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Research article

Dual roles of hydroxyl radicals and effects of competition on ozonation kinetics of two phenazone-type pollutants

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ABSTRACT

Ozonation has been proved to be a promising approach for eliminating emerging pollutants in wastewater. In previous studies, emerging pollutants including diverse pharmaceuticals were found to exhibit significantly different ozonation reactivity. However, how the structural differences of emerging pollutants determine ozonation reactivity and mechanisms are still ambiguous. In this work, ozonation of dimethylaminophenazone (DMP) and acetylaminophenazone (AAA) with the same parent structure of phenazone but different substitution groups was investigated, in order to probe influencing mechanisms of structural differences on ozonation reactivity. Results show that DMP reacts with ozone and HO• almost 2 and 1 order of magnitude faster than AAA, respectively. At pH 8, HO• accelerates ozonation of DMP, but decreases ozonation of AAA. Competition simultaneously decreases degradation rate of the two phenazones, but effects on AAA are more significant than that on DMP. According to theoretical calculation results, differences in ozonation reactivity and mechanisms of the two phenazones can be mainly attributed to different substitution groups. The dimethylamino group in the structure of DMP increases the ozonation reactivity of phenazone by increasing reaction orbital energies and altering reaction sites, while the acetylamino group in the structure of AAA decreases the reaction orbital energy and therefore lowers the reactivity.

1. Introduction

The occurrence of a huge number of pharmaceuticals and their active metabolites in aquatic environments becomes an issue of increasing concerns, as these pollutants potentially cause ecological risks to aquatic organisms and humans. Among the pharmaceuticals the most commonly detected in aquatic environments are analgesics [1]. Phenazone-type drugs including phenazone and derivatives like dipyrone are frequently prescribed analgesics. According to Chinese statistical data, several thousand tons of dipyrone were produced in 2011 [2]. In other countries, phenazone-type drugs are also widely used, and often detected in wastewater effluents and surface waters [1,3–5]. An environmental risk assessment using hazard indexes shows that phenazone-type pollutants rank among the most relevant pharmaceuticals for invertebrates and algae [6]. In aquatic environments, some dipyrone metabolites can transform to persistent and toxic photolytic products [7]. Conventional wastewater treatment plants were found to remove only up to 30% of phenazone and less than 40% of acetylaminophenazone (AAA) [8], which is a final metabolite of dipyrone and frequently detected in wastewater and environmental waters [4,9,10]. Some widely used phenazones, e.g.

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phenazone, propyphenazone and dimethylaminophenazone (DMP), degrade fast through chlorination [11–13]. Unfortunately, chlorinated products were formed [11] and a high *N*-nitrosodimethylamine formation potential was observed for DMP [14], raising concerns on potential ecotoxicity. In a previous work, phenazone was found to react fast with O_3 with a bimolecular rate constant (k_{O3}) of 6.2 × 10^5 M^{-1} s^{-1} (pH = 7) [17], implying that ozonation might be an alternative approach for eliminating these pollutants in wastewater. However, for other widely detected phenazones, the ozonation reactivity and mechanisms are scarcely known.

Ozonation is well-known for its efficiency in eliminating diverse emerging organic pollutants, e.g. pharmaceuticals and personal care products (PPCPs) [15]. A fast elimination of emerging pollutants during ozonation can be attributed to oxidation by ozone molecule (O_3) and/or its hydrolytic product, hydroxyl radicals (HO•) [16]. Due to structurally differences, the reactivity of PPCPs reacting with O_3 ranges several orders of magnitude [17]. Even some PPCPs and their metabolites having the same parent structure but different substitution groups may show different ozonation reactivity. For example, N(4)-acetylsulfamethoxazole reacts with O_3 more than 3 orders of magnitude slower than sulfamethoxazole [18]. The role of HO• during ozonation differs among PPCPs. For example, direct O_3 oxidation plays an essential role in ozonation of many antibiotics at a neutral pH range [18]. But for ibuprofen reacting slowly with O_3, HO• oxidation becomes more important than direct O_3 oxidation [19]. These indicate that the ozonation reactivity of PPCPs could be highly dependent on molecular structures.

The ozonation kinetics of PPCPs was previously observed to be influenced by pH, organic matters, and anions, etc. [20–22] By employing individual k_{O3} values, ozonation rates of PPCPs in real wastewater were usually predicted by considering influence of wastewater matrix [23]. However, in real wastewater, numerous PPCPs of different ozonation reactivity coexist. The ozonation rates of PPCPs may be not only influenced by water matrix, but also by coexisting PPCPs, as PPCPs show diverse reactivity in ozonation [15,17]. However, the influence mechanism of coexisting PPCPs at molecular level is largely ambiguous.

In this work, individual and competition ozonation kinetics of two phenazones were investigated, including DMP and AAA. The two phenazones have the same parent structure of phenazone but different substitution groups on the pyrazole ring. The work shows that the substitution groups influenced strongly on the ozonation reactivity of phenazones, and moreover determined the role of HO• and competition effects. In order to elucidate the influence mechanisms of the substitution groups, theoretical computations were performed for characterizing locations of the frontier molecular orbitals (FMO) that related with ozonation. The calculation results show that the substitution groups determine electrophilic reactivity and reacting sites of DMP and AAA.

2. Materials and methods

2.1. Materials

AAA (purity of 97%, Alfa Aesar), DMP (purity of 97%, Acros Organics), 4-methoxycinnamic acid (MC, purity of 99%, Aldrich) and *p*-chlorobenzoic acid (*p*CBA, purity of 98%, J&K) were used as received. Methanol and acetonitrile were of HPLC grade. Other agents used were of analytical grade (A.R. grade, >99% pure). Ultrapure water was produced with a Milli-pore filtration system (Billerica, USA).

2.2. Kinetic experiments

Ozonation experiments were performed in a cylindrical reactor at room temperature of 20 ± 2 °C. Ozone was generated with an ozone generator (OL80F/DST, Ozone services, Canada), and passed into the reactor continuously at a constant feed concentration. Initial concentrations of AAA and DMP are 0.01 mM except that in competition experiments, where initial concentrations of the two compounds were halved in order to maintain the ratio of pollutants to import ozone. Kinetic experiments were performed at different pH conditions (3, 8 and 10) adjusted with phosphate, phosphoric acid and NaOH, in the presence of HO• scavengers, including *tert*-butyl alcohol (*t*-BuOH, 0.1 M), HCO_3^- (1.6 mM), Br^- (0.06 mM), and NO_2^- (0.1 mM), and in a wastewater effluent (WWEf) sample collected at 50 m downstream from the wastewater discharge outlet in Liangshui River receiving sewage effluents in Beijing, China. The pH value and total organic carbon (TOC) of the wastewater sample was determined as 7.2 and 12 mg L^{-1}. All the experiments were repeated in duplicate or triplicate.

Second-order reaction rate constants of the phenazones with O_3 (k_{O3}) and HO• ($k_{HO•}$) were determined with competitive kinetic experiments employing MC and *p*CBA as reference compounds, respectively. Experiments were performed at equal concentrations of reference and target compounds, i.e. 0.01 mM. For determining k_{O3}, *t*-BuOH was added to scavenge HO•. For determining $k_{HO•}$, H_2O_2 (10% v/v) was added for improving HO• generation. k_{O3} and $k_{HO•}$ values are calculated according to equations (1) and (2), respectively.

$$k_{O3,p} = k_{O3,MC}\frac{\ln\frac{c_{t,p}}{c_{0,p}}}{\ln\frac{c_{t,MC}}{c_{0,MC}}} \quad (1)$$

$$k_{HO\cdot,p} = k_{HO\cdot,pCBA}\frac{\ln\frac{c_{t,p}}{c_{0,p}}}{\ln\frac{c_{t,pCBA}}{c_{0,pCBA}}} \quad (2)$$

where, $k_{O3,\,p}$ and $k_{HO•,\,p}$ are second-order reaction rate constants of the phenazones; $k_{O3,\,MC}$ and $k_{HO•,\,pCBA}$ are second-order reaction rate constants of the reference compounds.

2.3. Analytical methods

A HPLC-UV system (Waters, USA) employing a reverse-phase TC-C18 column (150 mm × 4.6 mm, 5 μm, Agilent, USA) was used for analyzing target and reference compounds. Mobile phases and detected wavelengths are methanol:H_2O (3:7), 254 nm for AAA, acetonitrile:H_2O (4:6), 254 nm for DMP, methanol:H_2O (4:6) with 0.1% H_3PO_4, 287 nm for MC, and methanol:H_2O (7:3) with 0.5‰ H_3PO_4, 236 nm for *p*CBA.

2.4. Calculation methods

Geometries of target compounds and phenazone were optimized based on density functional theory (DFT) at the B3LYP/6-31+G(d,p) level. Frequency analysis was performed at the same level to characterize the stationary points. FMO were calculated at the B3LYP/6-311+G(3df,2p) level for characterizing electrophilic reactivity and electrophile preferring attack sites. The integral equation formalism polarized continuum model based on the self-consistent-reaction-field [24] was employed in all calculations including geometry optimization. All DFT calculations were performed with Gaussian 09 software package [25].