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Production of Hydroxyl Radical via the Activation of Hydrogen Peroxide by Hydroxylamine

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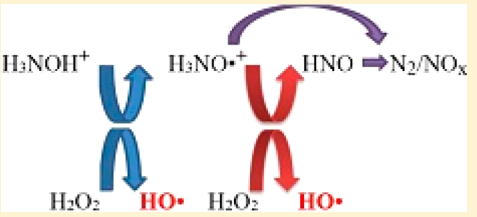
Supporting Information

ABSTRACT: The production of the hydroxyl radical (HO·) is important in environmental chemistry. This study reports a new source of HO· generated solely from hydrogen peroxide (H_2O_2) activated by hydroxylamine (HA). Electron paramagnetic resonance analysis and the oxidation of a HO· probe, benzoic acid, were used to confirm the production of HO·. The production of HO· increased with increasing concentrations of either HA or H_2O_2 as well as decreasing pH. The second-order rate constant for the reaction was $(2.2 \pm 0.2) \times 10^{-4}$ M^{-1} s^{-1}. HO· was probably produced in two steps: the activation of H_2O_2 by protonated HA and then reaction between the H_2O_2 and the intermediate protonated aminoxyl radical generated in the first step. Such a two-step oxidation can possibly be ascribed to the ionizable hydroxyl moiety in the molecular structure of HA, as is suggested by comparing the reactivity of a series of HA derivatives in HO· production. The results shed light on a previously unknown source of HO· formation, which broadens the understanding of its role in environmental processes.



INTRODUCTION

The hydroxyl radical (HO·) is a most reactive species which can oxidize most organic substrates unselectively.[1,2] It has been widely employed to degrade an enormous variety of recalcitrant and toxic contaminants in advanced oxidation processes (AOPs) such as the Fenton reaction, radiolysis, UV/H_2O_2 purification, O_3 oxidation, and electrochemistry.[3,4] The mechanisms of HO· generation and the involvement of HO· in redox reactions with contaminants in the environment have been investigated intensely for decades.[2−5] HO· is usually produced via metal-involved reactions such as the Fenton reaction or using energy-input systems as in H_2O_2/UV purification.[6,7] However, metal-independent and energy-input free production of HO· has been reported occasionally,[8−12] an intriguing and attractive finding.

The mechanism of metal-independent production of HO· is still under discussion, but it has been established that halogenated quinones and some reducing organic species such as ascorbic acid, phenols, hydroquinone and semiquinone moieties in reduced humic acid and biochar can enable the generation of active radicals with oxidants.[8−12] One of the underlying mechanisms involves nucleophilic attack of halogenated quinones by H_2O_2; their product then decomposes homolytically to produce HO·.[8] Another mechanism involves electron transfer. Ascorbic acid undergoes a two-step oxidation by H_2O_2 to yield HO· and dehydroascorbic acid with the formation of an intermediate ascorbyl radical,[9] and hydroquinone moieties in reduced humic acids are known to reduce O_2 to form H_2O_2 and semiquinones, which then react with the H_2O_2 to generate HO·.[10] Semiquinone-type persistent free radicals in biochar can react directly with H_2O_2 by single-electron transfer and reduce it to HO·.[11] Moreover, phenols can activate persulfate to form sulfate radicals, which are then transformed to HO· with hydroxide at alkaline pH or water at lower pH.[12] The common feature linking ascorbic acid, phenols, reduced humic acids, and biochar is the possession of ionizable hydroxyl moiety or a relevant C-centered radical which can participate in the production of HO·.[9−12]

Hydroxylamine (HA), a widely used reductant and antioxidant,[13] contains an ionizable hydroxyl moiety and can undergo electron transfer or H atom abstraction.[14−17] Previous work in our laboratory has indicated that it can accelerate Fe(II)/Fe(III) redox cycles to enhance the generation of reactive radicals dramatically in a Fenton system or an Fe(II)/peroxymonosulfate system.[18,19] Considering its similar reducing activity and the ionizable hydroxyl group, it is hypothesized that HA may activate H_2O_2 to form HO· without a transition metal. Radical species are very probably produced as intermediates in the electron transfer process between H_2O_2 and HA,[20] though the mechanism of HO· production involving HA and H_2O_2 is still unknown.

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The objectives of this study were to explore the potential of the reaction between HA and H_2O_2 as a new source of HO· and to reveal the mechanism involved. Electron paramagnetic resonance (EPR) technique and the oxidation of a HO· probe benzoic acid (BA) were used to illustrate the HO· production. The effects of pH and the concentrations of HA and H_2O_2 on HO· production were explored, and the potential pathways for HO· generation will be discussed. By studying HO· production by H_2O_2 with a series of HA derivatives (HAs), the role of ionizable hydroxyl moiety in the molecular structure of the HAs during the process was revealed and a plausible mechanism can now be proposed.

MATERIALS AND METHODS

Materials. All of the chemicals listed in Text S1 of the Supporting Information were used as purchased without further purification. Stock solutions of HA and its derivatives were all freshly prepared using deaerated Milli-Q water (deaerated using nitrogen).

Experimental Procedures. The EPR experiments were conducted at room temperature on a Bruker A200 300E instrument. Solutions of H_2O_2, HA, the spin-trapping agent 5,5-dimethyl-1-pyrroline N-oxide (DMPO), transition metal ions, HO· scavengers or iron chelators were mixed and deaerated with nitrogen. They were buffered at the desired pH with perchloric acid or acetate for the detection of HO·. The possible influence of perchloric acid on the system was negligible (Figure S1 and Text S2 in the Supporting Information). After mixing for about 1 min (±3 s), the sample solution was transferred into a 100 μL capillary tube, which was then fixed in the cavity of the EPR spectrometer. Ethyl *N*-hydroxycarbamate (a derivative of HA) was similarly mixed with H_2O_2 for the detection of relevant aminoxyl radicals.[21]

All of the other experiments were carried out in triangular flasks with constant stirring using a PTFE-coated magnetic stirrer in Milli-Q water adjusted to pH 3.0 with perchloric acid and deaerated with nitrogen throughout the experiments. The concentration of dissolved oxygen (DO) in the solution was below the detection limit of a DO meter (less than 0.31 μM). The solutions' temperature was maintained at 25 ± 0.5 °C. All of the experiments were performed at least in duplicate. In each run, HA, BA, perchloric acid, or *tert*-butanol were mixed in the desired dosages and the experiment was switched on by adding the desired dosage of H_2O_2. The pH changed less than 0.1 unit during the experiments. To avoid the interference of nitrogen in the detection of N_2O generated in the system, argon (Ar, 99.99%) instead of nitrogen was used to remove oxygen in the solution before the initiation of the reaction. The flasks were totally sealed to prevent the escape of N_2O from the solution and to guarantee the oxygen-free conditions during the process.

Sample Analysis. The concentrations of BA, *m*-hydroxybenzoic acid (MHBA), *o*-hydroxybenzoic acid (OHBA), and *p*-hydroxybenzoic acid (PHBA) were determined on high performance liquid chromatography (HPLC, Dionex Ultimate 3000) equipped with a reverse-phase C18 column. The pH was measured with a Denver Instrument Ultrabasic 10 pH meter. The concentration of DO was measured by a DO meter (Rex Electric Chemical, JPSJ-605). The H_2O_2 concentrations were measured by a colorimetric method using peroxidase and *N*,*N*-diethyl-*p*-phenylenediamine (DPD) on a PE Lambda 25 UV–vis spectrometer.[22] The HA samples were derivatized to acetone oxime using acetone and were subsequently extracted using methyl *tert*-butyl ether (MTBE). The acetone oxime concentrations were measured using a Shimadzu GC-2010 gas chromatograph with a flame ionization detector (FID) and N_2 as the carrier gas.[23] Ion chromatography (Dionex ICS-900) was employed for the detection of NO_2^- and NO_3^-. The concentration of dissolved N_2O was analyzed using a gas chromatograph (Agilent 7890) equipped with an electron capture detector (ECD) and a headspace sampler.[19,24] Additional details of the sample analysis procedures are presented in Text S3 of the Supporting Information.

RESULTS AND DISCUSSION

HO· Production. Figure 1a shows typical EPR signals of DMPO–OH during the reaction of HA with H_2O_2. The typical

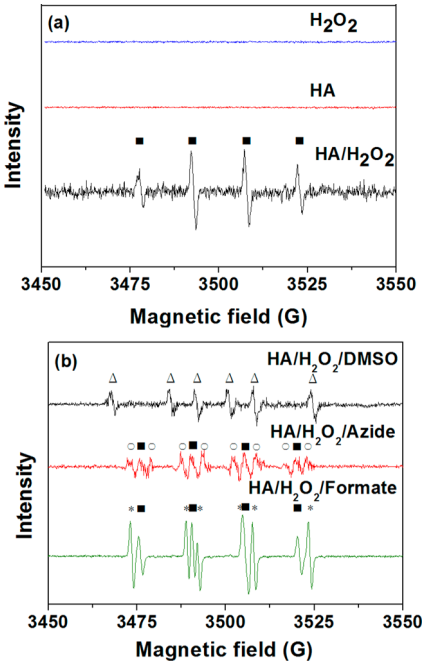

Figure 1. EPR signals of DMPO spin trapping adducts produced by (a) HA and H_2O_2, and (b) HA and H_2O_2 in the presence of HO· scavengers. Reaction conditions: $[DMPO]_0$ = 20.0 mM, $[H_2O_2]_0$ = 10.0 mM, $[HA]_0$ = 10.0 mM, $[scavengers]_0$ = 500.0 mM, pH = 3.0, 25 °C, DMPO–OH, ■; DMPO–CH_3, △; DMPO-N_3, ○; DMPO–CO_2, *.

DMPO–OH spin adduct ($a^H = a^N$ = 14.9 G), which has a specific quartet spectrum with peak height ratios of 1:2:2:1, indicates the formation of HO·.[25] It should be noted that a similar DMPO–OH signal may arise from the decomposition of DMPO-OOH and the nucleophilic addition to DMPO in the presence of Fe(III) or Cu(II).[26,27] Additional analysis was therefore carried out to confirm the production of HO·. Dimethyl sulfoxide (DMSO), azide, and formate react with HO· to generate methyl radicals (CH_3·), azidyl radicals (N_3·), and carbon dioxide anion radicals (CO_2^{-}·), respectively, as shown in the equations (eqs 1–3). These intermediate radicals can also be captured by DMPO to yield the corresponding DMPO–CH_3 (a^H = 23.4 G, a^N = 16.4 G), DMPO-N_3 ($a^H = a^N$ = 14.7 G), and DMPO–CO_2^- (a^H = 19.3 G, a^N = 15.9 G) spin adducts (eqs 4–6).[26] DMSO, azide, and formate were therefore adopted in the EPR study to verify the formation of HO·. The spin adducts of DMPO–CH_3, DMPO–N_3, and DMPO–CO_2^- were generated instead of DMPO–OH when excessive DMSO, azide or formate was present in the system, accompanied by a

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marked decrease in or disappearance of the DMPO−OH spin adducts (Figure 1b). These EPR results indicate the generation of HO· in the system.

$$HO\cdot + (CH_3)_2SO \rightarrow CH_3SO_2H + CH_3\cdot \quad (1)$$

$$HO\cdot + N_3^- \rightarrow OH^- + N_3\cdot \quad (2)$$

$$HO\cdot + HCO_2^- \rightarrow H_2O + CO_2^{-\cdot} \quad (3)$$

$$CH_3\cdot + DMPO \rightarrow DMPO{-}CH_3 \quad (4)$$

$$N_3\cdot + DMPO \rightarrow DMPO{-}N_3 \quad (5)$$

$$CO_2^{-\cdot} + DMPO \rightarrow DMPO - CO_2^- \quad (6)$$

Further evidence comes from the inhibition effect of *tert*-butyl alcohol (TBA), which is a strong HO· scavenger ($k_{TBA, HO\cdot}$ = 7.6 × 10^8 M^{-1} s^{-1}),[28] on the competition of HO· with BA, the HO· probe. Figure S2 shows almost complete inhibition of BA oxidation by 0.1 M TBA, suggesting the dominant contribution of HO· to BA oxidation in the system. Moreover, the *m*-hydroxybenzoic acid (MHBA), *o*-hydroxybenzoic acid (OHBA), and *p*-hydroxybenzoic acid (PHBA) are the primary intermediates, so their detection during the oxidation of BA also helps confirm the involvement of HO· in the system.[29,30] As is shown in Figure S3, MHBA, OHBA, and PHBA were all detected, further supporting the generation of HO·.

Possible Influence of Trace Transition Metal Ions. Trace transition metal impurities in the reagents may possibly have enhanced the generation of HO·. As can be seen from Figure S4, only iron could notably enhance the intensity of the HO· signal. This was readily excluded by using ferrozine and ferene as iron chelators.[26] Almost complete disappearance of the DMPO−OH signal in a traditional Fenton system when ferrozine or ferene is present, confirms their excellent iron complexing ability, as shown in Figure S5. In contrast, no significant decrease in the intensity of the HO· signal was observed in the HA−H_2O_2 reactions in the presence of sufficient ferrozine or ferene (Figure 2), indicating that trace iron was not responsible for the HO· production. The generation of HO· by the reaction of HA and H_2O_2 is indeed metal-independent.

Effect of pH. Figure 3 presents the profiles of DMPO−OH spin adducts at pH ranging from 2.0 to 6.0. The intensity of the

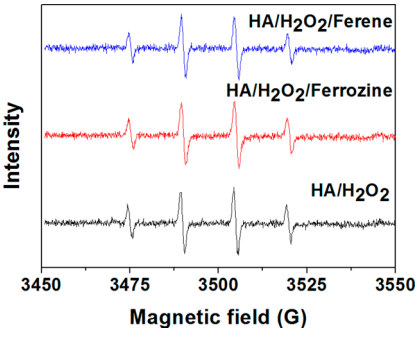

Figure 2. Effect of the iron chelating agents ferrozine and ferene on the EPR signals of DMPO−OH spin trapping adducts produced by HA and H_2O_2. Reaction conditions: $[DMPO]_0$ = 20.0 mM, $[H_2O_2]_0$ = 10.0 mM, $[HA]_0$ = 10.0 mM, $[ferrozine]_0$ = 50.0 μM, $[ferene]_0$ = 50.0 μM, pH = 3.0, 25 °C.

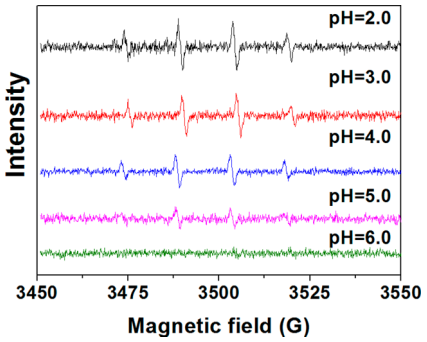

Figure 3. Effect of pH with acetate buffer on the EPR signals of DMPO−OH spin trapping adducts produced by HA and H_2O_2 in the pH range of 2.0 to 6.0. Reaction conditions: $[DMPO]_0$ = 20.0 mM, $[H_2O_2]_0$ = 10.0 mM, $[HA]_0$ = 10.0 mM, 25 °C.

HO· signal decreased with increasing pH, and it almost disappeared at pH values higher than 6.0.

The pK_a values for HA are 5.96 and 13.74.[31,32] When the pH is less than 5, the majority of the HA is in its protonated form (H_3NOH^+); it is mainly in its unprotonated form (H_2NOH) at pH values in the range of 7.0 to 12.0. The second-order rate constants for the reactions of HO· with H_3NOH^+ and H_2NOH are ≤5.0 × 10^8 M^{-1} s^{-1} and 9.5 × 10^9 M^{-1} s^{-1}, respectively,[33] so the scavenging of HO· by HA increases with increasing pH. In addition, some researchers have proposed that the protonated form of the hydroxylamino radical, the one-electron transfer intermediate of HA with a pK_a of about 4.2, reacts much faster with H_2O_2 than the unprotonated hydroxylamino radical to produce HO·.[17,33] Under strongly acidic conditions, most of the hydroxylamino radical is protonated, and thus the HO· production increased with decreasing pH. The pH might therefore affect HO· generation mainly through controlling the species distribution of HA and the intermediate hydroxylamino radical.

Effect of HA and H_2O_2 Concentrations. The EPR results presented in Figure S6 show that the concentration of HO· increased with increasing concentrations of either HA or H_2O_2, indicating the involvement of the two reagents in the HO· generation. The reaction between H_2O_2 and H_3NOH^+ was studied under acidic conditions by purging with N_2 constantly to minimize the influence of side reactions such as oxidation of unprotonated HA by HO·. Under those conditions the *k* was determined to be (2.2 ± 0.2) × 10^{-4} M^{-1} s^{-1} (Text S4 and Figure S7 of the Supporting Information), which seems relatively low.

Role of the Molecular Structure of the Hydroxylamines. The contribution of the series of hydroxylamine derivatives (HAs, shown in Figure 4) to HO· generation with H_2O_2 was investigated. Figure 5 shows the individual DMPO−OH spin adduct in each HAs−H_2O_2 reaction. HO· production was observed in the case of *N*-methyl hydroxylamine (*N*-methyl HA), *N*,*N*-dimethyl hydroxylamine (*N*,*N*-dimethyl HA), *N*-*tert*-butyl hydroxylamine (*N*-*tert*-butyl HA), *N*-benzyl hydroxylamine (*N*-benzyl HA) and *N*,*O*-dimethyl hydroxylamine (*N*,*O*-dimethyl HA). *N*-methyl HA, *N*,*N*-dimethyl HA and *N*-*tert*-butyl HA were even more efficient than HA in producing HO·, but *N*-benzyl HA and *N*,*O*-dimethyl HA were much less reactive. And no HO· was detected under the same conditions with the O-Substituted HAs, for example, *O*-methyl HA, *O*-*tert*-butyl hydroxylamine (*O*-*tert*-butyl HA) and *O*-benzyl hydroxylamine (*O*-benzyl HA). N-Substituted HAs showed much

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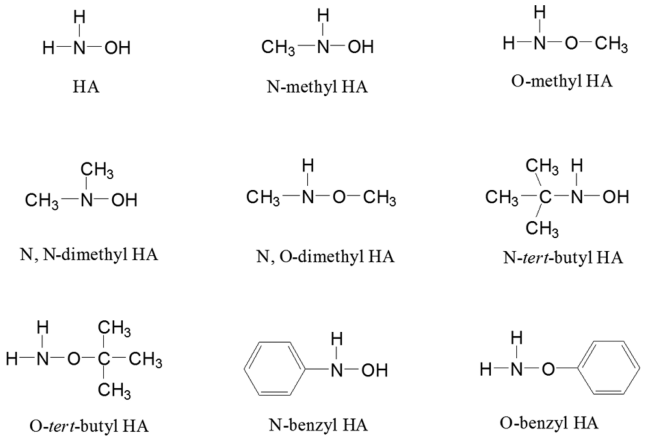

Figure 4. Chemical structures of the HAs used.

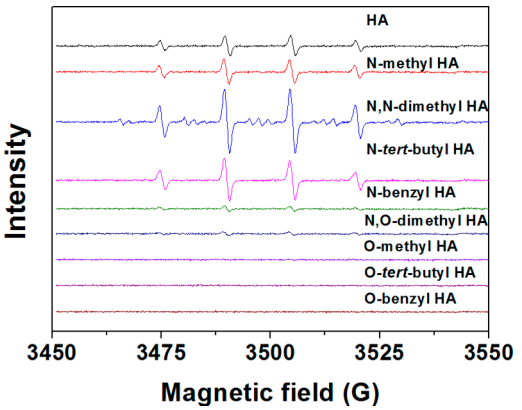

Figure 5. EPR signals of DMPO−OH spin trapping adducts produced by H_2O_2 and HAs. Reaction conditions: $[DMPO]_0$ = 20.0 mM, $[H_2O_2]_0$ = 10.0 mM, $[HAs]_0$ = 10.0 mM, pH = 3.0, 25 °C.

greater HO· generation than the O-Substituted HAs in the presence of H_2O_2. This suggests that the production of HO· by H_2O_2 and HAs is probably related to the −OH group in the structure of HAs.

Mechanism of HO· Generation. An intermediate aminoxyl radical (H_2NO·) or its isomer hydroxylamino radical (·HNOH) is formed during the oxidation of HA by a one-electron oxidant or an H atom abstractor.[34] Considering that the bond dissociation energy (BDE) of O−H in HA (75 to 77 kcal M^{-1}) is weaker than that of N−H (81 to 82 kcal M^{-1}),[34,35] H_2NO· is more easily generated and stable than ·HNOH.[34] When HO· is generated by the reaction of HA and H_2O_2 through one electron transfer under acidic conditions, H_2O_2 presumably reacts with protonated HA to produce HO· and an aminoxyl radical via eq 7. To verify this hypothesis, ethyl *N*-hydroxycarbamate, an HA derivative, was reacted with H_2O_2 instead of HA to generate a more intense EPR signal of its corresponding aminoxyl radical.[21] Despite its short lifetime,[35] the EPR signal shown in Figure 6 verified the generation of aminoxyl radical (a^N = 7.2 G, a^{N-H} = 11.4 G, a^{C-H} = 0.9 G) in the system,[21] supporting the pathway presented in eq 7.

The protonated form of the hydroxylamino radical ($pK_a \approx 4.2$) was reported to react with H_2O_2 much faster than the unprotonated hydroxylamino radical to produce HO· and nitroxyl (HNO).[17,33] However, the aminoxyl radical has been proven to be the dominating active intermediate in one-electron oxidation of HA aforementioned.[34] Thus, we proposed

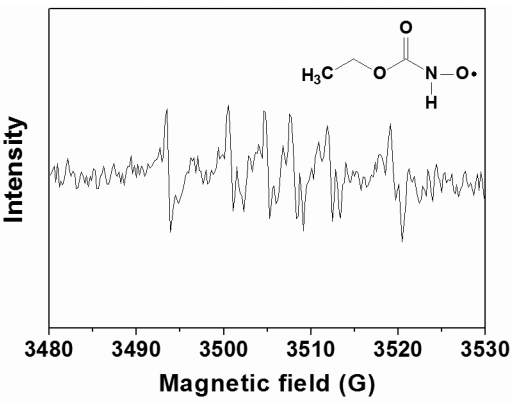

Figure 6. EPR signal of aminoxyl radical produced by H_2O_2 and ethyl *N*-hydroxycarbamate. Reaction conditions: [ethyl *N*-hydroxycarbamate]$_0$ = 50.0 mM, $[H_2O_2]_0$ = 50.0 mM, pH = 3.0, 25 °C.

that the protonated form of the aminoxyl radical would react with H_2O_2 much faster to produce HNO and HO· via eq 8.

$$H_2O_2 + H_3NOH^+ \rightarrow H_3NO^{\cdot +} + HO\cdot + H_2O \quad (7)$$

$$H_2O_2 + H_3NO^{\cdot +} \rightarrow HNO + HO\cdot + H_2O + H^+ \quad (8)$$

The aminoxyl radical and HNO, oxidation intermediates of HA, were ultimately converted to nitrogen and various nitrogen oxides (e.g., N_2O, NO_2^-, and NO_3^-) depending on the conditions.[34] The generation of gaseous products (N_2 and N_2O) mainly depends on the pH. The dimerization of unstable HNO to form N_2O is favored in strongly acidic conditions with the rate constant of $(4.5 \pm 2.7) \times 10^9$ M^{-1} s^{-1} (eq 9).[36−38] N_2 could be formed by the dimerization/cleavage of H_2NO· at pHs higher than 4.0 with a second-order rate constant of $(2.8 \pm 0.5) \times 10^8$ M^{-1} s^{-1} (eq 10).[17,20,34] In addition, reactions involving excess H_2O_2 might account for the production NO_3^-, and NO_2^- is probably formed as an intermediate (eqs 11−15).[17] N_2O was (Figure S8 determined in the system at pH 3.0 to verify the formation of HNO indirectly, as HNO is unstable and it spontaneously dimerizes and subsequently dehydrates to form N_2O with a high rate constant.[38] Figure S8 in the Supporting Information also shows the concentration of NO_2^- and NO_3^- generated in the HA and H_2O_2 reaction. The generation of NO_2^- and NO_3^- was not so evident, and the gaseous products N_2O increased with longer reaction time, supporting the formation of HNO and the two-step oxidation pathway for HO· generation (eqs 7 and 8).

$$2HNO \rightarrow N_2O + H_2O \quad (9)$$

$$2H_2NO\cdot \rightarrow N_2 + 2H_2O \quad (10)$$

$$H_2O_2 + HO\cdot \rightarrow HO_2\cdot/O_2\cdot^- + H_2O \quad (11)$$

$$H_2NO\cdot + O_2\cdot^- \rightarrow NO_2^- + H_2O \quad (12)$$

$$HO\cdot + NO_2^- \rightarrow NO_2\cdot + OH^- \quad (13)$$

$$NO_2\cdot + NO_2\cdot \rightarrow N_2O_4 \quad (14)$$

$$N_2O_4 + H_2O \rightarrow NO_2^- + NO_3^- + 2H^+ \quad (15)$$

According to the former two-step oxidation hypothesis, the theoretical stoichiometric ratio of HA consumption to H_2O_2 depletion is 0.5 not only for protonated HA but also for the intermediate protonated aminoxyl radical reacting with H_2O_2

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(eqs 7 and 8). To estimate the actual stoichiometric ratio in the system, BA was employed to scavenge HO·. The amount of HA consumed was then much lower than that of H_2O_2 (Figure 7a).

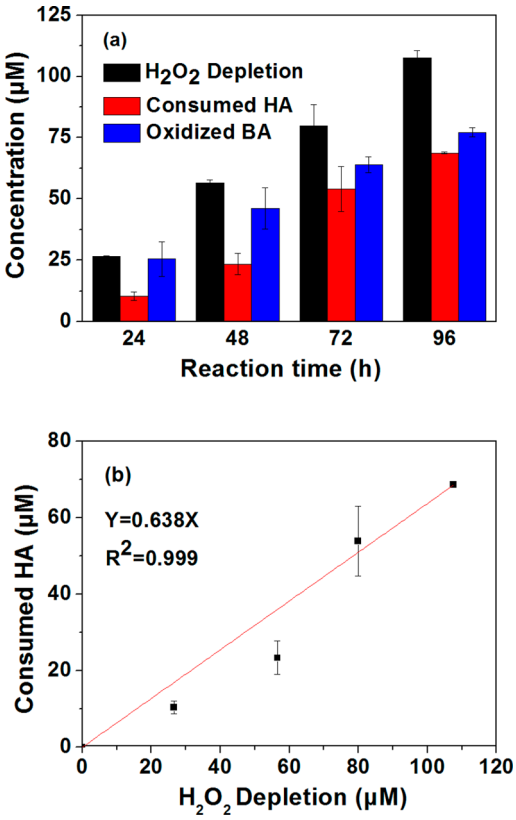

Figure 7. (a) The concentration changes of reagents and (b) the ratio of HA consumption to H_2O_2 depletion during the oxidation of BA by HA and H_2O_2. Reaction conditions: $[BA]_0$ = 0.4 mM, $[H_2O_2]_0$ = 0.4 mM, $[HA]_0$ = 0.4 mM, pH = 3.0, 25 °C.

The slope in Figure 7b shows that the stoichiometric ratio of HA consumption to H_2O_2 depletion was about 0.638, supporting the statement on the two major steps (eqs 7 and 8) involved in the reaction between HA and H_2O_2.

Figure 7a also shows the relationship between the oxidized BA and H_2O_2 depletion during the process. More than 95% of the depleted H_2O_2 was transformed to HO· to attack BA within 24 h. However, the ratio of oxidized BA to H_2O_2 depletion gradually decreased during the process. This may be because H_2O_2 competes with HO· to form NO_2^- and NO_3^- (eqs 11−15 and Figure S8),[17] and some of the HO· that is consumed by the HA as the second-order rate constants of BA and HA with HO· are 4.3×10^9 M^{-1} s^{-1} and $\leq 5.0 \times 10^8$ M^{-1} s^{-1}, respectively.[1,34] Furthermore, the second-order kinetic constants for HO· attacking OHBA and PHBA are 2.7×10^{10} M^{-1} s^{-1} and 8.0×10^9 M^{-1} s^{-1}, respectively,[1,30] suggesting that HBAs are more reactive with HO· than BA. The total amounts of MHBA, OHBA, and PHBA only accounted for about half of the observed BA oxidation (Figure S3), so those primary products (OHBA, MHBA, and PHBA) formed in the system further compete with BA for HO· and yield other intermediate products as the reaction progresses.[39] Thus, the estimated concentration of HO· at 1.49×10^{-16} M based on the BA degradation kinetics (Figure S9) ought to be lower than the actual one in the system.

The two-step oxidation hypothesis is further demonstrated by the role of the molecular structure of the HAs (Figure 5). N-Substituted HAs with ionizable hydroxyl moiety showed much greater HO· generation than O-Substituted HAs. The BDE of the N−H bonds in HAs is 81 to 82 kcal M^{-1}, while the BDE of O−H bonds in the N-Substituted HAs illustrated here is less than 77 kcal M^{-1}.[35] Such N-Substituted HAs tend to yield aminoxyl radicals (R_2NO·) and HO· when reacting with H_2O_2, and the aminoxyl radicals may yield oxoammonium (RN═O) and HO· through reacting with H_2O_2 in acidic conditions. Furthermore, the substitution of −OH by methoxyl on the N atom weakens the N−H bond, leading to a low yield of R_2NO·.[33−35] So N-Substituted HAs have much higher reactivity with H_2O_2 to produce HO· than O-Substituted ones. In addition, *N,O*-dimethyl HA shows insignificant reactivity to produce HO· because O-Substituted HAs can undergo only one-step oxidation with H_2O_2 to yield ·NROR and HO·. Consequently, it is hypothesized that the ionizable hydroxyl (−OH) moiety attached to an N atom of HAs is transformed to an ═O moiety through the formation of an intermediate −O·. This may then be responsible for the production of HO· with H_2O_2.

Implication. This study has demonstrated a previously unrecognized pathway for the formation of HO· from HA and H_2O_2. These results highlight the significance of reactions between H_2O_2 and HA which might be catalyzed rapidly by some transition metals.[14−16,38] It is therefore expected that HO· generation via eqs 7 and 8 will be greatly enhanced. Indeed, previous work in our laboratory has partially confirmed such a hypothesis in the case of Fenton reactions in the presence of HA.[18] H_2O_2 and/or superoxide radicals (e.g., HO_2·) are ubiquitous in the aquatic environment,[40,41] and the HA-like intermediates can be formed through the biodegradation of nitrogen-containing species (e.g., nitrogen fixation, nitrification, and denitrification).[35,42] The findings of this study may therefore help to elucidate the redox dynamics of contaminants in natural processes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b00483.

Four texts and nine figures are available with further information about the materials and additional data (PDF)

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Notes

The authors declare no competing financial interest.

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