Temperature Dependence of the Reaction Between the Hydroxyl Radical and Organic Matter

G. McKay, M.M. Dong, J. Kleinman, S.P. Mezyk, and F.L. Rosario-Ortiz

Abstract The temperature-dependent bimolecular rate constants for the reaction of the hydroxyl radical (HO•) with organic matter (OM) ($k_{\mathrm{OM-HO\bullet}}$) have been measured for three natural organic matter (NOM) isolates and three bulk effluent organic matter (EfOM) samples using electron pulse radiolysis and thiocyanate competition kinetics. The range of values for the room temperature $k_{\mathrm{OM-HO\bullet}}$ was $1.21–9.37 \times 10^8\ \mathrm{M_C}^{-1}\ \mathrm{s}^{-1}$, with NOM isolates generally reacting slower than EfOM samples. The NOM isolates had an average apparent activation energy of 19.8 kJ mol^{-1}, while the EfOM samples had an average value slightly lower (14.3 kJ mol^{-1}), although one NOM isolate (Elliot Soil Humic Acid, 29.9 kJ mol^{-1}) was a factor of 2 times greater than other samples studied. These apparent activation energies are the first determined for OM and HO•, and the Arrhenius plots obtained for NOM isolates (lowest $R^2 > 0.993$) suggest that no significant structural changes are occurring over the temperature range 8–41°C. In contrast, the greater scatter (lowest $R^2 > 0.903$) observed for the EfOM samples suggests that some structural changes may be occurring. These results provide a deeper fundamental understanding of the reaction between OM and HO• and will be useful in quantifying HO• reactions in natural and engineered systems.

Keywords Hydroxyl radical • Organic matter • Reactivity • Temperature dependence

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Introduction

The reactions between the hydroxyl radical (HO•) and organic compounds in water are of great importance in natural and engineered systems. For example, HO• is one of the most important reactive species in the indirect photolytic decay of organic contaminants in natural systems. In these photolytic processes, HO• is formed via photolysis of nitrate, the Fenton reaction, and the absorption of light by organic matter (Vione et al. 2006). The HO• radical is also the main reactive species in the application of advanced oxidation processes (AOPs) for treatment of water and wastewater. The source of HO• in these systems depends on the specific technology being used. Oxidizing AOPs typically generate HO• and include O_3/UV, O_3/H_2O_2, TiO_2/hν, ZnO/hν, H_2O_2/UV, pulsed UV, and photo-Fentons, while other processes such as electron-beam irradiation, supercritical water, electrohydraulic cavitation, and sonolysis generate a mixture of the hydroxyl radicals, hydrated electrons (e^-_{aq}), and hydrogen atoms (H•).

The objective of this study was to evaluate the temperature dependence of the reaction between HO• and OM. Three natural organic matter (NOM) isolates, including Elliot soil humic acid (ESHA), Pony Lake fulvic acid (PLFA), and Suwannee River standard fulvic acid I (SRFA), and three effluent organic matter (EfOM) samples were examined in this work. The OM was characterized by size exclusion chromatography (SEC). From the temperature-dependent kinetic data, activation energies (Ea) and entropic parameter ($\Delta S^{\circ\ddagger}$) were estimated.

Materials and Methods

The three NOM samples were prepared by dissolving IHSS standards in 5 mM K_2HPO_4 buffer, adjusted to pH 7.0 using $HClO_4$ or NaOH (5 M). Three EfOM samples (samples A–C) were collected from a series of membrane bioreactor pilot reactors operating at different retention times. Upon collection, these wastewater samples were filtered through 0.7-μm glass fiber filters to remove particulate matter. All samples studied were shipped overnight to the Radiation Laboratory, University of Notre Dame, in ice-chilled coolers and kept cold until analysis.

Details of the kinetics experiments are shown elsewhere (Rosario-Ortiz et al. 2008).

Results and Discussion

Rate Constant Measurements. HO• was produced using pulse radiolysis. The radiolysis of pure water or low-concentration solutions produces a suite of radicals and other species according to the stoichiometry (Buxton et al. 1988):

$$\mathrm{H_2O} \ \backslash/\backslash/\backslash/ - >[0.28]\ \mathrm{HO\bullet} + [0.06]\ \bullet\mathrm{H} + [0.27]\ \mathrm{e} -_{\mathrm{aq}} + [0.05]\ \mathrm{H_2} + [0.07]\ \mathrm{H_2O_2} + [0.27]\ \mathrm{H^+} \quad (1)$$

where the bracketed numbers are G-values (yields in μmol/J) for each species produced. Prior to the kinetic experiments, samples were pre-saturated with N_2O in order to quantitatively convert the $e^-{}_{aq}$ and •H radicals to HO• (Buxton et al. 1988).

Temperature-dependent rate constants were plotted according to the Arrhenius equation, which allowed for determination of the activation energy:

$$\ln(k) = -\frac{E_a}{R} + \ln(A) \quad (2)$$

This relationship is well established for reactions of HO• with compounds of lower molecular weight than OM. Based on the fitted pre-exponential factor terms, the change in entropy between the reactants and transition state ($\Delta S^{\circ\ddagger}$) can be obtained via the equation

$$A = \frac{k_B T}{h} e^{\Delta S^{\circ\ddagger}\neq/\mathrm{R}} \quad (3)$$

where k_B is Boltzman's constant and h is Planck's constant. The usefulness of $\Delta S^{\circ\ddagger}$ is in its ability to compare the change in entropy due to reactant organization (necessary for a reaction to occur) and the change in entropy due to any disaggregation of OM that occurs at the transition state.

Temperature Dependence for OM Isolates. Room temperature $k_{\mathrm{NOM-HO\bullet}}$ values for ESHA, SRFA, and PLFA were 1.21, 2.06, and 6.90 $M_C{}^{-1}$ s^{-1}, respectively.

Figure 1 presents Arrhenius plots for ESHA, SRFA, and PLFA. These samples exhibited excellent linearity ($R^2 > 0.993$) in the range of temperatures studied, indicating that varying the temperature did not result in significant configurational changes to the structure of the NOM isolates. It has been hypothesized that the $k_{\mathrm{OM-HO\bullet}}$ values are impacted by OM's three-dimensional configuration. For example, if not all carbon atoms are accessible to HO• due to the formation of a macrostructure, then the average $k_{\mathrm{OM-HO\bullet}}$ in these units would be lowered. However, the lack of deviation from Arrhenius behavior indicates that as the temperature changed, no significant configurational changes occurred, which is consistent with current theories that suggest that the interactions between OM building blocks are quite strong. Any OM disaggregation, which would present more surface area per carbon available to HO•, would be expected to exhibit an increased reactivity with increasing temperature. Table 1 presents the analogous Arrhenius parameters for all NOM isolates. The activation energies ranged from 15.18 to 29.93 kJ mol^{-1}, with PLFA and SRFA about a factor of two less than that of ESHA. This difference was interesting, considering that ESHA has the greatest aromatic carbon content, has the highest average molecular weight (AMW) of the NOM isolates, and is a humic acid, while SRFA and PLFA are fulvic acids. If some disaggregation of ESHA occurs,

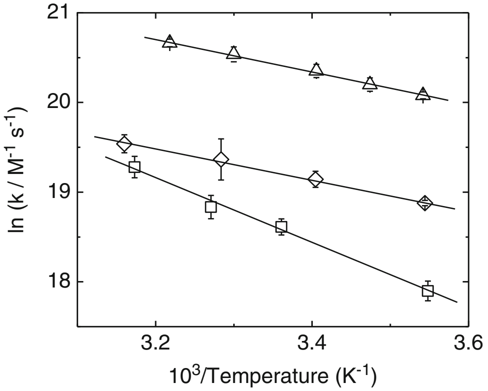

Fig. 1 Arrhenius plots for ESHA (□), SRFA (◇), and PLFA (Δ) at pH 7.1. *Solid lines* correspond to a weighted linear corresponding to activation energies of 29.93, 14.42, and 15.18 kJ mol^{-1}

Table 1 Arrhenius activation energies and thermodynamic data for selected NOM and EfOM samples

Sample	E_a (kJ mol^{-1})	$\Delta S^{\circ\neq}$ (J K^{-1} mol^{-1})
ESHA	29.93 ± 1.73	+0.21 ± 0.01
SRFA	14.42 ± 0.67	−5.43 ± 0.06
PLFA	15.18 ± 0.49	−3.91 ± 0.03
Sample A	15.16 ± 1.32	−3.85 ± 0.08
Sample B	10.71 ± 2.02	−5.42 ± 0.18
Sample C	16.95 ± 1.67	−3.14 ± 0.08

perhaps it does so more than PLFA and SRFA, resulting in greater activation energy; however, any increased reactivity due to disaggregation has not resulted in a deviation from Arrhenius behavior.

Temperature Dependence for EfOM. The room temperature $k_{\text{EfOM}-\text{HO}\bullet}$ values for Samples A, B, and C were 7.39, 9.37, and 6.79 M_C^{-1} s^{-1}, respectively. On average, the values for $k_{\text{EfOM}-\text{HO}\bullet}$ were greater than $k_{\text{NOM-HO}\bullet}$, which is consistent with previous findings.

The corresponding Arrhenius activation energies for EfOM ranged from 10.71 to 16.95 kJ mol^{-1} as shown in Table 1.

In general, the activation energies for the EfOM samples had larger standard deviations than for the NOM isolates, suggesting that EfOM could be disaggregating at higher temperatures (and aggregating at low temperatures), which might be expected when considering that EfOM is relatively more heterogeneous than NOM isolates. We have also calculated transition-state entropies ($\Delta S^{\circ\ddagger}$) based on the fitted pre-exponential factors (Table 1). Negative $\Delta S^{\circ\ddagger}$ values would be expected based on the more ordered transition state as compared to the reactants, and the values of this study for most of the OM samples ranged from −3.91 to −5.43 J mol^{-1}K^{-1}. In contrast, the single positive value for ESHA (0.21 J mol^{-1} K^{-1}) suggests that some additional entropic increase occurs in the HO• oxidation. Although hypothetical, we attribute this additional increase to ESHA having a more aggregated structure than PLFA or SRFA. This could be due to the higher molecular weight and greater aromatic character of ESHA. Higher molecular weight, combined with strong intermolecular forces between aromatic moieties, might produce a more ordered reactants' structure for ESHA, therefore resulting in a greater $\Delta S^{\circ\ddagger}$, assuming a similar transition state for NOM reactions with HO•.

Conclusions

In conclusion, activation energy measurements can be made for OM. NOM isolate's Arrhenius plots exhibited better linearity than EfOM's, suggesting that EfOM could be disaggregating as temperature increases, while NOM isolates are remaining relatively intact with increasing temperature. In addition, the positive $\Delta S^{\circ\ddagger}$ value for ESHA suggests that it has a more organized structure than other NOM isolates. Future research will continue to explore the temperature dependence of other NOM isolates.

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