Bimolecular Rate Constants between Levoglucosan and Hydroxyl Radical: Effects of pH and Temperature

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Bimolecular rate constants for levoglucosan and hydroxyl radical were determined at various temperatures and pHs using competitive kinetics. Hydrogen peroxide was used as the radical source, and benzoic acid was used as a competitive radical scavenger. The rate constants at 20 °C were 7.9×10^8 to $2.4 \times 10^9 \, \text{M}^{-1} \, \text{s}^{-1}$ between pH 3.0 and 8.0 and showed little variation as a function of temperature between 10 and 40 °C.

The hydroxyl radical ($^\bullet$OH) is a potent oxidant in aquatic environments. The lifetimes of many organic compounds are controlled by their relative reactivity with $^\bullet$OH.[1] The bimolecular rate constant between any given compound and $^\bullet$OH ($k_{\text{Org,OH}}$), and the steady-state concentration of $^\bullet$OH ($[^\bullet\text{OH}]_{\text{ss}}$) determine the reactivity, as shown below.

$$^\bullet\text{OH} + \text{Organic compound} \xrightarrow{k_{\text{Org,OH}}} \text{Product} \qquad (1)$$
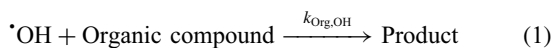
$$\text{Lifetime of organic compound} \quad 1/(k_{\text{Org,OH}}[^\bullet\text{OH}]_{\text{ss}}) \qquad (2)$$

To better estimate the lifetime of a given compound in nature, it is necessary to determine the rate constants for its reaction with $^\bullet$OH in different aquatic environments. For example, the pH of seawater is about 8.0, whereas cloud waters affected by anthropogenic activities can have pH values as low as 2.9.[2] Pristine rain water at equilibrium with current CO_2 levels of 380 ppm has a calculated pH of 5.6. The temperature of aquatic environments can also range from below freezing to boiling.

Levoglucosan (1,6-anhydro-β-D-glucose) is one of the main polar chemicals emitted into the atmosphere during biomass combustion. Levoglucosan is reported to be relatively stable in the environment and thus is often used as a tracer for biomass burning.[3,4] For example, Kundu et al.[5] used levoglucosan as a tracer to study aerosols during an intensive biomass-burning period in Brazil and found that the ratios between dicarboxylic acids and levoglucosan concentrations were higher during the daytime than at night, suggesting that photochemical reactions are important for dicarboxylic acid formation.

The current study determined the bimolecular rate constants between levoglucosan and $^\bullet$OH ($k_{\text{Lev+OH}}$) at various pH and temperature conditions, using competitive kinetics. In this technique, aqueous reactant solutions were illuminated with 313-nm light.[6] The solutions contained 100 µM levoglucosan, various concentrations of benzoic acid (BA; including both C_6H_5COOH and $C_6H_5COO^-$) as a competitive scavenger of $^\bullet$OH, and 100 µM hydrogen peroxide as a source of $^\bullet$OH. The solution pH was adjusted to 3.0, 5.5, or 8.0 using an appropriate phosphate buffer solution. Phosphate buffers were chosen

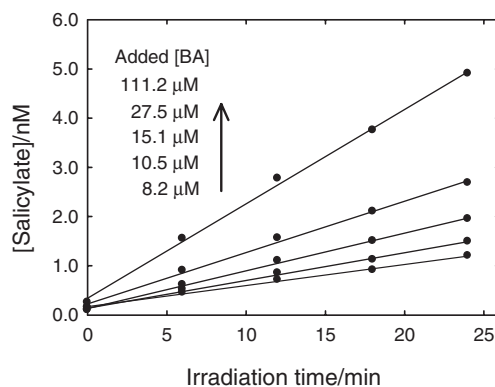**Figure 1.** Examples of salicylate formation with different initial concentrations of BA at pH 5.5 and 20 °C, with [Levoglucosan] = 100 µM and [H_2O_2] = 100 µM.

because the reaction rate of $^\bullet$OH with phosphate is much slower than those with levoglucosan and BA. The concentration of levoglucosan in the initial reaction mixture was held constant, while the BA concentration was varied. The rate of formation of salicylate, one of the products of $^\bullet$OH and BA, was a function of the fraction of $^\bullet$OH reacting with BA, which in turn was a function of BA concentration. Salicylate concentrations were determined by HPLC using a fluorescence detector (excitation at 320 nm, emission at 400 nm).[6] Calibration curves were made on each day of the experiments by adding standard sodium salicylate solution to pure water. Figure 1 shows examples of the salicylate formation kinetics observed with this technique. Formation rates of salicylate were calculated using a least-squares fit of the data in Figure 1, which show an increase in salicylate formation with increasing concentrations of BA.

With our illumination system, the $^\bullet$OH formation rate from the photolysis of 100 µM H_2O_2 is estimated to be about $8 \times 10^{-11} \, \text{M} \, \text{s}^{-1}$. Since we illuminated the solutions up to 24 min only, the total $^\bullet$OH formed in 24 min was about $1.15 \times 10^{-7} \, \text{M}$. Even if all the total $^\bullet$OH reacted with levoglucosan, only 0.1% of 100 µM levoglucosan would have been destroyed. Therefore, the initial concentration of 100 µM levoglucosan can be assumed to remain constant during the 24-min illumination period. Note that levoglucosan does not absorb 313-nm light; consequently, no direct photolysis occurred under these experimental conditions. In addition, no salicylate was detected after irradiating a 100 µM levoglucosan solution at 313 nm for 24 min.

As the bimolecular rate constants of BA were also affected by the temperature and pH of the reaction mixture, rate constants

were calculated at different temperatures and pHs using previously published data.[7] The bimolecular rate constants reported by Ashton et al.[7] for reactions of C_6H_5COOH (BAH) and $C_6H_5COO^-$ (BA$^-$) with $^{\bullet}OH$ were relatively unaffected by temperature between 20 and 200 °C. Considering that the acid dissociation constant (pK_a) of BAH is 4.2, the mole fractions of BAH and its conjugate base BA$^-$ at a specific pH were calculated and taken into account in the rate constant calculation shown below.

$$k_{BA+OH} = (\alpha_{BAH})(k_{BAH+OH}) + (\alpha_{BA^-})(k_{BA^-+OH}) \qquad (3)$$

$$\alpha_{BAH} = [H^+]/(K_a + [H^+]) \qquad (4)$$

$$\alpha_{BA^-} = 1 - \alpha_{BAH} \qquad (5)$$

where α_{BA} and α_{BA^-} are the mole fractions of BAH and BA$^-$, respectively, at a given pH. A scavenging rate constant, which represents the product of the bimolecular rate constant and the concentration of levoglucosan, k_{Lev+OH}[Levoglucosan], was determined from the relationship between [BA] and the formation rate of salicylate. Thus, k_{Lev+OH} could be calculated at a given levoglucosan concentration. The Supporting Information provides a detailed derivation of the equations and rate constants used in this study.[8]

Table S2 in the Supporting Information summarizes the values of k_{Lev+OH} as a function of pH and temperature.[8] At least three replicate experiments were conducted to determine the rate constants at each specific pH and temperature. For example, k_{Lev+OH} at 20 °C (293 K) was $(0.79 \pm 0.11) \times 10^9\,M^{-1}\,s^{-1}$ ($n = 5$) at pH 3.0, $(2.4 \pm 0.28) \times 10^9\,M^{-1}\,s^{-1}$ ($n = 4$) at pH 5.5, and $(1.6 \pm 0.08) \times 10^9\,M^{-1}\,s^{-1}$ ($n = 4$) at pH 8.0. The mean values of k_{Lev+OH} at pH 3.0 were always slightly smaller than those calculated at pH 5.5 or 8.0 at the same temperature. Hoffmann et al.,[3] the only study in the primary literature to have determined k_{Lev+OH}, reported a value of $(2.4 \pm 0.3) \times 10^9\,M^{-1}\,s^{-1}$ at 298 K (25 °C) using laser flush photolysis; however, because the solution pH was not given, it is not possible to directly compare this value with the present values. In the current study, when the pH of the solution was not controlled with a buffer solution, the measured pH of a solution for the conditions of Hoffmann et al.[3] (45 µM levoglucosan and 100 µM H_2O_2) was 6.2. Assuming that the pH of the solution used by Hoffmann et al.[3] was approximately 6.2, their reported value was similar to the k_{Lev+OH} value reported here at pH 5.5 and 293 K.

Figure 2 shows an Arrhenius plot of $\ln(k_{Lev+OH})$ versus $1/T$. Linear regression analyses revealed relatively low slopes across the pH range. Using the mean values at each temperature, the activation energy (E_a) for the reaction between levoglucosan and $^{\bullet}OH$ was calculated at each pH; the E_a (±standard error) was $12 \pm 9.6\,kJ\,mol^{-1}$ at pH 3.0, $2.3 \pm 4.8\,kJ\,mol^{-1}$ at pH 5.5, and $27 \pm 10\,kJ\,mol^{-1}$ at pH 8.0. The E_a values for k_{Lev+OH} were small. For example, the bimolecular rate constant of a reaction with $E_a = 10\,kJ\,mol^{-1}$ changes by only 16% with a temperature change of 10 °C, assuming that all of the coefficients in the Arrhenius equation are the same. Thus, the E_a values calculated in this study suggest that the rate constants for levoglucosan and $^{\bullet}OH$ are influenced little by changes in temperature between 10 and 40 °C.

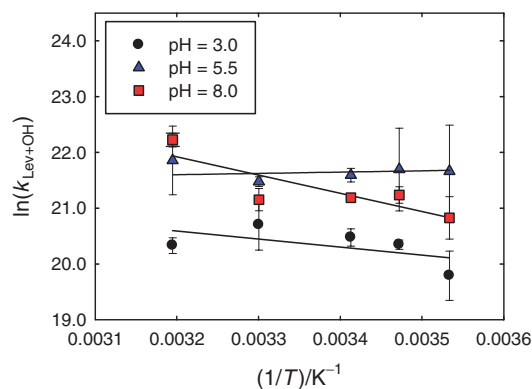**Figure 2.** An Arrhenius plot showing $\ln(k_{Lev+OH})$ as a function of $1/T$ at pH 3.0, 5.5, and 8.0. Error bars indicate one standard deviation about the mean.

Hoffmann et al.[3] studied reaction rates between levoglucosan and $^{\bullet}OH$, $NO_3^{\bullet}$, and $SO_4^{\bullet-}$, concluding that the reaction with $^{\bullet}OH$ was the major degradation pathway. In natural systems, $[^{\bullet}OH]_{ss}$ can vary widely; nevertheless, assuming that $[^{\bullet}OH]_{ss}$ is $10^{-14}\,M$ in the atmospheric liquid phase,[2] eq 2 predicts the lifetime of levoglucosan to be about 13.2 h. Although previous studies have indicated that levoglucosan is relatively stable in the atmosphere,[4] its calculated lifetime is relatively short. One should take this into consideration when using levoglucosan as the sole tracer for biomass burning.

References and Notes
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8 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.