Kinetics and Mechanism of Degradation of Reactive Radical-Mediated Probe Compounds by the UV/Chlorine Process: Theoretical Calculation and Experimental Verification

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ABSTRACT: The UV/chlorine process, by combining chlorination with UV irradiation, has been recently considered as a highly efficient advanced oxidation process (AOP) technology in water treatment. Nitrobenzene (NB), benzoic acid (BA), and p-chlorobenzoic acid (pCBA) are widely used as model probe compounds in the UV/chlorine system to calculate the second-order rate constants of the specific radical reaction with target contaminants by a competitive kinetics method. A comprehensive understanding of probe compounds’ reaction mechanism with reactive radicals is critical for investigation of the UV/chlorine reaction system. Here, we evaluated the radical-mediated reaction kinetics and mechanism of NB, BA, and pCBA in the UV/chlorine process using theoretical calculations and experimental studies. The main reactive radicals *OH, *ClO, and *Cl in the UV/chlorine process for the initial reaction with NB, BA, and pCBA can be explained by H-abstraction and addition pathways. The $\Delta E^{\text{CI}}$ values for the *OH reaction with NB, BA, and pCBA were in the range of 5.0–8.0, 3.7–8.2, and 3.4–8.2 kcal mol$^{-1}$, respectively. The $\Delta E^{\text{CI}}$ values for *ClO and *Cl reactions with these three probe compounds were higher than those of *OH, indicating slower *ClO- and *Cl-initiated reactions than that of the *OH-initiated reaction. The theoretically calculated radical-mediated reaction kinetic rate constants ($k_{\text{CI}}$) for NB, BA, and pCBA were $4.58 \times 10^{-3}$, $1.28 \times 10^{-3}$, and $1.6 \times 10^{-2}$ s$^{-1}$, respectively, which was consistent with the experimentally determined pseudo-first-order rate constant ($k_{p,\text{CI}}$) in the UV/chlorine process. Interestingly, theoretical calculations showed that *ClO and *Cl played an important role in subsequent reactions of NB-OH radicals, converting to hydroxylated and chlorinated products, which were further confirmed by experimental products’ identification. The findings from this study indicated that quantum chemistry calculations provide an effective means to investigate the reaction kinetics and mechanism of chemicals in the UV/chlorine process.

1. INTRODUCTION

Conventional drinking water and wastewater treatment systems are based on the UV irradiation or chlorination disinfection process to inactivate pathogenic microorganisms and control waterborne diseases. To remove emerging contaminants and reduce disinfection byproducts (DBPs), various advanced oxidation processes (AOPs) are frequently used in water and wastewater treatment systems. The UV/chlorine process, by combining chlorination with UV irradiation, has been recently considered as a highly efficient AOP technology. There are many reactive radicals produced by the UV/chlorine process: *OH and *Cl are produced via the chain initiation homolytic cleavage reaction after UV irradiation of HOCl; other reactive radicals (*ClO, *Cl$^-$, *HOCI$^-$) are produced by chain transitive sets. For example, *Cl can react with water to produce *HOCI and with Cl$^-$ to produce *Cl$^-$; the *OH can react with HOCl to produce *ClO. The *OH is a nonselective radical with a strong oxidation capacity. The *Cl can be generally more selective than *OH and preferentially react with compounds containing electron-rich moieties. The *ClO has been found to also play an important role in the degradation of some pharmaceuticals during the UV/chlorine process. These diverse reactive radicals in the UV/chlorine process make it efficient to degrade a wide range of contaminants in water. It is thus essential to inquire into the contributions of these reactive radicals in the UV/chlorine process. Various model probe compounds have been used to quantify the concentrations of selected radicals and calculate the second-order rate constants of specific reactive radicals. For example, nitrobenzene (NB), benzoic acid (BA), and p-chlorobenzoic acid (pCBA) are commonly used as probe compounds in the UV/chlorine process. NB and pCBA are...
probe compounds of •OH since they have very low reactivity with •Cl and •Cl₂. The compound BA is usually used as the probe compound of •Cl by calculating the difference in the reaction rate constants with NB in the UV/
Furthermore, the kinetics of reactive species in the UV/chlorine process can be mathematically modeled by considering different elementary reactions. There are some uncertainties in calculating the contributions.
of reactive radicals based on these probe compounds; therefore, more understanding of their reaction kinetics and mechanism is still needed.

It is known that quantum chemistry is an effective method to understand the mechanism of chemical reaction by calculating the charge distribution, molecular properties, and potential energy surfaces of reactions. Many studies have shown that density functional theory (DFT) is a powerful tool to calculate reaction pathways, kinetics, and byproducts of target compounds under specific ambient conditions.\textsuperscript{22,23} According to DFT calculations, *OH and *Cl initial reactions were via *OH (*Cl) addition to unsaturated bonds or H-abstraction with target compounds in the atmosphere or an aquatic environment.\textsuperscript{24–26} Thus, the reaction mechanism of reactive species with target compounds in the UV/chlorine process can be further investigated using DFT calculations.

The purpose of this study is to elucidate the kinetics and products (Ps) of the main reactive radicals (*OH, *ClO, and *Cl) reaction with selected probe compounds (NB, BA, and pCBA) in the UV/chlorine process by DFT calculations. The impact of an aqueous solvent was simulated by the implicit solvation model and explicit water molecules. The theoretically calculated results were verified by the experimental data, and the feasibility of using these probe compounds to determine the kinetics of contaminants in the UV/chlorine process was also discussed.

2. RESULTS AND DISCUSSION

2.1. Initial Reactions of Reactive Radicals with Probe Compounds. The UV/chlorine process produces reactive species such as *OH, *Cl, *Cl\textsubscript{2}, *ClO, *O, etc. Generally, the *OH and *Cl reactions contribute substantially to persistent chemical degradation, while the roles of other reactive species such as *Cl\textsubscript{2} and *O are negligible.\textsuperscript{27} Furthermore, the *ClO-related reactive species, generated by the reaction between chlorine and *OH/*Cl, play a major role in addition to *OH and *Cl for containment degradation.\textsuperscript{29} Therefore, the initial reaction of *OH, *ClO, and *Cl in the UV/chlorine process was mainly investigated by DFT calculation in the following sections. By taking into account the pKa of these three probe compounds (NB at 3.98, BA at 4.19, and pCBA at 3.97, Figure S2), NB is in the molecular form within the studied pH value (pH = 7.0), while BA and pCBA are in the anionic form, denoted BA\textsuperscript{−} and pCBA\textsuperscript{−}, respectively. Thus, NB, BA\textsuperscript{−}, and pCBA\textsuperscript{−} were selected for further DFT calculations. The optimized molecular structures of NB, BA, BA\textsuperscript{−}, pCBA, and pCBA\textsuperscript{−} are shown in Figure S3.

2.1.1. Initial Reactions of *OH. Schematic potential energy surfaces (ΔE\textsubscript{PES}, kcal mol\textsuperscript{−1}) of 11 reaction pathways were first calculated for NB, BA\textsuperscript{−}, and pCBA\textsuperscript{−} reactions with *OH, including five H-abstraction pathways and six *OH-addition pathways. Considering the symmetrical sites of C\textsubscript{2}−C\textsubscript{6} and C\textsubscript{2}−C\textsubscript{1} in our probe compounds, only three H-abstraction pathways and four *OH-addition pathways are shown in Figure 1. The complete ΔE\textsubscript{PES} data and the corresponding reaction enthalpy between reactant (RC) and intermediate (IM) values (ΔH\textsubscript{P}, kcal mol\textsuperscript{−1}) are provided in Table S4. For the NB reaction with *OH, the overall ΔE\textsubscript{PES} values for the *OH-addition pathways are lower than those of the H-abstraction pathways (Figure 1a), similar to the antiviral drug acyclovir reacting with *OH.\textsuperscript{28} The *OH addition at parapositions (C\textsubscript{2} and C\textsubscript{6}) with a ΔE\textsubscript{PES} value of 5.0 kcal mol\textsuperscript{−1} is the most favorable reaction pathway, followed by *OH addition at orthopositions (C\textsubscript{1} and C\textsubscript{6}) pathways (5.3 kcal mol\textsuperscript{−1}) and the paraposition (C\textsubscript{1}) pathway (5.3 kcal mol\textsuperscript{−1}). The remaining C\textsubscript{2} *OH-addition pathway and H-abstraction pathways are less favorable with ΔE\textsubscript{PES} values of 7.1−8.0 kcal mol\textsuperscript{−1}, and the H-abstraction at orthoposition (C\textsubscript{1} and C\textsubscript{6}) pathways (8.0 kcal mol\textsuperscript{−1}) is the least favorable reaction pathway. Figure 1b shows ΔE\textsubscript{PES} surfaces for the reaction pathways of BA\textsuperscript{−} with *OH. It is similar to the NB reaction with *OH; the main reaction pathway for BA\textsuperscript{−} is also *OH addition. In contrast, the most favorable pathways for BA\textsuperscript{−} reaction with *OH are metaposition (C\textsubscript{2} and C\textsubscript{6}) *OH-addition pathways (3.7 kcal mol\textsuperscript{−1}) and the paraposition (C\textsubscript{1}) *OH-addition pathway (3.8 kcal mol\textsuperscript{−1}), followed by orthoposition (C\textsubscript{1} and C\textsubscript{6}) *OH-addition pathways (5.7 kcal mol\textsuperscript{−1}). The highest ΔE\textsubscript{PES} is the C\textsubscript{1} *OH-addition pathway (8.2 kcal mol\textsuperscript{−1}), even higher than H-abstraction pathways. As shown in Figure 1c, there is little difference between ΔE\textsubscript{PES} of H-abstraction pathways and *OH-addition pathways (3.4−8.2 kcal mol\textsuperscript{−1}) for the pCBA\textsuperscript{−} reaction with *OH. Furthermore, metaposition (C\textsubscript{2} and C\textsubscript{6}) *OH-addition pathways (3.4 kcal mol\textsuperscript{−1}) are the most favorable pathways. On the whole, *OH-addition is the main pathway for the *OH reaction with NB, BA\textsuperscript{−}, and pCBA\textsuperscript{−}, and the *OH-addition pathway at metapositions (C\textsubscript{2} and C\textsubscript{6}) is the most favorable pathway. The pCBA\textsuperscript{−} reaction with *OH has the lowest ΔE\textsubscript{PES} values, followed by BA\textsuperscript{−} and NB. Moreover, all of the reaction pathways are thermodynamically spontaneous (ΔH\textsubscript{P} < 0).

2.1.2. Initial Reactions of *ClO. Schematic ΔE\textsubscript{PES} surfaces of reaction pathways that include five H-abstraction pathways and six *ClO-addition pathways are depicted in Figure 2. The complete potential energy data and corresponding ΔH\textsubscript{P} values are shown in Table S5. Like the *OH, the overall ΔE\textsubscript{PES} values for the *ClO-addition pathways are also lower than those of the H-abstraction pathways for the NB reaction with *ClO (Figure 2a). The *ClO addition at orthoposition (C\textsubscript{1} and C\textsubscript{6}) pathways of NB are the most favorable reaction pathways with an ΔE\textsubscript{PES} of 9.7 kcal mol\textsuperscript{−1}, followed by *ClO addition at the paraposition (C\textsubscript{1}) pathway (12.8 kcal mol\textsuperscript{−1}), metaposition (C\textsubscript{2} and C\textsubscript{6}) pathways (13.4 kcal mol\textsuperscript{−1}), and the C\textsubscript{1} pathway (13.3 kcal mol\textsuperscript{−1}). The H-abstraction pathways of NB are less favorable, with ΔE\textsubscript{PES} in the range of 16.1−18.8 kcal mol\textsuperscript{−1}. Figure 2b shows ΔE\textsubscript{PES} surfaces for the reaction pathways of BA\textsuperscript{−} and *ClO. The main reaction pathway is also the *ClO-addition reaction with ΔE\textsubscript{PES} between 10.0 and 11.4 kcal mol\textsuperscript{−1}. However, all of the H-abstraction pathways have similar ΔE\textsubscript{PES} (17.6−18.0 kcal mol\textsuperscript{−1}). For the pCBA\textsuperscript{−} reaction with *ClO, *ClO addition is the dominant pathway (Figure 2c). Additionally, the *ClO-addition pathways at orthopositions (C\textsubscript{1} and C\textsubscript{6}, 9.7 kcal mol\textsuperscript{−1}) are the most favorable pathways. In general, *ClO addition is the main pathway for the *ClO reaction with NB, BA\textsuperscript{−}, and pCBA\textsuperscript{−}. The orthoposition (C\textsubscript{1} and C\textsubscript{6}) *ClO-addition pathways are the most favorable pathways for these three probe compounds, which are different from the *OH initial reactions. The BA\textsuperscript{−} reaction with *ClO has the lowest ΔE\textsubscript{PES} values, followed by pCBA\textsuperscript{−} and NB. About the ΔH\textsubscript{P} values, all of the H-abstraction reaction and *ClO-addition pathways at metapositions (C\textsubscript{2} and C\textsubscript{6}) and the C\textsubscript{1} position are positive, meaning that these are endothermic reactions; the other *ClO-addition pathways are negative, meaning that they are exothermic reactions. Compared with
The reactions among NB, BA\(^-\), pCBA\(^-\), and *Cl are slower.

### 2.1.3. Initial Reactions of *Cl.

It has been reported that *Cl addition to the phenyl group is unlikely to happen.\(^{27,31}\) Thus, only H-abstraction reaction pathways are shown in Figure 3. The complete potential energy data and the corresponding \(\Delta H^0\) values are shown in Table S6. For the H-abstraction reaction of the NB reaction with *Cl (Figure 3a), the paraposition (C\(_1\)) pathway (6.5 kcal mol\(^{-1}\)) is the most favorable reaction site, and the others are less favorable (12.5–16.4 kcal mol\(^{-1}\)). For the BA\(^-\) reaction with *Cl (Figure 3b), H-abstraction only reacted at orthoposition (C\(_4\) and C\(_5\)) pathways (15.6 e kcal mol\(^{-1}\)). The potential energy surface scan results showed that the total energy increased as the hydrogen atom at C\(_1\) (C\(_2\) and C\(_3\)) positions moved far away from the carbon atom when *Cl approached. As revealed by Figure 3c, metaposition (C\(_2\) and C\(_3\)) pathways (8.2 kcal mol\(^{-1}\)) are more favorable than the orthoposition (C\(_4\) and C\(_5\)) H-abstraction pathways (16.8 kcal mol\(^{-1}\)) for the pCBA\(^-\) reaction with *Cl. The \(\Delta H^0\) values showed that most of the *Cl-initiated reactions are endothermic reactions. In the main, the *Cl-initiated reactions are slower than those of *OH for NB, BA\(^-\), and pCBA\(^-\). Besides, the *Cl-initiated reactions are faster than that of *ClO for NB and pCBA\(^-\) but opposite for BA\(^-\).

#### 2.1.4. Impact of Explicit Water on the Initial Reactions.

The impact of 1–4 explicit water molecules on initial reactions was investigated by the SMD model. The reaction of NB with *OH, *ClO, and *Cl at the paraposition (C\(_1\)) was chosen as an example (Figure 4 and Table S7). The theoretically calculated results showed that water molecules do not participate in the initial reaction but only connect with each other and NB by hydrogen bonds. These hydrogen bonds lead to the stability of the complex system. As shown in Figure 4a, the \(\Delta E^0\) values fluctuated with the addition of 1–4 water molecules for the addition reaction of NB with *OH and converged to a value slightly higher than the initial \(\Delta E^0\) value. A similar result was also found in a previous study, where the explicit water molecules only form hydrogen bonds. With the explicit water (1–4 H\(_2\)O), the \(\Delta G^0\) values of the tris(2-chloroisopropyl) phosphate reaction with *OH increased slightly.\(^{32}\) For the addition reaction of NB with *ClO (Figure 4b), the addition of 1–4 water molecules decreased the \(\Delta E^0\) values. It means that water molecules will promote this reaction. However, water molecules significantly inhibited the reaction of NB with *Cl (Figure 4c) since the \(\Delta E^0\) values increase with the addition of 1–4 water molecules. Although the \(\Delta E^0\) values can be impacted by explicit water molecules, the most favorable reaction pathway is invariant.\(^{33,34}\)

#### 2.2. Kinetics Calculation of Initial Reactions.

The reaction kinetics rate constants \(k_{CP,OH}\) for reactive radical-mediated probe compounds’ degradation were calculated based on the DFT-calculated \(k\) values (M\(^{-1}\) s\(^{-1}\)) and steady-state concentrations of reactive radicals (M). The \(k\) was calculated by considering the contribution of all of the reaction sites for NB, BA\(^-\), and pCBA\(^-\) reactions with reactive radicals *OH, *ClO, and *Cl. Tables S4–S6 show \(k\) of each reaction site with reactive radicals. As shown in Table 1, the DFT-calculated \(k_{CP,OH}\) values of NB, BA\(^-\), and pCBA\(^-\) are about 10\(^{8}\)–10\(^{9}\) M\(^{-1}\) s\(^{-1}\), while the \(k_{CP,ClO}\) and \(k_{CP,Cl}\) still have 10\(^{8}\)–10\(^{9}\) M\(^{-1}\) s\(^{-1}\). Thus, the initial reaction with *OH is the most important pathway for NB, BA\(^-\), and pCBA\(^-\) in the UV/chlorine process. However, the other two radicals (*ClO and *Cl) are not important.

![Figure 3](https://doi.org/10.1021/acsonew margins 15%2C15%2C20%2C20) Relative potential energies (\(\Delta E^0\), kcal mol\(^{-1}\)) of initial reactions among NB, BA\(^-\), pCBA\(^-\), and *Cl. The molecular structures in (a) and (b) represent *OH addition and H-abstraction at the paraposition (C\(_1\)) and those in (c) represent *OH addition and H-abstraction at the metaposition (C\(_2\)). H means H-abstraction, and A means *OH addition.
*Cl) can also react with these three compounds. According to previous studies, the steady-state concentration of reactive radicals can be determined by probe compounds or simulated by calculating the kinetic model. Here, we use the same order of magnitude for the steady-state concentration of reactive radicals ([OH]) = 1 × 10^{-14} M; ([ClO]) = 1 × 10^{-10} M; ([Cl]) = 1 × 10^{-15} M) due to the similar UV/chlorine experimental conditions. The reaction kinetic rate constant (k_{C}^{CP}, s^{-1}) was calculated by eq 1

\[ k_{C}^{CP} = k_{CP-OH} \times [\text{OH}]_{SS} + k_{CP-ClO} \times [\text{ClO}]_{SS} + k_{CP-Cl} \times [\text{Cl}]_{SS} \]  

where C means calculated and CP means compounds, referring to NB, BA−, or pCBA−. The k_{C}^{CP} values for NB, BA−, and pCBA− were 4.58 × 10^{-3}, 1.28 × 10^{-3}, and 1.6 × 10^{-2} s^{-1}, respectively. The k_{C}^{CP} values are consistent with the experimentally determined pseudo-first-order rate constants (k_{BP}^{CP}) in UV/chlorine experiments (see Section 2.4). It means that *OH, *ClO, and *Cl played a major role in the UV/chlorine process to degrade these three probe compounds. The results illuminated that it is reliable to calculate the rate constants (M^{-1} s^{-1}) of target contaminants according to the ΔE^{0,φ} values in the initial reactions.

2.3. Subsequent Reactions of Nitrobenzene-Oh Radicals. All these three probe compounds have substituted benzene group; thus, we took NB as an example. The subsequent reaction pathways of NB are similar and referable for BA− and pCBA−. Among the reaction pathways of NB with *OH, *ClO, and *Cl, the dominant reaction is NB with *OH because of the lowest ΔE^{0,φ}. Then, the chemically activated nitrobenzene-OH radicals (NB-OH) can subsequently react with *OH, *ClO, and *Cl. There are two kinds of NB-OH: one is the activated intermediate produced by the *OH-addition reaction (NB-OH-A), and the subsequent reactions with three radicals are H-abstraction at active sites; the other is the activated intermediate produced by the H-abstraction reaction (NB-OH-H), and the subsequent reactions are three radicals getting closer to active sites and forming a chemical bond. Figure 5 shows schematic ΔE^{0,φ} surfaces of the NB-OH reaction with *OH, *ClO, and *Cl at the paraposition (C1). The other reactions at metapositions (C2 and C6), orthopositions (C3 and C5), and the C4 position are shown in Figure S4. All of the ΔE^{0,φ} and ΔE^{φ} values for NB-OH reactions are provided in Table S8. The results showed that the NB-OH-H reaction with *OH, *ClO, and *Cl is barrierless. The potential energy surface scan results showed that the total energy decreased as *OH, *ClO, and *Cl approached NB-OH-H. The ΔE^{φ} values demonstrated that the relative stability and proportion of the products are on the order of NB-OH > NB-Cl > NB-ClO, as shown in Figure 5. The NB-OH-A reactions with *OH, *ClO, and *Cl have corresponding transition states (TSs), and the general trend for the favorable H-abstraction reaction of NB-OH-A with the radical is *OH > *ClO > *Cl. Subsequent reactions of paraposition (C1), metaposition (C2 and C6), and orthoposition (C3 and C5) conform to this rule, except for the C4 position. For the reaction NB-OH-A with *OH (*ClO and *Cl) at the C4 position, the ΔE^{0,φ} values are much higher than those of the other positions, indicating the less favorable reaction site. Thus, the theoretically calculated transformation products of NB were chlorinated-NB and hydroxyl-NB, and hydroxyl-NB was the main product (Figure 5). There was little difference in

\[ \Delta E^\phi \text{ (kcal mol}^{-1}\text{)} \]  

\[ \text{NB} \quad \text{OH} \quad \text{TS 3 H}_2\text{O} \quad \text{TS 1 H}_2\text{O} \quad \text{TS 4 H}_2\text{O} \quad \text{TS 0 H}_2\text{O} \quad \text{TS 2 H}_2\text{O} \]  

\[ \Delta E^\phi \text{ (kcal mol}^{-1}\text{)} \]  

\[ \text{NB} \quad \text{ClO} \quad \text{TS 0 H}_2\text{O} \quad \text{TS 1 H}_2\text{O} \quad \text{TS 2 H}_2\text{O} \quad \text{TS 3 H}_2\text{O} \quad \text{TS 4 H}_2\text{O} \]  

\[ \Delta E^\phi \text{ (kcal mol}^{-1}\text{)} \]  

\[ \text{NB} \quad \text{Cl} \quad \text{TS 2 H}_2\text{O} \quad \text{TS 1 H}_2\text{O} \quad \text{TS 3 H}_2\text{O} \quad \text{TS 4 H}_2\text{O} \quad \text{TS 0 H}_2\text{O} \]  

Figure 4. Relative potential energies (ΔE^φ, kcal mol^{-1}) of initial reactions between NB and *OH, *ClO, and *Cl with the addition of 1–4 explicit water molecules. (a) *OH reacted with NB by *OH addition at the C1 position. (b) *ClO reacted with NB by *ClO addition at the C1 position. (c) *Cl reacted with NB by H-abstraction at the C1 position.
Table 1. Theoretically Calculated and Experimentally Determined Degradation Rate Constants for Reactive Radical-Initiated Reactions of Nitrobenzene (NB), Benzoic Acid (BA−), and p-Chlorobenzoic Acid (pCBA−) in the UV/Chlorine Process

| compounds |  \( k_{CP-OH} \) M\(^{-1}\) s\(^{-1} \) |  \( [\text{OH}]_{ss} \) M |  \( k_{CP-ClO} \) M\(^{-1}\) s\(^{-1} \) |  \( [\text{ClO}]_{ss} \) M |  \( k_{CP-Cl} \) M\(^{-1}\) s\(^{-1} \) |  \( [\text{Cl}]_{ss} \) M |  \( k_{RR} \) s\(^{-1} \) |
|------------|---------------------------------|--------------------|---------------------------------|--------------------|---------------------------------|--------------------|------------------|
| NB         | 1.75 × 10\(^{11}\)            | 10\(^{-14}\)        | 2.56 × 10\(^7\)                | 10\(^{-10}\)        | 2.70 × 10\(^9\)                | 10\(^{-13}\)        | 4.58 × 10\(^{-3}\) |
| BA−        | 1.05 × 10\(^{12}\)            | 2.32 × 10\(^7\)    | 1.83 × 10\(^9\)                | 3.13 × 10\(^7\)    | 2.8 × 10\(^{-2}\)              | 3.78 × 10\(^{-3}\)  | 1.6 × 10\(^{-2}\) |
| pCBA−      | 1.28 × 10\(^{12}\)            | 3.13 × 10\(^7\)    | 3.0 × 10\(^9\)                 | 1.28 × 10\(^{-2}\) | 1.6 × 10\(^{-2}\)              | 5.92 × 10\(^{-3}\)  | 5.92 × 10\(^{-3}\) |

\(^{a}\) \([\text{OH}]_{ss}, [\text{ClO}]_{ss} \) and \([\text{Cl}]_{ss}\) are steady-state concentrations of reactive radicals; \( k_{CP} \) and \( k_{RR}\) are theoretically calculated and experimentally determined radical-mediated reaction kinetic rate constants, respectively; \( k_{CP-OH}, k_{CP-ClO}\) and \( k_{CP-Cl}\) are DFT-calculated second-order rate constants for the compound reaction with *OH, *ClO, and *Cl, respectively.

\[ \Delta E^0,\text{kl} \text{ kcal mol}^{-1} \text{ between different substitution sites of NB in the *OH-addition reaction, so that the conversion rates of the three hydroxyl products were uniform.} \]

In the UV/chlorine reaction system, all of the studied radicals contributed to the initial or subsequent reactions with NB. Although the reaction for NB with *OH is the main reaction in the UV/chlorine process by comparing the DFT-calculated rate constants (M\(^{-1}\) s\(^{-1}\)) in the initial reactions with three reactive radicals, the contribution of *ClO cannot be negligible when considering the steady-state concentration of three reactive radicals (Table 1). For the subsequent reactions of *NB-OH with *OH, *ClO, and *Cl, *Cl is generally more reactive than *OH in subsequent reactions of *NB-OH-A (Figure S5). The barrier-free reactions of *NB-OH-H indicated that the concentration of reactive radicals should be the determinant of these reaction pathways. Overall, both *ClO and *Cl cannot be ignored in NB degradation by the UV/chlorine process. Thus, the contributions calculated by NB for contaminants are probably overestimated because NB was deemed to only react with *OH. \(^{7,10,35}\)

2.4. UV/Chlorine Experimental Verification. The three probe compounds NB, BA, and pCBA were degraded by the UV/chlorine process, UV irradiation, and chlorination in pH 7.0 phosphate-buffered solutions (Figure S5). The pseudo-first-order degradation rate constants, \( k_{CP-ClO}, k_{CP-Cl} \) (s\(^{-1}\), CP means NB, BA, and pCBA), for corresponding treatments were obtained by eqs 2–4. The pseudo-first-order degradation rate constants of reactive radicals (\( k_{RR}\)) were obtained by eq 5.

\[ \ln \left( \frac{|CP|_{UV/Cl}}{|CP|_0} \right) = -k_{CP-Cl} \times t \] (2)

\[ \ln \left( \frac{|CP|_{UV}}{|CP|_0} \right) = -k_{CP-OH} \times t \] (3)

\[ \ln \left( \frac{|CP|_{UV}}{|CP|_0} \right) = -k_{CP-ClO} \times t \] (4)

\[ k_{RR} = k_{CP-ClO} - k_{CP-Cl} \] (5)

As shown in Figure S5a–c, the three probe compounds NB, BA, and pCBA were persistent in the chlorination treatment and only slightly decreased in UV irradiation. The UV/chlorine process dramatically increased the NB, BA, and pCBA degradation. Thus, the obtained \( k_{RR}\) (s\(^{-1}\)) values for NB, BA, and pCBA were 1.13 × 10\(^{-3}\) s\(^{-1}\), 3.78 × 10\(^{-3}\) s\(^{-1}\), and 5.92 × 10\(^{-3}\) s\(^{-1}\), respectively (Table 1). For the NB, BA, and pCBA mixture system (Figure S5d), the pseudo-first-order rate constants of these three compounds were 1.16 × 10\(^{-3}\) s\(^{-1}\), 3.57 × 10\(^{-3}\) s\(^{-1}\), and 5.77 × 10\(^{-3}\) s\(^{-1}\), respectively, which only have very little difference from that of individual degradation.

The experimentally determined \( k_{RR}\) values only have very minor difference with DFT-calculated \( k_{CP}\), which indicated that theoretical calculation is a suitable method to investigate the reaction kinetics and mechanism of chemicals in the UV/chlorine process. There are three aspects to explain this minor difference. As mentioned above, water molecules can promote the *ClO reaction and inhibit the *Cl reaction (Section 2.1.4). Thus, \( k_{CP-ClO}\) is undervalued and \( k_{CP-Cl}\) is overvalued. This may be one of the reasons for the deviation between \( k_{CP}\) and \( k_{RR}\). On the other hand, there are some deviations for the steady-state concentration of reactive radicals by kinetic model
simulation (Table 1), leading to the difference in the kinetic rate constant calculation. It is noted that intermediates like hydroxylated NB, etc. undergo faster direct photolysis in the system due to the stronger absorption and higher quantum yields. As those intermediates interfere with the conversion of many radicals in the system, the degradation kinetics of probe compounds should also be influenced.

Six transformation products (4-nitrophenol (4-NB-OH), 3-nitrophenol (3-NB-OH), 2-nitrophenol (2-NB-OH), 1-chloro-2-nitrobenzene (2-NB-Cl), 1-chloro-3-nitrobenzene (3-NB-Cl), and 1-chloro-4-nitrobenzene (4-NB-Cl)) were detected by ultrahigh-performance liquid chromatography-quadrupole time-of-flight mass spectrometry (UHPLC-QTOF-MS) with a photodiode array (PDA) detector for NB degradation in the UV/chlorine process (Figure S6a and Table S9). The corresponding extracted ion chromatograms and mass spectra, mass/mass spectra, are shown in Figures S7–S13, Supporting Information. These six transformation products in experimental samples were quantitatively detected by the PDA detector (Figure S6b) with standards, which are consistent with the HPLC results (Figure S14). The 3-NB-Cl and 4-NB-Cl were first produced, while the 2-NB-Cl and hydroxyl products (4-NB-OH, 3-NB-OH, and 2-NB-OH) were accumulated after reaction for 8 h (Figure S6b). In terms of the accumulation of each product, the main transformation product was the hydroxyl product. It is consistent with the DFT-calculated result of NB (Table S13), which means that the theoretically calculated results were reliable.

2.5. Environmental Implications. Many studies have been attempted to clarify the mechanism of different reactive radicals in the UV/chlorine process by the kinetic model based on first-principles and/or elementary reactions. However, our study indicated that DFT calculations can be extended to elucidate the degradation mechanism of contaminants with a similar structure in the UV/chlorine process, and the reaction rate constants and transformation products can be illustrated based on theoretical calculations.

The NB, BA, and pCBA are widely used as probe compounds to calculate the second-order rate constants of compounds’ reactions with reactive radicals in the UV/chlorine process. The *OH has been proved as the most important reactive radical in the UV/chlorine process. For initial reactions of NB, BA, and pCBA with reactive radicals, *OH has a higher second-order rate constant than those of *ClO and *Cl. However, *ClO and *Cl also play an important role in the UV/OH reactions for converting transformation products. Especially when considering the steady-state concentrations of various reactive radicals, *[ClO]o has been reported to be 3–4 orders of magnitude higher than *[OH]o and the contribution of *ClO and *Cl cannot be neglected in NB degradation by the UV/chlorine process. Thus, the contributions for *OH in competitive kinetic experiments calculated by NB are probably overestimated because NB is deemed to only react with *OH. Different pH, wavelength, and coexisting components in the UV/chlorine process will lead to the variation of these reactive radicals, which can affect the reaction rates and transformation products of selected contaminants. Further studies should investigate the interaction mechanism using theoretical calculations and experimental verification.

3. CONCLUSIONS

The kinetics and mechanism of the main reactive radicals (*OH, *ClO, and *Cl) in the UV/chlorine process reactions with selected probe compounds (NB, BA, and pCBA) have been elucidated by DFT calculation. The reactive radicals react with these three probe compounds via radical-addition and H-abstraction pathways. The DFT-calculated first-order rate constants (kfi) can be explained by the sum of initial reaction rate constants for *OH, *ClO, and *Cl reactions with each probe compound. The obtained rate constants (kfi) were consistent with the experimentally determined pseudo-first-order rate constants (kPC) in the UV/chlorine process. Within the initial reaction, water molecules do not participate in the H-abstraction reaction and the *OH-addition reaction. Water molecules only connect with other H2O and NB by hydrogen bonds, which can affect the calculated reaction rates of the NB reaction with *OH, *ClO, and *Cl. Besides the initial reactive radical reactions, the subsequent reaction for *NB-OH with *OH, *ClO, and *Cl is the chain termination reaction, which can be calculated to predict its transformation products. Six NB products (4-nitrophenol, 3-nitrophenol, 2-nitrophenol, 1-chloro-2-nitrobenzene, 1-chloro-3-nitrobenzene, and 1-chloro-4-nitrobenzene) were detected for NB degradation in the UV/chlorine process, which confirmed the DFT-predicted transformation products.

4. MATERIALS AND METHODS

4.1. Electronic Structure Calculation. The geometry optimizations and harmonic frequency calculations of all reactants (RCs), products (Ps), intermediates (IMs), and transition states (TSs) were calculated at the hybrid density functional M06-2X/6-311+G(d,p) level. With the exception of TSs having only one imaginary frequency, all of the stationary points (RCs, Ps, IMs, and complexes) have real frequencies. Intrinsic reaction coordinate (IRC) calculations at the same level were employed to construct the minimum-energy path (MEP) that confirmed TSs connected with corresponding local minima points on the potential energy surface. Zero point energy correction was calculated at the M06-2X/6-311+G(3df,2pd) level. Furthermore, three functionals (B3LYP, M06-2X, and ωB97) were tested to find a balance between time-consuming and computational accuracies at the 6-311+G(3df,2pd) level based on the optimized geometries from M06-2X/6-311+G(d,p) and then compared with the results that were optimized at the M06-2X/6-311+G(3df,2pd) level (Table S1, Supporting Information). Finally, an optimum method M06-2X was selected for our target system. All of the molecular structure and energy calculations were performed with the Gaussian 16 program package.

4.2. Simulating the Effects of Water. The impact of an aqueous solvent was simulated by two approaches: implicit solvation model and explicit water molecules. Specifically, the implicit solvation model based on density (SMD) was adopted to correct the long-range interactions between the target system and the aqueous solvent. The SMD model based on the self-consistent-reaction-field method was used to calculate the water effect at the M06-2X/6-311+G(3df,2pd) level. For consideration of simulating the effect of explicit water molecules, 1–4 water molecules were added in the target system based on the implicit solvation model so as to correct both short-range and long-range interactions.
4.3. Kinetics Calculation. For the initial reactions of nitrobenzene (NB), benzoic acid (BA), and p-chlorobenzoic acid (pCBA) with *OH, *ClO, and *Cl, the second-order rate constants $k_i$ (M$^{-1}$ s$^{-1}$) were calculated using the transition state theory (TST) with the Wigner transmission coefficient.\(^\text{42}\) Equation 6 was educed from the thermochemistry in Gaussian.

$$k_i = \sigma k_i T \left( \frac{RT}{B_1} \right)^{\Delta E_i \sigma / (\hbar \gamma E_i T)}$$

(6)

where $\sigma$ is the reaction-path degeneracy, $k_i$ is the Boltzmann constant, $T$ is temperature (K), $h$ is Planck’s constant, $R$ is the universal gas constant, $P_0$ is the standard state pressure (Pa), $\Delta n = n - 1$, where $n$ is the number of molecules involved in the reaction, $\Delta E_i ^\sigma$ is the corrected relative potential energy between TSs and RCs, and $k_i$ is the Wigner transmission coefficient, calculated by eq 7.

$$k_i = 1 + \frac{1}{24} \left( \frac{\hbar \gamma^*_i}{k_i T} \right)^2$$

(7)

where $\gamma^*_i$ is the imaginary frequency (cm$^{-1}$) of the TSs. The total second-order rate constant was the sum of $k_i$ for each site of NB, BA, and pCBA reacted with *OH, *ClO, and *Cl, respectively denoted $k_{NB-OH}$, $k_{NB-ClO}$, $k_{NB-Cl}$, $k_{BA-OH}$, $k_{BA-ClO}$, $k_{BA-Cl}$, $k_{CBA-OH}$, $k_{CBA-ClO}$, and $k_{CBA-Cl}$.

4.4. Experimental Section. Nitrobenzene (NB, >99%), benzoic acid (BA, >99%), p-chlorobenzoic acid (pCBA, >99%), and sodium hypochlorite solution (NaOCl) with available chlorine 4.0–5.0% were purchased from Sigma-Aldrich. Their stock solutions were prepared using deionized water (18.2 MΩ cm) and kept at 4 °C. HPLC-grade methanol and acetonitrile were obtained from Merck (Germany).

The degradation experiments of NB, BA, and pCBA by the UV/chlorine process were conducted in an internal illuminating photocochemical reactor (Figure S1) with a low-pressure mercury lamp (254 nm, 10 W). The UV photon fluence rate was determined at 1.9 μE (Einstein) L$^{-1}$ s$^{-1}$ using an iodide/iodate chemical actinometer.\(^\text{43,44}\) The temperature was maintained at 25 ± 1 °C with a recirculating cooling water system. The 2 μM target compound (NB, BA, and pCBA) was first spiked into pH 7.0 phosphate-buffered solutions (10 mM, 400 mL); then, the NaOCl stock solution was added to achieve an initial chlorine concentration of 100 μM. At different irradiation time intervals, 1 mL of the reaction solution was collected and quenched with 10 μL of Na$_2$S$_2$O$_3$ (50 mM) to measure the residual concentration of NB, BA, or pCBA by high-performance liquid chromatography (HPLC).\(^\text{45}\) meanwhile, another 1 mL of the reaction solution was collected to measure the residual concentration of free available chlorine using the N,N-diethyl-1,4-phenylenediamine sulfate (DPD) method.\(^\text{46}\) The control experiments of chlorination and UV photolysis were also conducted. All experiments were performed in triplicate. Besides, a mixture system including NB, BA, and pCBA was used to investigate their competition features. Moreover, a higher concentration of NB (800 μM) with chlorine (40 mM) was used to detect its transformation products in the UV/chlorine process.

The concentrations of three target compounds (NB, BA, and pCBA) were analyzed on an Agilent 1260 Infinity LC system equipped with a diode array detector (Agilent Technologies). The transformation products of NB in the UV/chlorine process were analyzed with their standards using an Agilent 1260 Infinity LC system equipped with a diode array detector (Tables S2 and S3) and Waters Xevo G2-XS QTOF quadrupole time-of-flight mass spectrometry (UHPLC-QTOF-MS) equipped with a photodiode array detector (see Text S1).
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Notes
The authors declare no competing financial interest.

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REFERENCES

(1) Krasner, S. W. The formation and control of emerging disinfection by-products of health concern. Philos. Trans. R. Soc. A 2009, 367, 4097−4095.

(2) Richardson, S. D.; Plewa, M. J.; Wagner, E. D.; Schoeny, R.; DeMarini, D. M. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research. Mutat. Res., Rev. Mutat. Res. 2007, 636, 178−242.

(3) Legrini, O.; Oliveros, E.; Braun, A. M. Photochemical processes for water-treatment. Chem. Rev. 1993, 93, 671−698.

(4) Esplugas, S.; Gimenez, J.; Contreras, S.; Pascual, E.; Rodriguez, M. Comparison of different advanced oxidation processes for phenol degradation. Water Res. 2002, 36, 1034−1042.

(5) Yang, B.; Ying, G. G.; Zhao, J. L.; Liu, S.; Zhou, L. J.; Chen, F. Removal of selected endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) during ferrate(VI) treatment of secondary wastewater effluents. Water Res. 2012, 46, 2194−2204.

(6) Yang, X.; Sun, J.; Fu, W.; Shang, C.; Li, Y.; Chen, Y.; Gan, W.; Fang, J. PPCP degradation by UV/chlorine treatment and its impact on DBP formation potential in real waters. Water Res. 2016, 98, 309−318.

(7) Kong, X.; Wu, Z.; Ren, Z.; Guo, K.; Hou, S.; Hua, Z.; Li, X.; Fang, J. Degradation of lipid regulators by the UV/chlorine process: Radical mechanisms, chlorine oxide radical (CIO•)-mediated transformation pathways and toxicity changes. Water Res. 2018, 137, 242−250.

(8) Feng, Y. G.; Smith, D. W.; Bolton, J. R. Photolysis of aqueous free chlorine species (HOCI and OCI−) with 254 nm ultraviolet light. J. Environ. Eng. Sci. 2007, 6, 277−284.

(9) Remucal, C. K.; Manley, D. Emerging investigators series: the efficacy of chlorine photolysis as an advanced oxidation process for drinking water treatment. Environ. Sci.: Water Res. Technol. 2016, 2, 565−579.

(10) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. Critical review of rate constants for reactions of hydrated electrons, hydrogen-atoms and hydroxyl radicals (−OH/−O•) in aqueous-solution. J. Phys. Chem. Ref. Data 1988, 17, 513−886.

(11) Guo, K.; Wu, Z.; Shang, C.; Yao, B.; Hou, S.; Yang, X.; Song, W.; Fang, J. Radical Chemistry and Structural Relationships of PPCP Degradation by UV/Chlorine Treatment in Simulated Drinking Water. Environ. Sci. Technol. 2017, 51, 10431−10439.

(12) Wu, Z.; Fang, J.; Xiang, Y.; Shang, C.; Li, X.; Meng, F.; Yang, X. Roles of reactive chlorine species in trimethoprim degradation in the UV/chlorine process: Kinetics and transformation pathways. Water Res. 2016, 104, 272−282.

(13) Watts, M. J.; Linden, K. G. Chlorine photolysis and subsequent OH radical production during UV treatment of chlorinated water. Water Res. 2007, 41, 2871−2878.

(14) Xiang, Y.; Fang, J.; Shang, C. Kinetics and pathways of ibuprofen degradation by the UV/chlorine advanced oxidation process. Water Res. 2016, 90, 301−308.

(15) Forsyth, J. E.; Zhou, P.; Mao, Q.; Asato, S. S.; Meschke, J. S.; Dodd, M. C. Enhanced inactivation of Bacillus subtilis spores during solar photolysis of free available chlorine. Environ. Sci. Technol. 2013, 47, 12976−12984.

(16) Wang, W. L.; Wu, Q. Y.; Huang, N.; Wang, T.; Hu, H. Y. Synergistic effect between UV and chlorine (UV/chlorine) on the degradation of carbamazepine: Influence factors and radical species. Water Res. 2016, 88, 190−198.

(17) Bulman, D. M.; Mezyk, S. P.; Remucal, C. K. The impact of pH and Irradiation Wavelength on the Production of Reactive Oxidants during Chlorine Photolysis. Environ. Sci. Technol. 2019, 53, 4450−4459.

(18) Fang, J.; Fu, Y.; Shang, C. The roles of reactive species in micropollutant degradation in the UV/free chlorine system. Environ. Sci. Technol. 2014, 48, 1859−1868.

(19) Zhou, S.; Zhang, W.; Sun, J.; Zhu, S.; Li, K.; Meng, X.; Luo, J.; Shi, Z.; Zhou, D.; Crittenden, J. C. Oxidation Mechanisms of the UV/Free Chlorine Process: Kinetic Modeling and Quantitative Structure Activity Relationships. Environ. Sci. Technol. 2019, 53, 4335−4345.

(20) Chuang, Y.-H.; Chen, S.; Chinn, C. J.; Mitch, W. A. Comparing the UV/Monochloramine and UV/Free Chlorine Advanced Oxidation Processes (AOPs) to the UV/Hydrogen Peroxide AOP Under Scenarios Relevant to Potable Reuse. Environ. Sci. Technol. 2017, 51, 13859−13868.

(21) Wang, D.; Bolton, J. R.; Hofmann, R. Medium pressure UV combined with chlorine advanced oxidation for trichloroethylene destruction in a model water. Water Res. 2012, 46, 4677−4686.

(22) Zhang, H.; Xie, H.; Chen, J.; Zhang, S. Prediction of hydrolysis pathways and kinetics for antibiotics under environmental pH conditions: a quantum chemical study on cephradine. Environ. Sci. Technol. 2015, 49, 1552−1558.

(23) Zhang, S. Y.; Yu, G.; Chen, J. W.; Zhao, Q.; Zhang, X. J.; Wang, B.; Huang, J.; Deng, S. B.; Wang, Y. J. Elucidating ozonation mechanisms of organic micropollutants based on DFT calculations: Taking sulfamethoxazole as a case. Environ. Pollut. 2017, 220, 971−980.

(24) Xie, H. B.; Li, C.; He, N. J.; Wang, C. J.; Zhang, S.; Chen, J. Atmospheric chemical reactions of monoethanolamine initiated by OH radical: mechanistic and kinetic study. Environ. Sci. Technol. 2014, 48, 1700−1706.

(25) Xie, H. B.; Ma, F.; Wang, Y.; He, N. J.; Yu, Q. Q.; Chen, J. Quantum Chemical Study on Cl-Initiated Atmospheric Degradation of Monoethanolamine. Environ. Sci. Technol. 2015, 49, 13246−13255.

(26) Gao, Y.; Ji, Y.; Li, G.; An, T. Mechanism, kinetics and toxicity assessment of OH-initiated transformation of triclosan in aquatic environments. Water Res. 2014, 49, 360−370.

(27) Zhang, Y. N.; Wang, J.; Chen, J.; Zhou, C.; Xie, Q. Phototransformation of 2,3-Dibromopropyl-2,4,6-tribromophenyl ether (DPTE) in Natural Waters: Important Roles of Dissolved Organic Matter and Chloride Ion. Environ. Sci. Technol. 2018, 52, 10490−10499.

(28) Cui, Y.; Ding, Z.; Sun, Y.; Yi, Y.; Xu, F.; Zhang, Q.; Wang, W. A theoretical study of OH radical-initiated atmospheric oxidation of 1-chloronaphthalene. Chem. Phys. Lett. 2018, 699, 40−47.

(29) Sun, P.; Lee, W. N.; Zhang, R.; Huang, C. H. Degradation of DEET and Caffeine under UV/Chlorine and Simulated Sunlight/Chlorine Conditions. Environ. Sci. Technol. 2016, 50, 13265−13273.

(30) An, T.; An, J.; Gao, Y.; Li, G.; Fang, H.; Song, W. Photocatalytic degradation and mineralization mechanism and toxicity assessment of antivirus drug acyclovir: Experimental and theoretical studies. Appl. Catal., B 2015, 164, 279−287.

(31) Ma, F.; Ding, Z.; Elm, J.; Xie, H. B.; Yu, Q.; Liu, C.; Li, C.; Fu, Z.; Zhang, L.; Chen, J. Atmospheric Oxidation of Piperazine Initiated
(32) Li, C.; Chen, J.; Xie, H. B.; Zhao, Y.; Xia, D.; Xu, T.; Li, X.; Qiao, X. Effects of Atmospheric Water on ·OH-initiated Oxidation of Organophosphate Flame Retardants: A DFT Investigation on TCPP. *Environ. Sci. Technol.* **2018**, *52*, 9801−9809.

(33) Wang, B.; Cao, Z. How water molecules modulate the hydration of CO₂ in water solution: insight from the cluster-continuum model calculations. *J. Comput. Chem.* **2013**, *34*, 372−378.

(34) Pliego, J. R., Jr. Basic hydrolysis of formamide in aqueous solution: a reliable theoretical calculation of the activation free energy using the cluster-continuum model. *Chem. Phys.* **2004**, *306*, 273−280.

(35) Nowell, L. H.; Hoigne, J. Photolysis of aqueous chlorine at sunlight and ultraviolet wavelengths-II. hydroxyl radical production. *Water Res.* **1992**, *26*, 599−605.

(36) Kamath, D.; Minakata, D. Emerging investigators series: ultraviolet and free chlorine aqueous-phase advanced oxidation process: kinetic simulations and experimental validation. *Environ. Sci. Water Res. Technol.* **2018**, *4*, 1231−1238.

(37) Wu, Z.; Guo, K.; Fang, J.; Yang, X.; Xiao, H.; Hou, S.; Kong, X.; Shang, C.; Yang, X.; Meng, F.; Chen, L. Factors affecting the roles of reactive species in the degradation of micropollutants by the UV/chlorine process. *Water Res.* **2017**, *126*, 351−360.

(38) Ye, B.; Li, Y.; Chen, Z.; Wu, Q.-Y.; Wang, W.-L.; Wang, T.; Hu, H.-Y. Degradation of polyvinyl alcohol (PVA) by UV/chlorine oxidation: Radical roles, influencing factors, and degradation pathway. *Water Res.* **2017**, *124*, 381−387.

(39) Yin, R.; Ling, L.; Shang, C. Wavelength-dependent chlorine photolysis and subsequent radical production using UV-LEDs as light sources. *Water Res.* **2018**, *142*, 452−458.

(40) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A. J.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16*, revision B.01; Gaussian, Inc.: Wallingford, CT, 2016.

(41) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the SolventDefined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009**, *113*, 6378−6396.

(42) Thermochemistry in Gaussian. [http://gaussian.com/thermo/](http://gaussian.com/thermo/) (accessed June 23, 2020).

(43) Bolton, J. R.; Stefan, M. I.; Shaw, P. S.; Lykke, K. R. Determination of the quantum yields of the potassium ferrioxalate and potassium iodide−iodate actinometers and a method for the calibration of radiometer detectors. *J. Photochem. Photobiol., A* **2011**, *222*, 166−169.

(44) Cai, W. W.; Peng, T.; Yang, B.; Xu, C.; Liu, Y. S.; Zhao, J. L.; Gu, F. L.; Ying, G. G. Kinetics and mechanism of reactive radical mediated flunazol degradation by the UV/chlorine process: Experimental and theoretical studies. *Chem. Eng. J.* **2020**, *402*, No. 126224.

(45) Lee, Y.; von Gunten, U. Oxidative transformation of micropollutants during municipal wastewater treatment: comparison of kinetic aspects of selective (chlorine, chlorine dioxide, ferrate VI, and ozone) and non-selective oxidants (hydroxyl radical). *Water Res.* **2010**, *44*, 555−566.

(46) Moore, H. E.; Garmendia, M. J.; Cooper, W. J. Kinetics of monochloramine oxidation of N,N-diethyl-p-phenylenediamine. *Environ. Sci. Technol.* **1984**, *18*, 348−353.