

Determination of hydroxyl radicals with salicylic acid in aqueous nitrate and nitrite solutions

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Abstract: The qualitative and quantitative analyses of reactive oxygen species are essential to determine their steady-state concentration and related reaction mechanisms in environmental aquatic systems. In this study, salicylic acid was employed as an innovative molecular probe of hydroxyl radical(OH) generated in aqueous nitrate and nitrite solutions through photochemical reactions. Kinetic studies showed that the steady-state concentrations of OH in aqueous NO_3^- (10 mmol/L, pH = 5) and NO_2^- (10 mmol/L, pH = 5) solutions under ultraviolet irradiation were at a same magnitude, 10^{-15} mol/L. Apparent quantum yields of OH at 313 nm were measured as 0.011 and 0.07 for NO_3^- and NO_2^- respectively, all comparable to the results of previous studies.

Keywords: photochemistry; hydroxyl radical; salicylic acid; nitrate; nitrite

Introduction

The qualitative and quantitative analyses of reactive oxygen species(ROS) are essential to determine their steady-state concentration and related reaction mechanisms in natural waters and photochemical systems of advanced oxidation processes (Foote, 1995; Legrini, 1993). ROS include singlet oxygen, superoxide/hydroperoxyl radical, hydrogen peroxide, hydroxyl radical, and organic peroxy radicals.

Employing molecular probe techniques combined with laboratory spectroscopy studies is a very powerful tool to detect and identify the ROS. A large number of literatures have reported that cumene (Mill, 1980), butyl chloride (Haag, 1985), anisole(Zepp, 1992), benzene, 2-propane, formate (Warneck, 1988), benzoic acid, and methanol (Zhou, 1990) can be used as the probe of OH in aqueous solutions.

A substantial body of work has established that the photolysis of nitrate and nitrite can be significant sources of OH in waters. In this paper we have employed a new molecular probe, salicylic acid (SA) to determine the photochemically produced OH. The steady-state concentrations and apparent quantum yields of OH were estimated for aqueous nitrate and nitrite solutions.

1 Materials and methods

All reagents were of analytical grade and distilled water was used throughout. All the photoreactions were carried out in a NDC-3 photochemical reaction chamber(Nanjing University) equipped with a mercury lamp and a quartz water cooler. The cooler was immersed in a borosilicate glass sleeve, which was filled with an aqueous solution of 1 mmol/L potassium chromate in 2.3% potassium carbonate, to isolate the light of wavelength 313 nm. A fan was mounted in the chamber for cooling so that the temperature was controlled at 20—30 °C.

1.1 Irradiation and analysis procedures

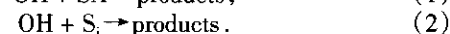
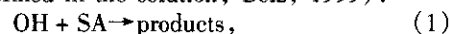
Salicylic acid was added into aqueous NaNO_3 (10 mmol/L, pH = 5) solutions at a series of concentrations (7.24 $\mu\text{mol/L}$ —0.724 mmol/L), and added into NaNO_2 (10 mmol/L, pH = 5) solution at a concentration of 7.24 $\mu\text{mol/L}$.

Hydrochloric acid and sodium hydroxide were used to adjust the pH where necessary.

The 10-ml tube containing the reaction solution was placed upon the outer surface of the glass sleeve. After irradiation for 0 and 4 h with UV light(313 nm), the sample solutions, which were sampled at 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, and 4 h, were diluted and analyzed by HPLC (Hewlett Packard series 1050) with a Hypersil BDS C_{18} (200 \times 4.6 mm, 5 μ) column using methanol/water(60:40 = v: v) as eluent and a UV detector(at 300 nm). The ultraviolet absorption spectra were recorded on a UV-Vis spectrophotometer (Shimadzu UV-2201) using a quartz cuvette(1 cm path length).

1.2 Measurement of steady-state concentration of OH in NO_3^- solution

According to the previous studies (Zafriou, 1979a; Warneck, 1988), the NO_3^- system produced OH photochemically. The hydroxyl radicals decayed following two pathways(Eq. (1) and Eq. (2)), i. e. reaction with the probe(SA) and with the substrate or other active species(S_i) (e. g., ONOO^- formed in the solution; Beiz, 1999).



Then, the following equations apply:

$$d[\text{OH}]/dt = F - [\text{OH}] \left(\sum k_{B_i} [\text{S}_i] + k_B [\text{SA}] \right), \quad (3)$$

$$d[\text{SA}]/dt = - k_B [\text{OH}][\text{SA}], \quad (4)$$

where F is the formation rate of OH in the photochemical system, and k_{B_i} represents the rate constant of the reaction of S_i and OH.

Invoking the steady-state approximation for OH provides its steady-state concentration:

$$[\text{OH}]_{ss} = F / \left(\sum k_{B_i} [\text{S}_i] + k_B [\text{SA}] \right). \quad (5)$$

Substitution of Eq. (5) into Eq. (4) then furnishes an expression relating the initial rate of SA loss, R , to its initial concentration $[\text{SA}]_0$:

$$R = - d[\text{SA}]/dt = F k_B [\text{SA}]_0 / \left(\sum k_{B_i} [\text{S}_i] + k_B [\text{SA}]_0 \right). \quad (6)$$

At sufficiently high SA concentration ($k_B [SA]_0 \gg \sum k_{Bi} [S_i]$), R asymptotically approaches the OH formation rate F and becomes approximately independent of $[SA]_0$. The above equation can be linearly transformed as follows:

$$1/R = 1/F + \sum k_{Bi} [S_i] / (k_B F) (1/[SA]_0). \quad (7)$$

Plotting $1/R$ versus $1/[SA]_0$ provides a straight line with the slope (Sl) and intercept (Int) given by

$$Sl = \sum k_{Bi} [S_i] / (k_B F), \quad (8)$$

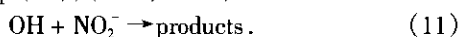
$$Int = 1/F. \quad (9)$$

Knowing k_B , we can obtain $[OH]_{ss}$ in the absence of SA from Eq.(5),

$$[OH]_{ss} = F / \sum k_{Bi} [S_i] = 1 / (k_B Sl). \quad (10)$$

1.3 Measurement of steady-state concentration of OH in NO_2^- solution

The ultraviolet-visible spectrum of NO_2^- solution studied in this study (10 mmol/L, pH = 5) has a maximum absorption at 354 nm. Zafiriou *et al* reported that NO_2^- is reactive in producing OH radicals under irradiation (Zafiriou, 1979b). The OH radicals produced from NO_2^- decayed in two pathways, namely reaction with SA (Eq.(1)) and with the substrate NO_2^- (Eq.(11)) (Beiz, 1999).



The steady-state concentration of OH can be expressed as:

$$[OH]_{ss} = F / (k_{NO_2^-} [NO_2^-] + k_B [SA]), \quad (5')$$

where $k_{NO_2^-}$ is the rate constant of Eq.(11).

In this work, the SA concentration was sufficiently low that $[OH]_{ss}$ was unaffected ($k_B [SA]_0 \ll k_{NO_2^-} [NO_2^-]$). Then the rate of SA loss is proportional to $[SA]$,

$$d[SA]/dt = -k_p [SA], \quad (12)$$

with $k_p = k_B [OH]_{ss}$.

Integration of Eq.(12) gives

$$\ln ([SA]/[SA]_0) = -k_p t. \quad (13)$$

Plotting $\ln [SA]$ versus irradiation time provides a straight line with the slope k_p . Knowing k_B , we can calculate the steady-state concentration of OH generated in the system.

1.4 Apparent quantum yields of OH

The incident light flux, I_0 , was measured by the standard ferric oxalate actinometer (Ranby, 1975). It was about 2.1×10^{-5} Einstein/s.

Apparent quantum yield for OH (Φ_{OH}), defined as the number of OH formed per photon absorbed by the system, could be expressed as follows:

$$\Phi_{OH} = F / I_0 (1 - 10^{-Abs}), \quad (14)$$

where Abs is the absorbance of the system studied at 313 nm.

2 Results and discussion

2.1 The suitability of SA as a molecular probe of OH

In principle, an ideal molecular probe needs to satisfy several criteria (Foote, 1995). First, the probe should react selectively with a single ROS so that identification is unequivocal. Second, the probe should react rapidly with the ROS, so that high concentrations of probe are not needed to compete effectively with other ROS decay routes. Third, the analysis of the probe or its products should be analytically tractable and highly sensitive. Fourth, the probe should not absorb light extensively in the spectral region of interest; if not completely transparent, it must be relatively inert to direct photolysis and must not initiate any unintended photochemistry.

We have confirmed the reaction of SA and OH in a preliminary experiment according to a colorimetric method

(Halliwell, 1976). Since there is no evidence for the reactions of SA with other ROS in the systems studied, we are sure of the specificity of this reaction with a second order kinetic coefficient (k_B) as large as $2.2 \times 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ (Buxton, 1988). We have studied the direct photolysis of SA (72.4 $\mu\text{mol/L}$) under different irradiation conditions. There was no apparent photolysis of SA under irradiation of a medium-pressure mercury lamp with water filter ($> 290 \text{ nm}$) for 4 h at pH of 2 and 5 (Fig.1). The photolyzed ratio of SA at pH = 12 was about 19% after 2 h. We attributed the result to its ionized speciation, which was similar to the case of phenols (Zika, 1987). At pH 5, there was no apparent photolysis of SA under 313 nm-irradiation (Fig.1). SA photolyzed rapidly under irradiation of a medium-pressure mercury lamp without any filters. The above results mean that SA can be used as a molecular probe of OH in this study.

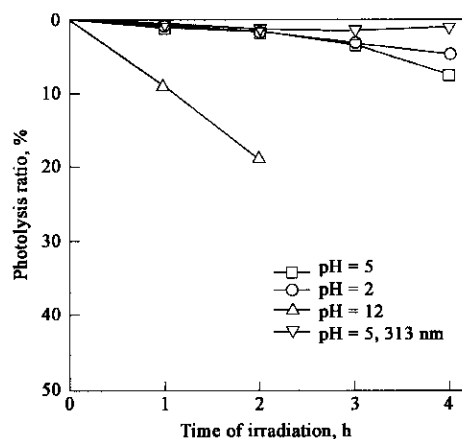


Fig.1 The direct photolysis of SA at different pH values

2.2 steady-state concentrations of OH in NO_3^- and NO_2^- solutions

Because for all NO_3^- solutions of various initial concentrations we obtained the linear correlation between $[SA]$ and irradiation time (Fig.2), with R better than 0.97, the loss rate (R) could be calculated by the difference of SA concentrations divided by the irradiation time. From the plots of $1/R$ versus $1/[SA]_0$ (Fig.3), combined with Eq.(10), the steady-state concentration of OH in aqueous nitrate solution was calculated as $2.23 \times 10^{-15} \text{ mol/L}$.

As for the NO_2^- system, the plot of $\ln [SA]$ versus time gave a slope, or k_p , of 0.242 h^{-1} (Fig.4). Using $k_B = 2.2 \times 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$, we obtained the steady-state concentration of OH of $3.06 \times 10^{-15} \text{ mol/L}$.

2.3 Apparent quantum yield of OH in the photochemical systems

Substitution of Eq.(9) into Eq.(14), it provides the expression of Φ_{OH} for NO_3^- system:

$$\Phi_{OH} = 1 / Int I_0 (1 - 10^{-Abs}). \quad (15)$$

Using $Int = 3.14 \times 10^7 \text{ M}^{-1} \cdot \text{s}$ (Fig.3), $Abs = 0.067$, and $I_0 = 2.1 \times 10^{-5} \text{ Einstein s}^{-1}$, we obtained $\Phi_{OH} = 0.011$ at 313 nm.

According to Equations (1) and (5'), we can get the expression of Φ_{OH} for NO_2^- system:

$$\Phi_{OH} = [OH]_{ss} (k_{NO_2^-} [NO_2^-] + k_B [SA]) / I_0 (1 - 10^{-Abs}). \quad (16)$$

Substitution of $[OH]_{ss} = 3.06 \times 10^{-15} \text{ mol/L}$, $k_{NO_2^-} = 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$, $k_B = 2.2 \times 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$, $[NO_2^-] = 10^{-2} \text{ mol/L}$, $[SA] = 7.24 \times 10^{-6} \text{ mol/L}$, and $Abs = 0.101$ into the above equation, the Φ_{OH} for NO_2^- system at 313 nm was calculated to

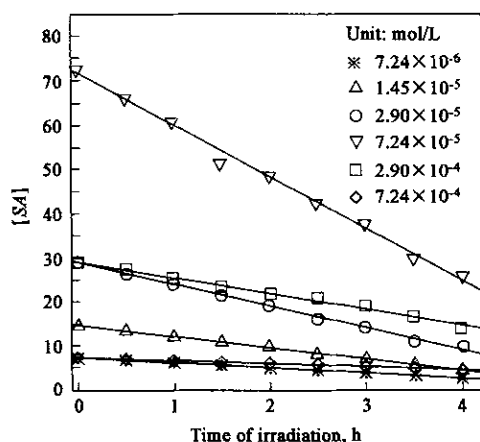


Fig. 2 The linearity between SA loss and irradiation time for NO_2^- systems

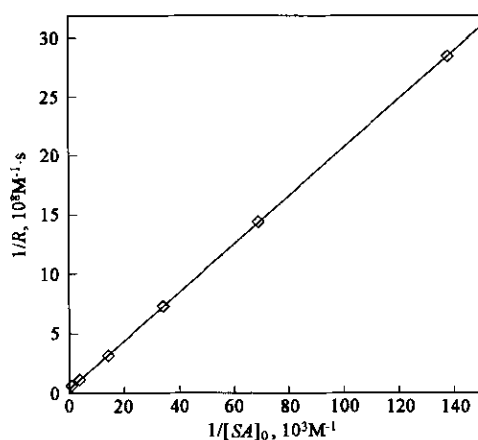


Fig. 3 Relationship between $1/R$ and $[\text{SA}]_0$ for NO_2^- system

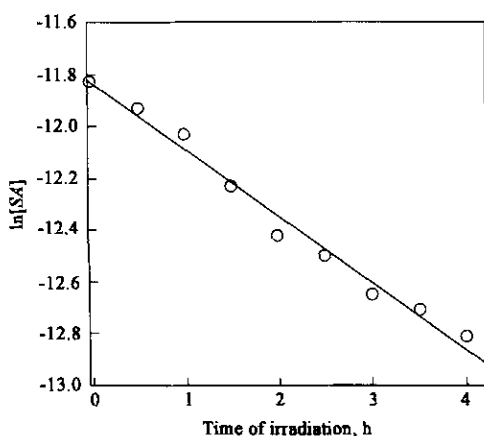


Fig. 4 The plot of $\ln[\text{SA}]$ vs. time for NO_2^- system (10 mmol/L) with SA added (7.24×10^{-6} mol/L) under 313 nm irradiation

be 0.07.

For NO_3^- systems, Zepp *et al.* have reported the mean quantum efficiency for OH production at 313 nm, which rises from 0.013 at 20 °C to 0.017 at 30 °C in the pH range of 6.2–8.2 (Zepp, 1987). Warneck and Wurzinger reported an OH quantum yield at 305 nm of $(9.2 \pm 0.4) \times 10^{-3}$ in the pH region of 5–12 (Warneck, 1988). Kieber *et al.* reported that the wavelength-dependent OH quantum yields ranged from 0.0007 to 0.014 for nitrate photolysis between 290 and 330 nm and from 0.024 to 0.078 for nitrite photolysis between 298 and 390 nm (Jankowski, 1999). Zellner *et al.* reported that in

NO_2^- system, $\Phi_{\text{OH}}(298 \text{ K}, 303 \text{ nm}) = 0.07 \pm 0.01$ for $4 \leq \text{pH} \leq 9$, and $\Phi_{\text{OH}}(298 \text{ K}, 351 \text{ nm}) = 0.046 \pm 0.009$ for $\text{pH} = 8$ (Zellner, 1990). Besides, Zafiriou's result is $\Phi_{\text{OH}} = 0.015 - 0.08$ and Alif's result is 0.07 at 313 nm for nitrite photolysis (Zafiriou, 1987; Alif, 1991). Our results are comparable with previous ones.

3 Conclusions

According to the criteria of an ideal probe, the validation of salicylic acid as a molecular probe of hydroxyl radical formed in aqueous nitrate and nitrite solutions is assuring. In this study, the steady-state concentrations of OH radicals generated in UV irradiated nitrate and nitrite solutions are at a same magnitude, 10^{-15} mol/L. Apparent quantum yields of OH at 313 nm are 0.011 and 0.07 for nitrate and nitrite ions respectively. However, we should keep it in mind that SA could not be applied to the photochemical systems under irradiation of less than 290 nm or basic solutions. If the limitations are out of the problem, addition of salicylic acid into the aquatic system being studied may be a useful tool to estimate the steady-state generation of hydroxyl radical and be helpful to determine the related reaction mechanisms in the system.

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