

Experimental Determination of Hydroxyl Radical Reactivity in Supercritical Water Using Pulse Radiolysis

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Complete mineralization of hazardous organic compounds to innocuous products can be achieved using supercritical water oxidation (SCWO). At typical SCWO process conditions (500 – 650 °C), free radical chemistry has been shown to be the dominant reaction path. Detailed Chemical Kinetic Mechanisms (DCKM), consisting of elementary free-radical reactions, have been used to model the oxidation of a number of organics in supercritical water, but with mixed success. Thus, there is the need for experimental verification of the rates of some of the elementary reactions that play a key role in the destruction of organic species in supercritical water. Using pulse radiolysis, we have measured the reactivity of hydroxyl radicals, which have been identified as one of the primary oxidizing species in supercritical water. In particular, we have measured the bimolecular rate constants (k_{bi}) of the hydrogen abstraction reaction between hydroxyl radical and methanol. In DCKM modeling of methanol destruction in supercritical water, this reaction has been shown to be one of the most important elementary steps. We find that the hydroxyl abstraction reaction follows Arrhenius behavior from ambient to 390 °C, but the bimolecular rate constants, k_{bi} , in the supercritical region are significantly greater than the values used in the DCKM modeling.

INTRODUCTION

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

A number of researchers have attempted to model SCWO processes with elementary free radical reaction mechanisms (e.g., [2,3]). Researchers find that hydrogen abstraction reactions by hydroxyl radical are a particularly important class of reactions [2,3]. These reactions are inevitably among the few rate determining steps in SCWO.

Here we seek to determine if 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. Thus, we measure directly the bimolecular rate constant for hydrogen abstraction by hydroxyl radical from methanol, a well-studied model compound [2-7], in water at conditions from ambient to supercritical.

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 monitor the hydrogen abstraction from methanol by hydroxyl radical using competitive kinetics, where hydroxyl radical addition to nitrobenzene is the probe

reaction. We generate the hydroxyl radical by pulse radiolysis. Previously, we and others [8,9] have studied the addition reaction between nitrobenzene and hydroxyl radical in subcritical and supercritical water.

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.

EXPERIMENTAL SECTION

I – MATERIALS, APPARATUS AND PROCEDURES

Nitrobenzene (Sigma-Aldrich, 99 + %) and methanol (Fisher Scientific, Certified A.C.S) were used as received. Water was filtered to 16 MΩ using a Millipore Reagent Water System at Notre Dame Radiation Laboratory. All solutions were saturated with N₂O (Mittler, 99.0 %, minimum) before irradiation.

The pulse radiolysis experiments were done with 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 [9].

Experiments were performed with continuous flow of the single phase aqueous solution to prevent the buildup of unwanted by products; this system has been described elsewhere [9]. One modification is that the feed solution was not degassed with N₂O continuously since methanol is so volatile. Rather, the methanol was added to the degassed solution and the feed vessel sealed. All the experimental data were obtained at a pressure of 250 bar, which ensures single phase operation. The highest concentrations of nitrobenzene and methanol used were just 7 and 3 mM, respectively, at ambient conditions so the physical properties of the aqueous solutions 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. These tests assured that there was no significant thermal degradation of either compound in the short residence times (on the order of 1-2 minutes) required for the experiments.

II – ANALYSIS OF COMPETITION KINETICS

Hydroxyl radical reacts with methanol to form water, as indicated by equation 1.



None of the species in reaction (1) has any significant absorbance in the ultraviolet-visible region. Therefore, we use competitive kinetic techniques, which require that $\cdot OH$ reactivity with a probe molecule, whose product can be detected easily, to determine the k_1 . Here we choose nitrobenzene as the reference solute since we have studied hydroxyl radical addition to nitrobenzene to form the easily detected hydroxycyclohexadienyl radical (equation 2) in subcritical and supercritical water [9].



Nitrohydroxycyclohexadienyl radical, $\cdot OHC_6H_5NO_2$, is detectable and has been characterized in subcritical and supercritical water [9]. In the current study, varying amounts of methanol

were added to the feed solution, while maintaining a particular probe concentration. The observed rate of disappearance of hydroxyl radical has three contributions: the desired reaction of $\cdot OH$ with methanol (equation 1), the reaction of $\cdot OH$ with the probe molecule (nitrobenzene) (equation 2), and any natural decay (k') (equation 3).



Thus, the rate of disappearance of $\cdot OH$ is shown in equation (4), and the pseudo-first-order rate constant (k_{obs}) for hydroxyl radical disappearance is shown in equation (5), where $k'' = k' + k_2[C_6H_5NO_2]$.

$$-\frac{d[\cdot OH]}{dt} = k'[\cdot OH] + k_2[C_6H_5NO_2][\cdot OH] + k_1[CH_3OH][\cdot OH] \quad (4)$$

$$k_{obs} = k' + k_2[C_6H_5NO_2] + k_1[CH_3OH] = k'' + k_1[CH_3OH] \quad (5)$$

Using the growth in the absorbance of the product, $\cdot OHC_6H_5NO_2$, 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 of the growth kinetics. The desired bimolecular rate constant, k_1 , 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 equation 5.

RESULTS AND DISCUSSION

Measurements of the bimolecular rate constants for the hydrogen abstraction of methanol by $\cdot OH$ were conducted at 250 bar and temperatures from 22 to 390 °C. 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. Mixture densities should be quite similar to these values since the highest nitrobenzene and methanol concentration used was just 7 and 3 mM at ambient

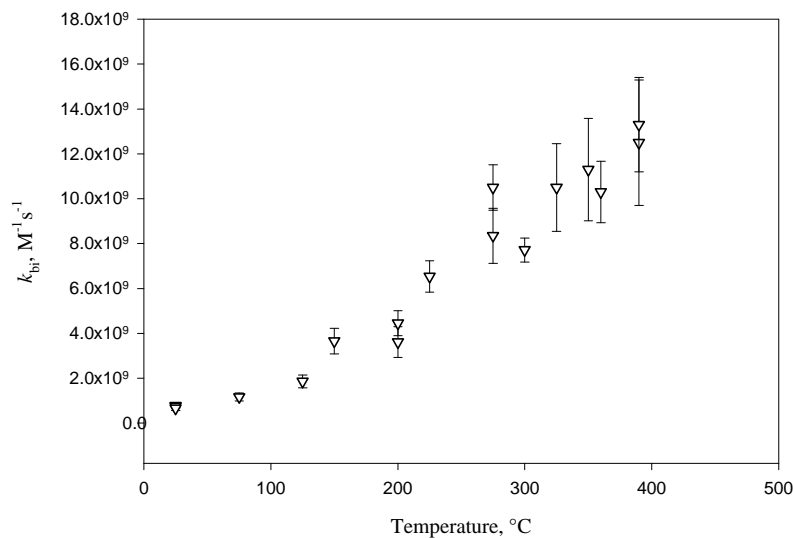


Figure 1: The effect of temperature on the bimolecular rate constant of the abstraction reaction of methanol by the hydroxyl radical at 250 bar.

conditions, respectively. Values of k_1 for the reaction of $\bullet\text{OH}$ with CH_3OH were obtained from the slopes of the k_{obs} versus CH_3OH concentration curves, according to equation 5. For a given temperature and pressure multiple data were taken at each nitrobenzene concentration. All data were used to determine the k_1 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. The final results, the bimolecular rate constants (k_1 is labeled as k_{bi} in the figures), are shown in Figure 1, along with the uncertainty at each temperature indicated by error bars. Our measured bimolecular rate constants from 22 to 390 °C clearly followed Arrhenius behavior, as shown in Figure 2.

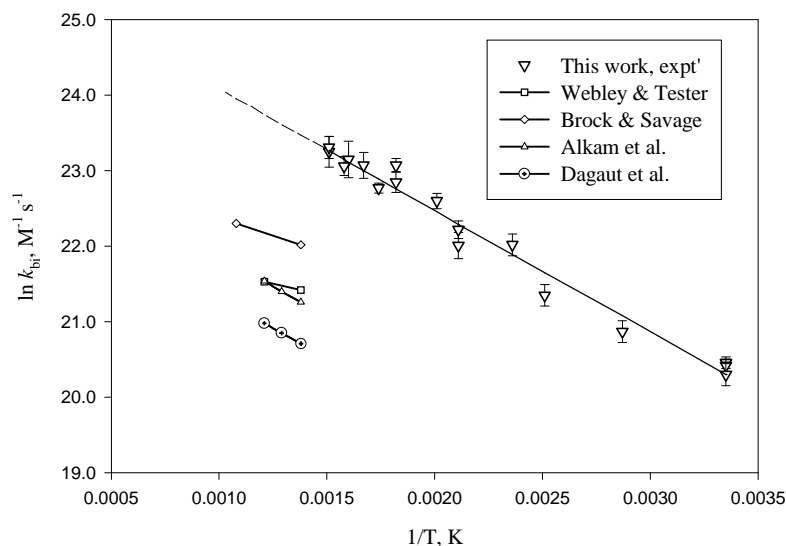


Figure 2: Arrhenius plot of the bimolecular rate constants for hydrogen abstraction from methanol in water, compared to values used in various modeling efforts (see text).

Design, control and optimization of SCWO reactors requires an understanding of the kinetic mechanism. Therefore, numerous researchers have used detailed chemical kinetics models and a variety of lumping strategies to describe overall destruction efficiencies of various organic compounds [2-7]. As mentioned above, hydrogen abstraction by $\bullet\text{OH}$ is frequently identified as an important class of reactions in SCWO, and this is certainly the case for methanol destruction [2-7]. Thus, we compare the measured values for the rate constants of 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 [2-7]. These researchers model the hydrogen abstraction reaction from methanol by $\bullet\text{OH}$ with an Arrhenius fit of the form:

$$k = A T^n \exp\left(-\frac{Ea}{RT}\right) \quad (6)$$

The SCWO studies were done at temperatures higher than those investigated in the current study. We were limited by poor signal quality at higher temperatures so some extrapolation was necessary. 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.

Each of the four detailed chemical kinetics models for methanol destruction by SCWO contain more than 56 elementary reactions. A wide variety of techniques are used to account for solution nonideality but 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 [7] used an activation energy less than half that obtained here, and their pre-exponential factor was only about a third of that measured here. This is shown clearly in Figure 2, which gives our data on an Arrhenius plot, as well as the rate constants predicted by the model of Webley and Tester [7] 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 [7] are significantly lower than those measured here. Also shown in Figure 2 are the rate constants used by Brock and Savage [2], Alkam et al. [4], and Dagaut et al. [3]. 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. 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 2).

Table 1: Comparison of the Arrhenius parameters for the hydrogen abstraction reaction of methanol by hydroxyl radical.

| | Pre-exponential factor, A, $M^{-1} s^{-1}$ | Activation Energy, E_a , kJ/mol | n | Temperature Range, °C |
|----------------------------|--|-----------------------------------|------|-----------------------|
| Current Work | 1.43E+11 | 13.3 | 0 | 22 – 390 |
| Elliot and McCracken, [10] | 1.05E+10 | 4.8 | 0 | 20 – 80 |
| Boock and Klein, [6] | 3.33E+08 | 16.1 | 0 | 300 |
| Webley and Tester, [7] | 5.01E+09 | 5.5 | 0 | 450 - 550 |
| Brock and Savage, [2] | 1.35E+10 | 7.9 | 0 | 450 - 650 |
| Alkam et al., [4] | 17.7 | -3.7 | 2.7 | 453 - 544 |
| Dagaut et al., [3] | 14.2 | -3.7 | 2.65 | 450 - 550 |

Klein and coworkers have used a lumping strategy that assumes every elementary reaction step belong to one of eight reaction families, one of which is hydrogen abstraction by radicals, in modeling oxidation of organic compounds in supercritical water [5,6]. Fitting the model to the experimental data, these researchers obtain a single pre-exponential 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, as well. While their activation energy is similar to

that obtained in this work, the pre-exponential factor is several orders of magnitude lower, yielding correspondingly low rate constants ($1.14 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ at 300 °C, compared to $1.13 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$, 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 $\bullet\text{OH}$ were measured in water at temperatures between ambient and 390 °C and at a pressure of 250 bar. $\bullet\text{OH}$ was generated using pulse radiolysis and the kinetics determined by monitoring the growth of the nitrohydroxycyclohexadienyl radical. The measured bimolecular rate constants showed Arrhenius temperature dependence from ambient to the supercritical region. 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 using the free radical mechanism models 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 this introduces significant uncertainty into those models.

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