet HC_6H_5NO_2$ will only affect the bimolecular rate constant for the reaction of •OH with methanol (determined as described in the Analysis of Competition Kinetics section above), if the reaction rate constant for the reaction of •H with methanol is comparable to the rate constant for the reaction of •H with nitrobenzene. At room temperatures the rate constant for •H reactivity with methanol is very small, 2.6×10^6 M^{-1} s^{-1},[41] compared to rate constant for the reaction of •H with nitrobenzene, 2.3×10^9 M^{-1} s^{-1}.[42] If this is also true at higher temperatures, then the pseudo-first-order rate constant for •H consumption (and subsequent $\bullet HC_6H_5NO_2$ formation) should *not* be a function of methanol concentration. So any component in the absorption that we measure that might come from $\bullet HC_6H_5NO_2$ should not depend on methanol concentration. As long as the rate constant for reaction of •H with methanol is small in comparison to the reaction of •H with nitrobenzene, then any contribution from the presence of •H should not affect the bimolecular rate constants for the reaction of •OH with methanol. This assumption was checked by force-fitting the growth curves at the higher temperatures with a double exponential. In all cases only one of the two exponential growth components depended on methanol concentration. Thus, we conclude that analyzing the data, as described in the section on Analysis of Competition Kinetics, will give correct values for the bimolecular rate constants for the hydrogen abstraction from methanol with hydroxyl radical.

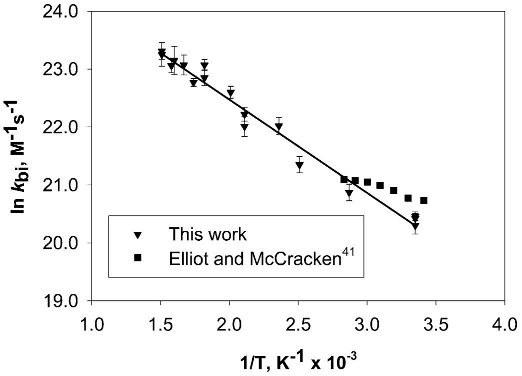

Figure 5. Arrhenius plot of the bimolecular rate constant vs 1/*T* obtained in this work in comparison to the results of Elliot and McCracken.[43]

TABLE 1: Comparison of the Arrhenius Parameters Used in Different Models for the Hydrogen Abstraction Reaction of Methanol by Hydroxyl Radical

	preexponential factor *A* (M^{-1} s^{-1})	activation energy E_a (kJ/mol)	n	temp range (°C)
present work	1.43×10^{11}	13.3	0	22−390
Elliot and McCracken[43]	1.05×10^{10}	4.8	0	20−80
Boock and Klein[28]	3.33×10^{8}	16.1	0	300
Webley and Tester[27]	5.01×10^{9}	5.5	0	450−550
Brock and Savage[8]	1.35×10^{10}	7.9	0	450−650
Alkam et al.[22]	17.7	−3.7	2.7	453−544
Dagaut et al.[11]	14.2	−3.7	2.65	450−550

Discussion

Arrhenius Behavior. Our measured bimolecular rate constants from 22 to 390 °C clearly followed Arrhenius behavior, as shown in Figure 5. Also shown on this graph are the data of Elliot and McCracken[43] taken at temperatures from 20 to 80 °C. Both sets of Arrhenius parameters are tabulated in Table 1. At 22 °C and 250 bar, our measured value of the bimolecular rate constant, $(7.32 \pm 0.75) \times 10^8$ M^{-1} s^{-1}, matches the literature values, 8.0×10^8 M^{-1} s^{-1} [36] and 8.3×10^8 M^{-1} s^{-1},[44] reasonably well. The literature values were taken at ambient temperature and pressure. As can be noted from Figure 5, there is some difference between our measured bimolecular rate constants and those of Elliot and McCracken, which were taken over a much smaller temperature range. Inherent uncertainty in the measurements (10−15% in our measurements) translates to a much larger uncertainty in activation energy when only a small temperature range is investigated (60 °C compared to the 368 °C range investigated here). Also, Elliot and McCracken's experiments[43] were carried out in N_2O-saturated 1 mol dm^{-3} KOH solutions, as compared to pure water in the current investigation. Unfortunately, we are aware of no other experimental results at elevated temperature for this reaction with which we can compare the current work.

Comparions with Detailed Chemical Kinetics Model Using Elementary Reaction Steps. Understanding the kinetic mechanism will be a key component in designing, controlling, and optimizing the SCWO reactors. Toward this end, numerous researchers have used detailed chemical kinetics models and a variety of lumping strategies to describe overall destruction efficiencies of various organic compounds.[4,8−21,28,29,45] Hydrogen abstraction by •OH is frequently identified as an important class

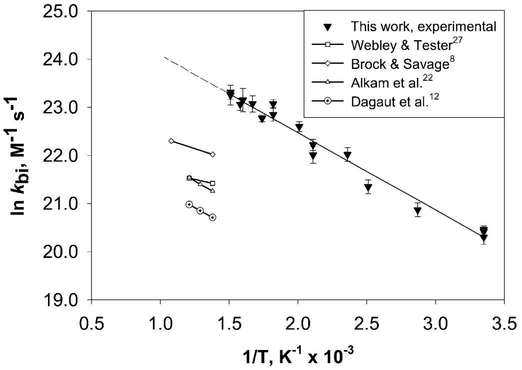

Figure 6. Arrhenius plot of the bimolecular rate constant obtained in this work in comparison to different models; our bimolecular rate constants were extrapolated to 700 °C by use of experimentally obtained Arrhenius parameters, as indicated by the dashed line.

of reactions in SCWO, and this is certainly the case for methanol destruction.[8,11,22,27] Thus, we compare the measured values for the rate constants for the hydrogen abstraction from methanol by hydroxyl radical with those used in the various kinetic models of the oxidation of methanol in supercritical water.

Four different research groups have studied the destruction of methanol during SCWO and modeled the process with a series of detailed elementary chemical reactions.[8,11,22,27] In all cases, the hydrogen abstraction reaction from methanol by •OH is modeled with an Arrhenius fit of the form

$$k = AT^{n} \exp\left(-\frac{E_{a}}{RT}\right) \tag{8}$$

The SCWO studies were done at temperatures higher than those investigated in the current study, which was limited by poor signal quality. Thus, some extrapolation will be required for the comparison. All of the SCWO experiments and modeling were done at pressures between 240 and 250 bar, which is similar to the 250 bar chosen for the current investigations.

The four detailed chemical kinetics models for methanol destruction by SCWO contain 56−184 elementary reactions. They use a wide variety of techniques to account for solution nonideality and all identify hydrogen abstraction from methanol by hydroxyl radical as a key reaction. The Arrhenius parameters used for the hydrogen abstraction from methanol by hydroxyl radical in those modeling studies are shown in Table 1, along with those determined experimentally for the same reaction in this work. Webley and Tester[27] used an activation energy less than half that obtained here, and their preexponential factor was only about a third of that measured here. The effect is seen more clearly in Figure 6, which shows our data on an Arrhenius plot, as well as the rate constants predicted by the model of Webley and Tester over the temperature range they investigated. Also shown is the Arrhenius fit of our data (solid line), extrapolated to slightly higher temperatures (dashed line). Clearly, the rate constants used in the detailed chemical kinetics model of Webley and Tester are significantly lower than those measured here. Also shown in Figure 6 are the rate constants used by Brock and Savage,[8] Alkam et al.,[22] and Dagaut et al.[12] In all cases, the bimolecular rate constants used in the models are significantly lower than those measured in this study. The Arrhenius parameters for these other models are also shown in Table 1. As with the Webley and Tester rate equation,[27] the activation energy and preexponential factor used by Brock and Savage[8] are significantly lower than the values found here. It is more difficult to compare the Arrhenius parameters used by Alkam et al.[22] and Dagaut et al.,[11] since they included an explicit temperature dependence in the expression. Nonetheless, it is clear from Figure 6 that their rate constants are quite low as well. In fact, the rate constants used by all four research groups at supercritical temperatures are not much higher than the well-known values at room temperature (see Figure 6).

Klein and co-workers[28,29,45] have used a somewhat different strategy in modeling oxidation of organic compounds in supercritical water. They use a lumping strategy that assumes every elementary reaction step belongs to one of eight reaction families, one of which is hydrogen abstraction by radicals. Fitting the model to the experimental data, these researchers obtain a single preexponential factor for each reaction family and use Evans−Polanyi relationships to correlate the activation energies with heats of reaction. Their Arrhenius parameters for hydrogen abstraction from methanol by hydroxyl radical are shown in Table 1. While the activation energy is similar to that obtained in this work, the preexponential factor is several orders of magnitude lower, yielding correspondingly low rate constants (1.14×10^{7} M^{-1} s^{-1} at 300 °C, compared to 1.13×10^{10} M^{-1} s^{-1}, which is the value that would be expected from the Arrhenius fit to our data).

Conclusions

The bimolecular rate constants for the hydrogen abstraction reaction of methanol by •OH were measured in water at temperatures between ambient and 390 °C and at a pressure of 250 bar. •OH was generated by pulse radiolysis and the kinetics determined by monitoring the growth of the nitrohydroxycyclohexadienyl radical. These are among the first direct measurements of the bimolecular rate constant of hydrogen abstraction reaction by hydroxyl radical in supercritical water. Hydrogen abstraction reaction by hydroxyl radical is one of a few important reactions in supercritical water oxidation.

The measured bimolecular rate constants showed Arrhenius temperature dependence from ambient to the supercritical region. The Arrhenius parameters and bimolecular rate constants obtained in the present work were compared to previous modeling efforts that use free radical reaction mechanism models of the SCWO of methanol. In all cases, the bimolecular rate constants for hydrogen abstraction from methanol by hydroxyl radical measured here (extrapolated to the slightly higher temperatures studied by the other researchers where necessary) are several orders of magnitude higher than those predicted by the models used by the other researchers. Since hydrogen abstraction by hydroxyl radical has been identified as a key reaction in SCWO, this may explain the mixed success that has been observed when the free radical mechanism models were used for the SCWO process. This suggests that the attempts used in the detailed kinetic mechanism models to correct for the lower temperature and nonideal solution conditions present at slightly supercritical conditions are likely not adequate, and the uncertainty this introduces into those models should be fully recognized when their utility is evaluated.

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