

Kinetics of Ozonation of Typical Sulfonamides in Water*

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Abstract

Objective To investigate the kinetic rate constants ozone and hydroxyl radicals towards two groups of antimicrobials —sulfadiazine (SD) and sulfamethoxazole (SMX).

Methods The solute consumption method was used to detect the rate constants of ozone alone with sulfadiazine and sulfamethoxazole, and tertiary butanol was selected as a scavenging agent and pH was adjusted to 2.5 by adding orthophosphate buffers (OB); and the competition kinetics studying method with nitrobenzene as a reference was applied to measure the rate constants of hydroxyl radicals towards sulfadiazine and sulfamethoxazole, and pH was adjusted to 7.0 by adding OB.

Results The rate constants of SD and SMX with ozone alone were $261 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$ and $303 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$ by calculating in low reaction system. The rate constants of hydroxyl radicals with SD and SMX were $2.2 \times 10^{10} \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$ and $2.7 \times 10^{10} \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$, respectively. Moreover, the rate constants of hydroxyl radicals with SMX were found to have increased from $3.6 \times 10^9 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$ to $2.8 \times 10^{10} \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$ with pH value rising from 5.0 to 7.8.

Conclusion SMX and SD are both refractory to ozone oxidation alone, and are liable to be degraded by hydroxyl radicals, and the rate constants of SMX with the hydroxyl radical slightly increases with pH rise.

Key words: Antibiotics; Sulfadiazine; Sulfamethoxazole; Kinetics; Rate constant; Ozone; Hydroxyl radicals

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INTRODUCTION

Antibiotics have been successfully and widely used to control and treat human diseases, as well as in veterinary practice since the discovery of penicillin in 1929. However, antibiotics are unable to be completely metabolized in human or animal bodies, and the treated subjects excrete a fraction of the administered dose as the unaltered parent compounds or acetylated metabolites^[1]. Consequently, these parts of antibacterial agents are eventually discharged into the environment where

they may be persistent in aquatic systems^[2]. Recently, various antibiotics have been detected in ground water, surface water or even drinking water^[1,3-4]. The long-term exposure of human beings to antibiotics even in trace amount has aroused concern since they have the potential to negatively affect non-target living organisms. The presence of antibacterial agents in water represents the gravest concern owing to a possibility of leading to the development of bacteria with resistant genes^[5-7] and the development of allergenic responses^[8].

Sulfonamides (SAs), a series of drugs containing

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the chemical structure of sulfanilic amide (Figure 1a), are a widely consumed class of administered antibacterial agents in animal husbandry as preventive and therapeutic agents for bacterial infections due to their low cost, broad spectrum of activity and effectiveness in growth promotion^[9-10]. Due to their persistence in the environment and their relatively high mobility, SAs have been found in water sources at concentrations of tens to hundreds of ng/L^[11].

To assure the safety of drinking water, serious efforts have been made to remove the antibacterial agents from the water source or drinking water in recently years. Ozone, due to its high oxidation potential, has been proven to be effective to degrade or remove the organic pollutants in water. It is suggested that ozone could also degrade pharmaceuticals in water^[12-13]. Nevertheless, till now, few researches on the kinetics of ozonation of antibacterial agents have been reported, and as a result the practical application of ozonation for the degradation of these agents has stagnated.

Two groups of SAs, sulfadiazine (SD), and sulfamethoxazole (SMX), were chosen as model antibacterial agents (Figure 1b and Figure 1c)

The present study is aimed to investigate the reaction rate constants of ozone and hydroxyl radicals (the decomposition product of ozone in water) towards SAs, and meanwhile to observe the effect of pH on the rate constants.

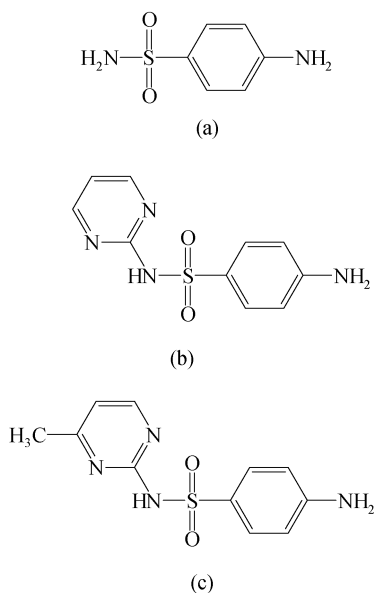


Figure 1. The chemical structure of sulfonamides. (a) sulfanilic amide; (b) sulfadiazine; (c) sulfamethoxazole.

MATERIALS AND METHODS

Reagents and Materials

The SD and SMX standards were purchased from National Institute for the Control of Pharmaceutical and Biological Products both with the purity of 99.9%. Nitrobenzene, sodium thiosulfate, potassium iodide and tert-butanol, obtained from Sinopharm Chemical Reagent Co., were all of analytical grade and used without further purification. Formic acid (>98.0% CNW Technologies GmbH) and acetonitrile (CNW Technologies GmbH) were of HPLC grade. All solutions were prepared with water purified by a Millipore Milli-Q UV Plus system ($R=18.2 \text{ M}\Omega\cdot\text{cm}$).

All glassware were dipped in the acidic potassium dichromate solution overnight, and then rinsed with tap water and pure water repeatedly.

Experimental Equipment

The ozonation experiments were carried out in semi-continuous mode. The cylindrical reactor (Figure 2) was made of glass with the inside diameter 50 mm, length of 700 mm, which was enclosed with sintered paper to avoid the light-decomposition effect. Ozone was generated by a corona discharge ozone generator (DHX-I, Harbin Jiujiu Electrochemistry Technology Co. Ltd. China) using air as feed gas. The ozone gas concentration was 0.45 mg/min with the constant flow rate of 400 mL/min at 293 K. The ozone was introduced into the reactor through a porous titanium sand plate laid at

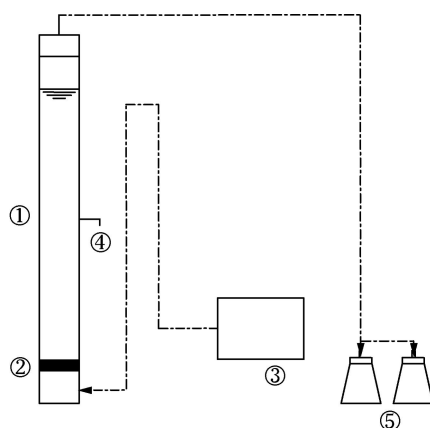


Figure 2. Schematic diagram of ozonation system. ① Ozonation reactor ② Aeration plate ③ Ozone generator ④ Sampling point ⑤ KI trap.

50 mm height higher than the bottom. The off gas was adsorbed by the potassium iodide solution. Before the experiment operation, 500 mL of pure water was first added into the reactor, and then ozonized for 5.5 min, which was proven to reach the constant ozone concentration in aqueous solution in the pre-test. The SA solution then was immediately added into the ozonated solution with the volume of less than 5 mL water samples were withdrawn at specific intervals for ozone concentration measurement and SA qualification. For the samples used for SA qualification, sodium thiosulfate was used to quench further oxidation.

Analytical Method

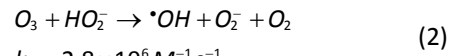
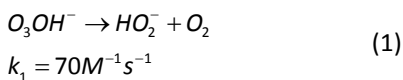
A High Performance Liquid Chromatography system (HPLC, Waters UV/Visible 2489, Waters e2695 Separation Module, Welch Materials, Inc.) and a 150 mm × 4.6 mm C₁₈ 5 μm reversed-phase column (Ultimate AQ-C18, Hypersil Gold, Supelco, Inc., Bellefonte, PA) were used to detect SD, SMX, and nitrobenzene. SD, SMX, and NB were analyzed at 265 nm with the mobile phase of 0.1% formic acid and acetonitrile (70:30, ratio by volume). The flow rate was 1 000 μL/min, and the retention times for SD, SMX, and NB were 3.5, 5.2, and 12.3 min, respectively. The concentrations of ozone in the gas and aqueous solution were determined by the iodometric titration method and indigo method, respectively^[14-15]. pH was adjusted by phosphate buffer and monitored by Metrohm pH Meter (Switzerland).

Kinetics Studying Method

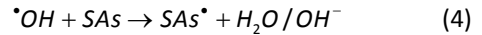
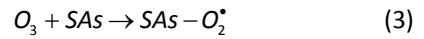
The solute consumption method and competition kinetic method^[16-17] were used to study the kinetics of ozone molecule and hydroxyl radicals with SAs. Nitrobenzene was chosen as reference compound. The rate constants of nitrobenzene with ozone molecule and hydroxyl radicals were reported to be $0.09 \pm 0.02 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$ and $3.9 \times 10^9 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$ ^[18-19].

RESULTS

In aqueous solution, ozone will be decomposed into hydroxyl radicals ($\cdot\text{OH}$) (see Equation 1-2) (unless under strong acidic pH condition), then in ozonation SAs should be oxidized by ozone and hydroxyl radicals will react with SAs in water (see Equation 3-4).



$$k_2 = 2.8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$$



The rate of depletion of SAs therefore is the consequence of its second order parallel reaction with dissolved ozone and with hydroxyl radicals:

$$-\frac{d[\text{SAs}]}{dt} = k_{\text{O}_3, \text{SAs}} [\text{SAs}] [\text{O}_3] + k_{\cdot\text{OH}, \text{SAs}} [\text{SAs}] [\cdot\text{OH}] \quad (5)$$

Where $k_{\text{O}_3, \text{SAs}}$ and $k_{\cdot\text{OH}, \text{SAs}}$ stand for the rate constants of ozone with SAs and hydroxyl radicals towards SAs, respectively. And $[\text{SAs}]$ stands for the concentration of SAs, $[\text{O}_3]$ stands for the concentration of ozone, $[\cdot\text{OH}]$ stands for the concentration of hydroxyl radicals, and t stands for the reaction time.

The kinetics of a gas-liquid ozonation process depends on the relative rates of physical absorption and chemical reaction. The kinetic regime is determined by the Hatta number, which represents the maximum rate of chemical reaction relative to the maximum rate of mass transfer. For a second order reaction the Hatta number is:

$$Ha_2 = \frac{\sqrt{k_2 D_A C_{Bb}}}{k_L} \quad (6)$$

In which k_2 is the decomposition rate constant of ozone, D_A is the diffusivity of ozone in water, C_{Bb} is the function of chemical and mass transfer of the organic compound.

When $Ha_2 < 0.3$, the reaction belongs to the slow speed reaction system; $0.3 < Ha_2 < 3$, the reaction belongs to the medium speed reaction system; $Ha_2 > 3$, the reaction belongs to the fast speed reaction system.

Kinetics of Ozone Molecule with SAs

To ensure that the ozone molecule acted as the sole oxidant, pH of the solution was adjusted to 2.5, and the 25 mg/L of *tert*-butanol was added to prohibit the hydroxyl radicals reaction. During the ozonation process, ozone was continuously purged into the solution to keep the ozone concentration constant; therefore the reaction could be simplified as the pseudo-first order reaction. It was also indicated that the reaction belonged to the slow speed reaction system with $Ha_2 < 0.1$. Accordingly, the Eq. 5 can be rewritten as follows:

$$-\ln\left(\frac{[\text{SAs}]_t}{[\text{SAs}]_0}\right) = -k_{\text{O}_3, \text{SAs}} [\text{O}_3] t \quad (7)$$

Here, $[\text{SAs}]_0$ and $[\text{SAs}]_t$ represent the initial and t time concentration of SAs. Using k' as the apparent

rate constant ($k' = k_{O_3, SAs}[O_3]$), the data represented in Figure 3 and Figure 4 allow the calculation of apparent rate constant of ozone molecule with SAs, which yields $261 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$ and $303 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$ for $k_{O_3, SD}$ and $k_{O_3, SMX}$, respectively, which are relatively low constants for the direct ozonation reaction. As is customary, the boundaries represent 95% confidence intervals. To further verify the accuracy of the experimental system, the kinetic of ozone molecule oxidization of nitrobenzene was also studied in the same experimental condition with the SAs tests. The value obtained in this work for the rate constant of $k_{O_3, Nitrobenzene}$ was $0.12 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$, which indicated that the kinetic data for ozonation of SAs were creditable.

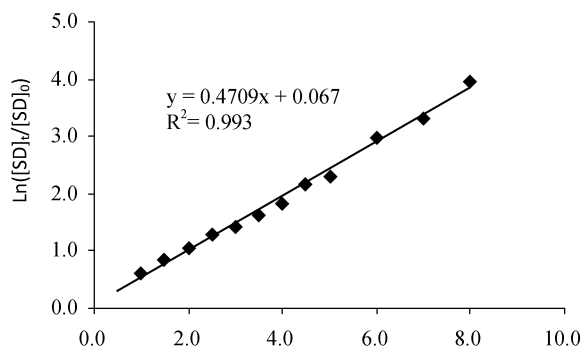


Figure 3. Pseudo first order kinetic plot of oxidation reaction of sulfadiazine by ozone alone.

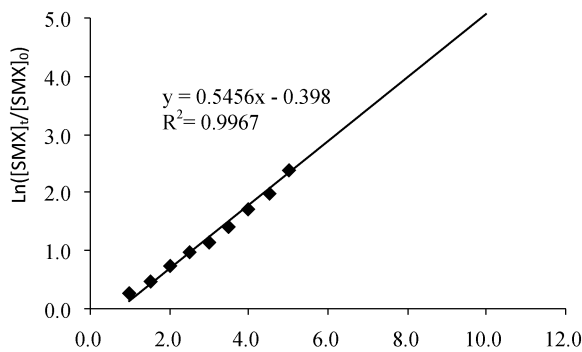


Figure 4. Pseudo first order kinetic plot of oxidation reaction of sulfamethoxazole by ozone alone.

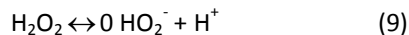
Kinetic of Hydroxyl Radicals with SAs

In this experiment, the O_3/H_2O_2 system was used to represent the hydroxyl radical reaction process, and pH was adjusted to 7.0 with phosphorous buffer. In O_3/H_2O_2 system, the Hatta number value is

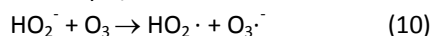
calculated based on Equation 7, which is different from the ozone alone system.

$$Ha_2 = \sqrt{\frac{k_{i2} 10^{pH-pK} C_{H_2O_2} D_{O_3}}{k_L (1 + 10^{pH-pK})}} \rightarrow \quad (8)$$

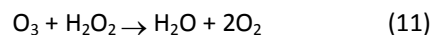
In which k_{i2} is the decomposition rate constant of ozone, $C_{H_2O_2}$ is the concentration of hydrogen peroxide, D_{O_3} is the diffusivity of ozone in water, K_L is the aqueous transfer coefficient. From Equation 7, the Hatta number is the function of solution pH and the concentration of H_2O_2 . Under the condition of pH 7.0 and with the concentration of H_2O_2 1 mmol/L, the Hatta number equals to 0.006, and it belongs to the slow speed reaction system. Under this pH condition, hydrogen peroxide will be decomposed into HO_2^- , and then the reactions occurring in the O_3/H_2O_2 oxidation systems are shown as Equation 9-11, while the reaction shown in Equation 1 could be ignored due to its low reaction rate constant.



$$pK_a = 11.8$$



$$k_3 = 2.2 \times 10^6 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$$



$$k_4 < 10^{-2} \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$$

As recommended by von Gunten and Elovitz, a R_{ct} value can be utilized to describe the molar concentration ratio of $\cdot OH$ to ozone during ozonation process as described in Equation 12^[20], and under different reaction conditions, including pH, alkalinity, DOC, temperature and others, the R_{ct} value is in the range of 10^{-7} - 10^{-9} [21]. Consequently, the concentration of SAs and NB at a specific reaction time (t) can be described by Equation 13-14. Then the reaction rate constant of SAs could be derived from Equation 15-16. Through fitting the experimental data shown in Figure 5 and Figure 6 with the above mathematical model, the rate constants of hydroxyl radicals with SD ($k_{\cdot OH, SD}$) and SMX ($k_{\cdot OH, SMX}$) under pH 7.0 are $2.2 \times 10^{10} \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$ and $2.7 \times 10^{10} \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$, respectively.

$$R_{ct} = \frac{\int [\cdot OH] dt}{\int [O_3] dt} \quad (12)$$

$$-\ln \frac{[SAs]_t}{[SAs]_0} = k_{\cdot OH, SAs} R_{ct} \int_0^t [O_3] dt \quad (13)$$

$$-\ln \frac{[NB]_t}{[NB]_0} = k_{\cdot OH, NB} R_{ct} \int_0^t [O_3] dt \quad (14)$$

$$\frac{k_{\cdot OH, SAs}}{k_{\cdot OH, NB}} = \ln \frac{[SAs]_t}{[SAs]_0} / \ln \frac{[NB]_t}{[NB]_0} \quad (15)$$

$$k_{OH,SAs} = k_{OH,NB} \times \left(\ln \frac{[SAs]_t}{[SAs]_0} / \ln \frac{[NB]_t}{[NB]_0} \right) \quad (16)$$

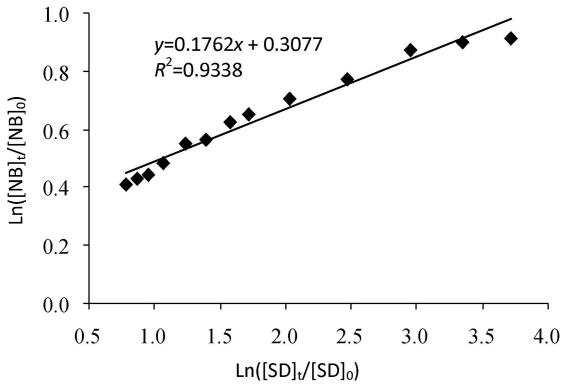


Figure 5. The relationship between $\ln([SD]_t/[SD]_0)$ and $\ln([NB]_t/[NB]_0)$.

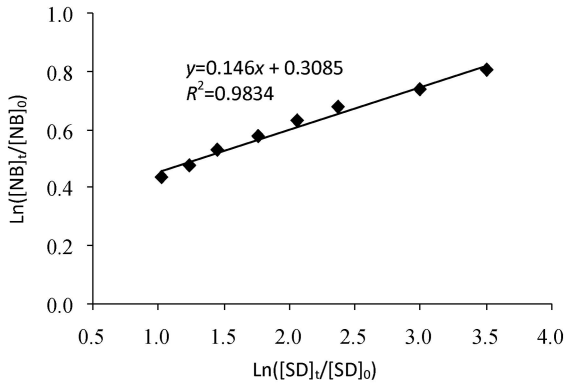


Figure 6. The relationship between $\ln([SMX]_t/[SMX]_0)$ and $\ln([NB]_t/[NB]_0)$.

Effect of pH on Rate Constants of Hydroxyl Radicals with SAs

The rate constants of hydroxyl radicals with SAs were observed under different pH conditions using phosphate as buffer, and the calculating results were summarized in Table 1. The rate constant obviously augmented with pH increase, though in a slight way.

Table 1. Rate Constants of Hydroxyl Radical Reaction under different pH Conditions

pH	Rate Constants ($\text{mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$)			
	SD	R^2	SMX	R^2
5.0	3.6×10^9	0.968	1.6×10^{10}	0.991
5.8	1.2×10^{10}	0.989	2.0×10^{10}	0.989
6.5	1.7×10^{10}	0.973	2.3×10^{10}	0.988
7.0	2.2×10^{10}	0.993	2.7×10^{10}	0.983
7.8	2.8×10^{10}	0.996	4.0×10^{10}	0.994

DISCUSSION

From the experimental data, it can be concluded that sulfadiazine and sulfamethoxazole are more liable to be oxidized by hydroxyl radicals, as compared with ozone alone oxidation. Although ozone has strong oxidative ability for its high oxidative potential of 2.07 V, it is inferior to hydroxyl radicals. Hydroxyl radicals are one of the most reactive free radicals and are deemed as one of the strongest oxidants with the oxidative potential of 2.85 V^[22-23]. And ozone, being a kind of powerful oxidant, is highly selective and reacts slowly with some organic compounds, and the reaction rate constants are typical in the range of $k_{O_3} = 1.0 - 10^3 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$; while hydroxyl radicals react non-selectively and immediately ($k_{OH} = 10^8 - 10^{10} \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$) with organic compounds^[16,20].

The reaction of ozone with aromatic ring system is highly electrophilic and selective, and the benzene ring is relatively reactive. From the structure of sulfanilamide (Figure 1), $-NH_2$ serves as an electron-donor group, which results in the promotion of the reaction activity of benzene ring with ozone; while $-SO_2$ is an electron-withdrawing group, and the weakening of the electron density of the benzene ring will lead to the prohibition of the reaction activity. Based on the experimental data, it is deduced that the weakening effect may be stronger than the promoting effect. For SD and SMX, the methyl group on SMX is relatively reactive and has electron donor effect, so SMX reacts faster with ozone than SD.

For the process of oxidizing SD and SMX with hydroxyl radicals, the fast reaction rate constants should be attributed to the unselective reaction pathway and the high oxidizing oxidative ability of hydroxyl radicals. Further, the hydroxyl radicals may initiate the inert hydrogen on benzene ring and generate some organic radicals by dehydrogenation^[24], the formed organic radicals may participate in the further oxidizing of the SD and SMX, which may also contribute to its fast reaction. The effect of pH on the reaction rate constants of hydroxyl radicals with SAs is due to the fact that the deprotonated SMZ species, known to have higher reactivity towards ozone compared to protonated species^[18], becomes predominant as the pH increases. In addition, from Equation 1 and 9, it can be seen that more hydroxyl radicals will be generated with the increase of pH. As reported by Staehelin^[25], the decomposition rate of

ozone will increase by two orders of magnitude when pH increases by one unit from pH 4.0.

CONCLUSIONS

Using solute consumption and competitive kinetic methods, the kinetics of ozonation of SAs were studied. It is evident that sulfadiazine and sulfamethoxazole are refractory by ozone alone oxidation, but are prone to be oxidized by hydroxyl radicals. From the kinetics data obtained, it is reasonable to deduce that the advanced oxidation process, which is characterized by the generation of hydroxyl radicals, should be effective to degrade the sulfadiazine and sulfamethoxazole from water.

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