Atmospheric oxidation mechanism and kinetics of indole initiated by \( \cdot OH \) and \( \cdot Cl \): a computational study

Jingwen Xue\(^1\), Fangfang Ma\(^1\), Jonas Elm\(^2\), Jingwen Chen\(^1\), and Hong-Bin Xie\(^1\)

\(^1\)Key Laboratory of Industrial Ecology and Environmental Engineering (Ministry of Education), School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China
\(^2\)Department of Chemistry and iClimate, Aarhus University, Langelandsgade 140, 8000 Aarhus C, Denmark

Correspondence: Fangfang Ma (maff@dlut.edu.cn) and Hong-Bin Xie (hbxie@dlut.edu.cn)

Received: 4 February 2022 – Discussion started: 26 April 2022
Revised: 4 July 2022 – Accepted: 29 July 2022 – Published: 7 September 2022

Abstract. The atmospheric chemistry of organic nitrogen compounds (ONCs) is of great importance for understanding the formation of carcinogenic nitrosamines, and ONC oxidation products might influence atmospheric aerosol particle formation and growth. Indole is a polyfunctional heterocyclic secondary amine with a global emission quantity almost equivalent to that of trimethylamine, the amine with the highest atmospheric emission. However, the atmospheric chemistry of indole remains unclear. Herein, the reactions of indole with \( \cdot OH \) and \( \cdot Cl \), and subsequent reactions of resulting indole radicals with \( O_2 \) under 200 ppt NO and 50 ppt HO\(_2\cdot\) conditions, were investigated by a combination of quantum chemical calculations and kinetics modeling. The results indicate that \( \cdot OH \) addition is the dominant pathway for the reaction of \( \cdot OH \) with indole. However, both \( \cdot Cl \) addition and H abstraction are feasible for the corresponding reaction with \( \cdot Cl \). All favorably formed indole radicals further react with \( O_2 \) to produce peroxy radicals, which mainly react with NO and HO\(_2\cdot\) to form organonitrates, alkoxy radicals and hydroperoxide products. Therefore, the oxidation mechanism of indole is distinct from that of previously reported amines, which primarily form highly oxidized multifunctional compounds, imines or carcinogenic nitrosamines. In addition, the peroxy radicals from the \( \cdot OH \) reaction can form N-(2-formylphenyl)formamide (C\(_8\)H\(_7\)NO\(_2\)), for the first time providing evidence for the chemical identity of the C\(_8\)H\(_7\)NO\(_2\) mass peak observed in the \( \cdot OH \) + indole experiments. More importantly, this study is the first to demonstrate that despite forming radicals by abstracting an H atom at the N site, carcinogenic nitrosamines were not produced in the indole oxidation reaction.

1 Introduction

Volatile organic compounds (VOCs) play a central role in air quality and climate change as their transformations are highly relevant for the formation of secondary organic aerosols (SOA), toxic air pollutants and ozone (O\(_3\)) (Ehn et al., 2014; Karl et al., 2018; Lewis Alastair, 2018; Li et al., 2019; Khare and Gentner, 2018; Ji et al., 2018). Therefore, an accurate description of the atmospheric transformation mechanism and kinetics of VOCs is essential to fully explore the global impacts of VOCs. Despite massive effort to understand the atmospheric fate of VOCs, current mechanism-based atmospheric models often underestimate SOA and O\(_3\) formation quantity. Therefore, the emission inventories or reaction mechanism employed in the models are either missing some vital primary VOCs or there remain an unrevealed reaction mechanism of currently known VOCs. Hence, it is crucial to identify unaccounted reaction pathways of known VOCs or the transformation mechanism of unconsidered VOCs with high concentrations.

Organic nitrogen compounds (ONCs) are a subgroup of VOCs that are widely observed in the atmosphere (Silva et al., 2008). Until now, about 160 ONCs have been detected in the atmosphere, accounting for 10 % of total gas phase nitrogen (excluding N\(_2\)) (Ge et al., 2011; Silva et al., 2008). Due to the adverse effects of ONCs on air quality (formation of particles via acid–base reactions or generation of toxic ni-
trosamines, nitramines, isocyanic acid and low volatile products via gas phase oxidation), the chemistry of ONCs has gained significant attention in recent years (Almeida et al., 2013; Chen et al., 2017; Lin et al., 2019; Nielsen et al., 2012; Zhang et al., 2015; Xie et al., 2014, 2015, 2017; F. F. Ma et al., 2018a, 2021b, 2019; Shen et al., 2019, 2020). Detailed transformation pathways of a series of ONCs, including low-molecular-weight alkyl amines (Nicovich et al., 2015; Xie et al., 2014, 2015; F. F. Ma et al., 2021b), aromatic aniline (Xie et al., 2017; Shiels et al., 2021), heterocyclic amines (Sen-Gupta et al., 2010; Ma et al., 2018a; Borduas et al., 2016b; Ren and Da Silva, 2019) and amides (Xie et al., 2017; Borduas et al., 2016a, 2015; Bunkan et al., 2016, 2015), have been investigated. These studies have shown that the functional groups connected to the NH$_x$ ($x = 0, 1, 2$) group highly affect the reactivity of ONCs and eventually lead to their different atmospheric impacts. Therefore, the comprehensive understanding the reaction mechanism of ONCs with various functional groups linked to the NH$_x$ group is of great significance in assessing the atmospheric impact of ONCs.

Indole is a polyfunctional heterocyclic secondary amine (Laskin et al., 2009). Atmospheric indole has various natural and anthropogenic sources including vegetation, biomass burning, animal husbandry, coal mining, petroleum processing and the tobacco industry (Q. Ma et al., 2021; Cardoza et al., 2003; Yuan et al., 2017; Zito et al., 2015). The global emission of indole is around 0.1 Tg yr$^{-1}$ (Misztal et al., 2015), which is almost equivalent to that of trimethylamine ($\sim 0.17$ Tg yr$^{-1}$) (Schade and Crutzen, 1995; Yu and Luo, 2014) which has the highest emission among the identified atmospheric amines. A field measurement study found that the concentration of indole can reach 1–3 ppb in ambient air during a springtime flowering event (Gentner et al., 2014). From a structural point of view, the -NH$_2$ group of indole is located at 9-center-10-electron delocalized $\pi$ bonds, possibly altering its reactivity compared with that of previously well-studied aliphatic amines and aniline. Therefore, considering the large atmospheric emission of indole and its unique structure compared with previously studied amines, the reaction mechanism of indole needs to be further evaluated to assess its atmospheric impacts. Furthermore, elucidating the reaction mechanism of indole will add to the fundamental understanding of the transformation mechanism of ONCs.

Hydroxyl radicals ($\cdot$OH) are considered to be the most important atmospheric oxidants governing the fate of most organic compounds (MacLeod et al., 2007). Previous experimental studies have investigated the reaction kinetics and identified the products of the $\cdot$OH + indole reaction. Atkinson et al. found that the rate constant ($k_{\text{OH}}$) of the $\cdot$OH + indole reaction is $1.54 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K, translating to a $20$ min lifetime of indole (Atkinson et al., 1995). Montoya-Aguilera et al. found that isatin and isatoic anhydride are the two dominant monomeric products for $\cdot$OH initiated reaction of indole. More importantly, they found that the majority of indole oxidation products can contribute to SOA formation with an effective SOA yield of $1.3 \pm 0.3$ under the indole concentration (200 ppb) employed in their chamber study (Montoya-Aguilera et al., 2017). Although the chemical formulas of some of the indole oxidation products have been detected, detailed mechanistic information, such as the products branching ratio of the $\cdot$OH initiated reaction of indole, remains unknown. Additionally, the lack of commercially available standards of some products presents a significant obstacle to identify the exact chemical identity of the products. Therefore, to fully understand the role of indole in SOA formation, it is essential to investigate the detailed atmospheric transformation of indole initiated by $\cdot$OH.

Besides reactions with $\cdot$OH, reactions with chlorine radicals ($\cdot$Cl) have been proposed to be an important removal pathway for ONCs due to the identification of new $\cdot$Cl containing species and the high reactivity of $\cdot$Cl (Wang et al., 2022; Li et al., 2021; Jahn et al., 2021; Xia et al., 2020; Young et al., 2014; Faxon and Allen, 2013; Riedel et al., 2012; Atkinson et al., 1989; Ji et al., 2013; Thornton et al., 2010; Le Breton et al., 2018). $\cdot$Cl initiated atmospheric oxidation of ONCs can lead to the formation of N-centered radicals, once a strong 2-center-3-electron (2c–3e) bond complex has been formed between $\cdot$Cl and NH$_x$ ($x = 1, 2$) (Mcke et al., 1996; Xie et al., 2015, 2017; Ma et al., 2018a). The formed N-centered radicals can further react with NO to form carcinogenic nitrosamines, increasing the atmospheric impact of ONC emissions (Xie et al., 2014, 2015, 2017; Ma et al., 2018a, 2021b; Onel et al., 2014a, b; Nielsen et al., 2012; Da Silva, 2013). As a secondary amine, indole reaction with $\cdot$Cl has the possibility of forming N-centered radicals and subsequently forming nitrosamines via the reaction with NO. Since the -NH$_2$ group of indole is embedded in a unique chemical environment compared with previously well-studied ONCs, the reaction mechanism of $\cdot$Cl with indole remains elusive. In addition, there are only a few studies concerning the reactions of polyfunctional heterocyclic ONCs with $\cdot$Cl.

In this work, we investigated the reaction mechanism and kinetics of indole initiated by $\cdot$OH and $\cdot$Cl by employing a combination of quantum chemical calculations and kinetic modeling. The initial reactions of $\cdot$OH and $\cdot$Cl with indole and the subsequent reactions with O$_2$ of resulting intermediates were further investigated.

2 Computational details

2.1 Ab Initio electronic structure calculations

All the geometry optimizations and harmonic vibrational frequency calculations were performed at the M06-2X/6-31+G(d,p) level of theory (Zhao and Truhlar, 2008). Intrinsic reaction coordinate calculations were performed to confirm the connections of each transition state between the corresponding reactants and products. Single point energy calcu-
lations were performed at the CBS-QB3 method based on the geometries at the M06-2X/6-31+G(d,p) level of theory (Montgomery et al., 1999). The combination of the M06-2X functional and CBS-QB3 method has successfully been applied to predict radical–molecule reactions (Guo et al., 2020; F. F. Ma et al., 2021a; Wang et al., 2018; Wang and Wang, 2016; Wu et al., 2015; Wang et al., 2017; Fu et al., 2020). $T_1$ diagnostic (Table S2 in the Supplement) values in the CCSD(T) calculations within the CBS-QB3 scheme for the intermediates and transition states involved in the key reaction pathways were checked for multifreference character. The $T_1$ diagnostic values for all checked important species in this work are lower than the threshold value of 0.045, indicating the reliability of applied single reference methods (Rienstra-Kiracofe et al., 2000). In addition, similar to our previous studies, a literature value of 0.8 kcal mol$^{-1}$ for the isolated ·Cl was used to account for the effect of spin-orbit coupling in the ·Cl + indole reaction (Nicovich et al., 2015; Xie et al., 2017; Ma et al., 2018a). Atomic charges of indole and pre-reactive complexes in the ·Cl + indole reaction are obtained by natural bond orbital (NBO) calculations (Reed et al., 1985). All calculations were performed within the Gaussian 09 package (Frisch et al., 2009). Throughout the paper, the symbols “R, RC, PC, TS, IM and P” stand for reactants, pre-reactive complexes, post-reactive complexes, transition states, intermediates and products involved in the reactions, respectively, and their subscripts denote different species. In addition, “A/B” was used to present the computational method, where “A” is the theoretical level for single point energy calculations and “B” is that for geometry optimizations and harmonic frequency calculations.

2.2 Kinetics calculations

MultiWell-2014.1 and MESMER 5.0 software were employed to investigate the kinetics for short time and long time reaction, respectively (Barker and Ortiz, 2001; Barker, 2001; Glowacki et al., 2012). For the initial reactions of ·OH and ·Cl with indole, the reaction kinetics were calculated within the MultiWell-2014.1 program. For the subsequent reactions of resulting primary intermediates, MESMER 5.0 was selected for simulating the reaction kinetics, since it has good performance for long time runs, especially for simulating the variation of the different intermediates over time. Both the MultiWell and MESMER codes employ the Rice–Ramsperger–Kassel–Marcus (RRKM) theory to calculate the reaction kinetics for reactions with intrinsic energy barriers (Holbrook, 1996; Robinson, 1972). The long-range transition-state theory (LRTST) with a dispersion force potential within the MultiWell-2014.1 program (Barker and Ortiz, 2001) or the inverse Laplace transformation (ILT) method within the MESMER 5.0 program was employed to calculate the reaction rate constants for the barrierless recombination reactions (from R to RC and P to PC) (Rienstra-Kiracofe et al., 2000). Computational details for performing LRTST and ILT calculations were described in our previous studies (F. F. Ma et al., 2021a, b; Guo et al., 2020; Ding et al., 2020). The parameters used in the LRTST calculations and Lennard-Jones parameters of intermediates estimated by the empirical method proposed by Gilbert and Smith (Gilbert and Smith, 1990) are listed in Tables S3 and S4, respectively. $N_2$ was selected as the buffer gas, and an average transfer energy of $\Delta E_d = 200$ cm$^{-1}$ was used to simulate the collision energy transfer between active intermediates and $N_2$. In addition, $\Delta E_d$ between 50–250 cm$^{-1}$ were selected to study energy transfer parameters effects. For the reactions involving H abstraction or H shift, tunneling effects were taken into account in all of the reaction rate constants calculations by using a one-dimensional unsymmetrical Eckart barrier (Eckart, 1930), and are discussed in the Supplement. The kinetic calculations were primarily performed at 298 K and 1 atm, with additional ones at 0.1, 0.4 and 0.7 atm in the troposphere relevant range to explore pressure effects. Variation in the energy transfer parameters and pressure resulted in only minor changes (< 0.1 %) in the calculated rate coefficients and branching ratios of the main reaction pathways (see details in the Supplement).

3 Results and discussion

3.1 Initial reactions of indole

In principle, ·OH and ·Cl could add to the unsaturated C–C bonds and benzene ring or directly abstract H atoms connected to either a C atom or the N atom of indole. Considering the planar $C_6$ structure of indole, ·OH and ·Cl addition to one side of indole was only considered here. However, although numerous attempts were made, we failed to locate the TSs and addition IMs of ·Cl addition to the C2, C3, C4, C7, C8 and C9 sites of indole (the numbering of the atoms is given in Fig. 1), suggesting that such additions are in fact unfeasible. Therefore, 7 H-abstraction pathways of ·OH and ·Cl, respectively, 8 ·OH-addition pathways and 2 ·Cl-addition pathways were considered for the ·OH and ·Cl with indole reactions. The schematic zero-point energy (ZPE) corrected potential energy surfaces of ·OH and ·Cl with indole reactions are presented in Fig. 1.

As can be seen in Fig. 1, each H-abstraction reaction pathway proceeds through an RC and PC, and the addition pathways through an RC for the ·OH and ·Cl with indole reactions. For the H-abstraction pathways, the activation energy ($E_a$) for the -NH- group for both reactions are at least 2.0 kcal mol$^{-1}$ lower than the corresponding $E_a$ values for the -CH- groups. This indicates that H abstraction from the -NH- group forming $C_6H_5N$ radicals and $H_2O$ or HCl is the most favorable among all the H-abstraction pathways. In addition, the activation energy for the H abstraction from the -NH- group in the ·Cl + indole reaction is much lower than the corresponding ·OH + indole reaction. This is consistent with previously reported reactions of other amines with ·OH.
and ·Cl (F. F. Ma et al., 2018a, 2021b; Xie et al., 2014, 2015, 2017; Tan et al., 2021; Ren and Da Silva, 2019; Borduas et al., 2015).

For the addition reactions, the most favorable reaction site differs for the indole + ·OH and indole + ·Cl reactions. Among all 8 ·OH addition pathways, ·OH addition to the C7 site of the C=C bond via TS1–7 forming IM1–7 is the most favorable pathway. Different from the reaction with ·OH, the additions of ·Cl to the C5 and C6 sites to form IM2–5 and IM2–6, respectively, are significantly more favorable. By comparing the $E_a$ values of the addition and H-abstraction pathways for both ·OH and ·Cl with indole reactions, it can be concluded that ·OH addition to the C7 site is the most favorable for the ·OH + indole reaction. All the ·OH + indole hydrogen abstraction reactions have high energy barriers. However, the additions of ·Cl to the C5 and C6 sites, as well as the ·NH-H abstraction, are all favorable due to their very low $E_a$ values for the ·Cl + indole reaction.

Interestingly, we found that all the pathways for the indole + ·Cl reaction can proceed via a stable 2c–3e bonded RC, which is different from that of the ·OH + indole reaction. Among all 2c–3e bonded RCs, only RC2–10 from the ·NH-abstraction pathway is formed between the N atom and ·Cl, while the others are formed between the C atom and ·Cl. Note that RC2–11, which forms from C atom and ·Cl, is the most stable among all the formed RCs in the ·Cl + indole reaction. To the best of our knowledge, this is the first time that such a stable 2c–3e bonded RC has been identified between the C atom and ·Cl. In addition, the energy of RC2–10 is higher than that of the traditional 2c–3e bonded RCs formed from alkylamine and ·Cl, which would result from the delocalization of lone pair electrons of the N atom. By analyzing the NBO charges of these nine RCs (Table S5), we found that significant charge transfer occurs between ·Cl and indole. The charge at the Cl atom for RC2–5, RC2–6, RC2–10, RC2–11, RC2–12, RC2–13, RC2–14, RC2–15 and RC2–16 are $0.35e$, $0.33e$, $0.31e$, $0.39e$, $0.35e$, $0.33e$, $0.39e$, $0.35e$ and $0.33e$, respectively, indicates that all RCs are charge-transfer complexes. Similar charge-transfer complexes were also found in our previous study of the ·Cl+piperazine reaction (Ma et al., 2018a).

With the master equation theory, the overall rate constants ($k_{OH}$ and $k_{Cl}$) and branching ratios ($\Gamma$) for all H-abstraction and ·OH/·Cl-addition pathways involved in the ·OH and ·Cl with indole reactions were calculated at 298 K and 1 atm. The calculated $k_{OH}$ and $k_{Cl}$ values of indole are $7.9 \times 10^{-11}$ and $2.9 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively. The calculated $k_{OH}$ value is close to the available experimental value of $1.5 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Atkinson et al., 1995), supporting the reliability of employed computational methods. Over the temperature range 230–330 K (Ma et al., 2018b), the calculated $k_{OH}$ and $k_{Cl}$ values have a negative correlation with temperature (Fig. S1 in the Supplement). Based on the calculated $\Gamma$ values of the ·OH and ·Cl with indole reactions (Table 1), it can be concluded that IM1–7 (77%) is the main product for ·OH + indole reaction, and IM2–5 (31%), IM2–6 (46%) and P2–10 (C$_3$H$_4$N radicals + Cl) (23%) are the main products for ·Cl + indole reaction. In addition, the calculated $\Gamma$ values of IM1–7, IM2–5, IM2–6 and P2–10 (C$_3$H$_6$N radicals + Cl) change negligibly with the variation in temperature, pressure and energy transfer parameters (see the Supplement). Therefore, we mainly considered the further transformation of IM1–7, IM2–5, IM2–6 and C$_3$H$_6$N radicals in the following part.

### 3.2 Subsequent reactions of addition intermediates

Similar to other C-centered radicals (Zhang et al., 2012; Guo et al., 2020; F. F. Ma et al., 2021a; Yu et al., 2016, 2017; Ji et al., 2017; Ding et al., 2020a), the intermediates IM1–7, IM2–5 and IM2–6 will subsequently react with O$_2$. Two different pathways (Fig. 2) were considered for the reactions of the intermediates IM1–7, IM2–5 and IM2–6 with O$_2$. One pathway is the direct hydrogen abstraction by O$_2$ from the C site connecting to the ·OH or ·Cl group forming P1–7–1 (C$_3$H$_4$NO + HO$_2$), P2–5–1 (C$_3$H$_6$NCI + HO$_2$) and P2–6–1 (C$_3$H$_6$NCI + HO$_2$); the other is the O$_2$ addition to the C sites with high spin density (see spin density distribution in Table S10) of the intermediates IM1–7, IM2–5 and IM2–6 to form peroxo radicals $Q$-iOO-a/s, where $Q$ stands for intermediates IM1–7, IM2–5 and IM2–6, and $i$ stands for the numbering of the C positions where O$_2$ is added. The O$_2$ molecule can be added to the same (syn, abbreviated as -s) and opposite (anti, abbreviated as -a) sides of the plane relative to the ·OH or ·Cl group. The C2, C4, C6 and C8 sites of IM1–7, C2, C4, C6 and C8 sites of IM2–5 and C3, C5, C7 and C9 sites of IM2–6 are high spin density sites susceptible to O$_2$ addition.

As can be seen from the energetic data shown in Fig. 2, O$_2$ addition to the C4 site of IM1–7 to form IM1–7-4OO-a/s ($-0.6/-0.6$ kcal mol$^{-1}$), C6 site of IM2–5 to form IM2–5-6OO-a/s ($-3.3/-2.0$ kcal mol$^{-1}$) and C5 site of IM2–6 to form IM2–6-5OO-a/s ($2.0/1.7$ kcal mol$^{-1}$) are the most favorable among all possible entrance pathways for the respective reactions. It deserves mentioning that the formation energy ($\Delta E$) of IM2–5-6OO-a/s and IM2–6-5OO-a/s are only about $9.0$ kcal mol$^{-1}$, which could indicate that they likely

<table>
<thead>
<tr>
<th>Pathways</th>
<th>Species</th>
<th>$\Gamma$</th>
<th>Species</th>
<th>$\Gamma$</th>
<th>Species</th>
<th>$\Gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>·OH + indole</td>
<td>IM1–2</td>
<td>0</td>
<td>IM1–3</td>
<td>0</td>
<td>IM1–4</td>
<td>5 %</td>
</tr>
<tr>
<td></td>
<td>IM1–5</td>
<td>12 %</td>
<td>IM1–6</td>
<td>3 %</td>
<td>IM1–7</td>
<td>77 %</td>
</tr>
<tr>
<td></td>
<td>IM1–8</td>
<td>1 %</td>
<td>IM1–9</td>
<td>1 %</td>
<td>P1–10</td>
<td>1 %</td>
</tr>
<tr>
<td></td>
<td>P1–11</td>
<td>0</td>
<td>P1–12</td>
<td>0</td>
<td>P1–13</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>P1–14</td>
<td>0</td>
<td>P1–15</td>
<td>0</td>
<td>P1–16</td>
<td>0</td>
</tr>
<tr>
<td>·Cl + indole</td>
<td>IM2–5</td>
<td>31 %</td>
<td>IM2–6</td>
<td>46 %</td>
<td>P2–10</td>
<td>23 %</td>
</tr>
<tr>
<td></td>
<td>P2–11</td>
<td>0</td>
<td>P2–12</td>
<td>0</td>
<td>P2–13</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>P2–14</td>
<td>0</td>
<td>P2–15</td>
<td>0</td>
<td>P2–16</td>
<td>0</td>
</tr>
</tbody>
</table>
re-dissociate back to the reactants IM$_{2-5}$/IM$_{2-6}$ and O$_2$, if IM$_{2-5}$/6OO-a/s and IM$_{2-6}$/5OO-a/s does not rapidly transform to other species.

For the further transformation of the formed peroxy radicals IM$_{1-7}$/4OO(a/s), IM$_{2-5}$/6OO(a/s) and IM$_{2-6}$/5OO(a/s), two transformation pathways were identified. The first pathway is cyclization reactions where the terminal O atom of -OO attacks the different C positions to form bicycle radicals $Q_{ij}$OO(-a/s) ($j$ stands for the number of the C positions attacked by terminal O atom). The second pathway is H shifts from -OH, -NH- and different -CH- sites to the terminal O atom to form various hydroperoxide radicals $Q$-iOO-OH(-a/s), $Q$-iOO-NH(-a/s) and $Q$-iOO-C$_k$H(-a/s) ($k$ stands for the number of the C positions from which H is shifted), respectively. For IM$_{1-7}$/4OO(a/s) and IM$_{2-5}$/6OO(a/s), forming IM$_{1-7}$/4OO-OH-s and IM$_{2-5}$/6OO-C5H-a via H-shift reactions are the most favorable, respectively. However, for IM$_{2-6}$/5OO(a/s), the cyclization

**Figure 1.** Schematic ZPE-corrected potential energy surface for the reactions of indole + ·OH (a) and indole + ·Cl (b) at the CBS-QB3//M062X/6-31+g(d,p) level of theory. The total energy of the reactants indole + ·OH and indole + ·Cl are set to zero, respectively (reference state).
reaction forming IM$_2$-6-52OO-a is the most favorable. It
is noted that the formed IM$_{1-7}$-4OO-OH-s from IM$_{1-7}$-
4OO(a/s) can barrierlessly transform to form C$_8$H$_8$NO$_2$ (N-
(2-formylphenyl)formamide) and \( \cdot \)OH (collectively denoted
P$_1$-7-4-1) via concerted C-C and O-O bonds rupture. The
further transformation of the peroxy radicals IM$_{1-7}$-4OO(-
a/s), IM$_{2-6}$-6OO(a/s) and IM$_{2-6}$-5OO(a/s) needs to over-
come barriers above 20.5 kcal mol$^{-1}$ (relative to their re-
spective peroxy radicals), indicating that the further transfor-
mation of IM$_{1-7}$-4OO(a/s), IM$_{2-5}$-6OO(a/s) and IM$_{2-6}$-
5OO(a/s) should be very slow.

Based on the energetic data of the favorable reaction path-
ways, MESMER modeling was employed to investigate the
reaction rate constants and fractional yields for the reactions
of IM$_{1-7}$, IM$_{2-5}$ and IM$_{2-6}$ with O$_2$. Similar to previous
studies (Guo et al., 2020; F. F. Ma et al., 2021a, b; Zhang et
al., 2012; Fu et al., 2020; Crounse et al., 2013; Veres et al.,
2020), bimolecular reactions with NO and HO$_2$ are consid-
ered as competitive pathways for the unimolecular reactions
of the peroxy radicals IM$_{1-7}$-4OO(a/s), IM$_{2-5}$-6OO(a/s) and
IM$_{2-6}$-5OO(a/s) by simply adding their pseudo-first-
order rate constants into the master equation modeling. Here,
applied pseudo-first-order rate constants for peroxy radi-
cals (IM$_{1-7}$-4OO(a/s), IM$_{2-5}$-6OO(a/s) and IM$_{2-6}$-5OO(-a/s))
reaction with NO and HO$_2$ are 0.06 and 0.02 s$^{-1}$, re-
spectively, corresponding to reactions occurring at 200 ppt
NO and 50 ppt HO$_2$ conditions (Hofzumahaus et al., 2009;
Yu et al., 2020; Praske et al., 2018). The reactions of per-
 oxy radicals with NO and HO$_2$ should form organoni-
trate/alkoxy radicals (collectively denoted NO-P$_n$, where
$\eta$ marks products from the different peroxy radical re-
actions) and hydroperoxide (HO$_2$-P$_n$), respectively. Pseudo-
first-order rate constants of IM$_{1-7}$, IM$_{2-5}$, and IM$_{2-6}$ with
O$_2$ are calculated to be $3.0 \times 10^7$ s$^{-1}$, based on the reac-
tion rate constants of IM$_{1-7}$, IM$_{2-5}$, and IM$_{2-6}$ with O$_2$
($6.0 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) and the concentration
of O$_2$ ([O$_2$] = $5.0 \times 10^{18}$ molecule cm$^{-1}$). The simulated time-
dependent fractional yields are presented in Fig. 3.

As can be seen in Fig. 3, after 100 s, the reactions of
IM$_{1-7}$, IM$_{2-5}$ and IM$_{2-6}$ with O$_2$ mainly form the organon
itrate/alkoxy radicals NO-P$_4$ (C$_8$H$_8$NO$_2$/C$_8$H$_8$NO$_2$-\( \cdot \)OH),
NO-P$_5$ (C$_8$H$_2$N$_2$O$_5$Cl/C$_8$H$_2$NClO$^-\cdot$) and NO-P$_3$
(C$_8$H$_2$N$_2$O$_5$Cl/C$_8$H$_2$NClO$^-\cdot$), followed by the formation of
hydroperoxide HO$_2$-P$_3$ (C$_8$H$_8$NO$_3$), HO$_2$-P$_4$ (C$_8$H$_8$NO$_2$Cl)
and HO$_2$-P$_5$ (C$_8$H$_6$NO$_2$Cl), respectively. For the reactions
of IM$_{2-5}$ and IM$_{2-6}$ with O$_2$, the main products formed are
NO-P$_{4/5}$ and HO$_2$-P$_{4/5}$. In contrast, the IM$_{1-7}$+O$_2$ reaction
also leads to the fragmental products P$_1$-7-4-1 (C$_8$H$_7$NO$_2$
and \( \cdot \)OH) besides the main products NO-P$_3$ and HO$_2$-P$_3$.
This difference in product branching ratios is due to the
fact that the peroxy radical IM$_{1-7}$-4OO(a/s) has a lower uni-
molecular reaction energy barrier than IM$_{2-5}$-6OO(a/s) and
IM$_{2-6}$-5OO(a/s). It should be noted that the C$_8$H$_8$NO$_2$
product has been detected in previous experimental study of

Figure 2. Reaction pathways and corresponding energetic data for
the reactions of IM$_{1-7}$ (a), IM$_{2-5}$ (b) and IM$_{2-6}$ (c) with O$_2$.
Units are in kcal mol$^{-1}$. 

11548  J. Xue et al.: Atmospheric oxidation mechanism and kinetics of indole initiated by \( \cdot \)OH and \( \cdot \)Cl
the \( \cdot \text{OH} + \) indole reaction (Montoya-Aguilera et al., 2017), supporting the validity of our computational results.

An obvious difference for these three reactions is that the reaction of IM\(_1\)-7 with O\(_2\) can form peroxy radicals IM\(_1\)-7-4OO(-a/s) with high yields during the reactions. However, the yields of the corresponding peroxy radicals IM\(_2\)-5-6OO(-a/s) and IM\(_2\)-6-5OO(-a/s) from the reactions of IM\(_2\)-5 and IM\(_2\)-6 with O\(_2\) are low. The difference mainly originates from the difference in the formation energy of these three peroxy radicals as shown in Fig. 2. The \( \Delta E \) values of IM\(_1\)-7-4OO(-a/s) (\(-19.1/-19.4 \text{ kcal mol}^{-1}\)) are much lower than those of IM\(_2\)-5-6OO(-a/s) (\(-9.0/-8.1 \text{ kcal mol}^{-1}\)) and IM\(_2\)-6-5OO(-a/s) (\(-9.6/-9.0 \text{ kcal mol}^{-1}\)). As discussed above, the high formation energy of IM\(_2\)-5-6OO(-a/s) and IM\(_2\)-6-5OO(-a/s) should make IM\(_2\)-5-6OO(-a/s) and IM\(_2\)-6-5OO(-a/s) return back to the reactants, explaining the reason for the lower yields of IM\(_2\)-5-6OO(-a/s) and IM\(_2\)-6-5OO(-a/s).

### 3.3 Subsequent reactions of C\(_8\)H\(_6\)N radicals from the H-abstraction pathway

Here, the bimolecular reaction with O\(_2\) was mainly considered for C\(_8\)H\(_6\)N radicals as its sole atmospheric fate. It was found that the spin density distribution was mainly centered at the C atoms (C4 (0.662), C6 (0.261), C8 (0.178)) and N atom (0.256), indicating that the C\(_8\)H\(_6\)N radical is delocalized. This is in contrast to previously studied N-centered radicals formed from alkylamine oxidation, which is highly localized (Xie et al., 2015, 2014; Ma et al., 2018a; Tan et al., 2021; Borduas et al., 2015). Therefore, O\(_2\) addition to the C4, C6, C8 and N1 sites (including attack from both sides) is considered for the reaction of the C\(_8\)H\(_6\)N radicals with O\(_2\). As can be seen in Fig. 4, O\(_2\) additions to the C4 site of the C\(_8\)H\(_6\)N radicals forming C\(_8\)H\(_6\)N-4OO-a/s with \( E_a \) of \(-0.3 \text{ kcal mol}^{-1}\) are the most favorable, translating to pseudo-first-order reaction rate constants of \(3.0 \times 10^7 \text{ s}^{-1}\). Such rate constants are about 7 orders of magnitude higher than that of typical N-centered radicals reacting with NO even under very high NO concentration (5 ppb). Therefore, C\(_8\)H\(_6\)N radicals do not react with NO to form carcinogenic

---

**Figure 3.** Calculated fractional yields of species (at 200 ppt NO and 50 ppt HO\(_2\)• conditions) as a function of time in the reactions of IM\(_1\)-7 (a), IM\(_2\)-5 (b), IM\(_2\)-6 (c) and C\(_8\)H\(_6\)N (d) with O\(_2\) at 298 K and 1 atm.
nitrosamines in any appreciable amount, which is different from the previously reported reaction mechanism of N-centered radicals formed from the reactions of alkylamines with \( \cdot \)Cl (Xie et al., 2015, 2014; Ma et al., 2018a). To the best of our knowledge, this is the first study to reveal that despite forming radicals by abstracting an H atom at the N site, carcinogenic nitrosamines were not produced in the indole oxidation reaction.

For the transformation of the formed \( \text{C}_8\text{H}_6\text{N}-4\text{OO-a/s} \) radicals, the ring closure reaction to form \( \text{C}_8\text{H}_6\text{N}-43\text{OO-a/s} \) is the most favorable, but it still needs to overcome a 27.8 kcal mol\(^{-1}\) energy barrier; therefore, the further transformation of the formed \( \text{C}_8\text{H}_6\text{N}-4\text{OO-a/s} \) should proceed very slowly. The \( \text{C}_8\text{H}_6\text{N}-4\text{OO-a/s} \) should mainly react with NO and HO\(_2\) to form NO-P\(_6\) and HO\(_2\)-P\(_6\). Detailed kinetics calculations (Fig. 3d) further confirm that the reaction of \( \text{C}_8\text{H}_6\text{N} \) radicals with O\(_2\) mainly form NO-P\(_6\) and HO\(_2\)-P\(_6\) under 200 ppt NO and 50 ppt HO\(_2\) conditions.

4 Comparison with available experimental results and atmospheric implications

This study found that \( \cdot \)OH and \( \cdot \)Cl initiated reactions of indole mainly form organonitrates, alkoxy radicals and hydroperoxide products with \( \text{N}-(\text{2-formylphenyl})\text{formamide} \) (\( \text{C}_8\text{H}_7\text{NO}_2 \)) as a minor product at 200 ppt NO and 50 ppt HO\(_2\) conditions. The formed closed-shell products have high oxygen-to-carbon ratios compared with indole and therefore are expected to have lower vapor pressures, likely being first generation products that can be further oxidized and contribute to the formation of SOA.

With our findings, a comparison was made with the available experimental study on \( \cdot \)OH initiated reaction of indole. The calculated \( k_{\text{OH}} \) value (7.9 \( \times \) 10\(^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)) of indole is consistent with the experimental value (15 \( \times \) 10\(^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)) (Atkinson et al., 1995), indicating the reliability of applied theoretical methods. A signal with the molecular formula \( \text{C}_8\text{H}_7\text{NO}_2 \) has been ob-
served in the mass spectrum in an experimental study by Montoya-Aguilera et al. (2017), supporting the formation of the predicted N-(2-formylphenyl)formamide. To the best of our knowledge, our study is the first to reveal the chemical identity of the mass spectrum signal as N-(2-formylphenyl)formamide, as opposed to the proposed 3-oxy-2-hydroxy-indole. In addition, monomeric products (isatin and isatoic anhydride) and dimer products have not been observed in our computational study. We speculate that they may be produced from the subsequent conversion of the formed alkoxy radicals, multi-generation reactions of organonitrates and hydroperoxide as well as self- or cross reactions of peroxy radicals (RO$_2$ + RO$_2$). Therefore, further studies are warranted to investigate the subsequent transformation of the formed alkoxy radicals, organonitrates and hydroperoxide, and the RO$_2$ + RO$_2$ reactions, to accurately describe the atmospheric impact of indole.

The calculated $k_{\text{Cl}}$ value of the indole + •Cl reaction is a factor of 3.7 higher than that of the indole + •OH reaction, and is close to the $k_{\text{Cl}}$ values for the reactions of alkylamines, heterocyclic amines and amides with •Cl (Xie et al., 2017, 2015; Ma et al., 2018a; Nicovich et al., 2015). The contribution of •Cl to the transformation of indole is calculated to be 36 %–36 % of •OH, assuming •Cl concentrations equal to 1 %–10 % of that of •OH (Wang and Ruiz, 2017; Nicovich et al., 2015; Xie et al., 2017, 2015; Ma et al., 2018a). Therefore, •Cl plays an important role in the overall transformation of indole. More importantly, •Cl initiated reaction of indole does not lead to the formation of carcinogenic nitrosamines although •Cl can favorably abstract the H atom from the N site to form C$_8$H$_6$N radicals, which is a plausible precursor of carcinogenic nitrosamines. Hence, to the best of our knowledge, this is the first study to reveal that despite forming radicals by abstracting an H atom at the N site, carcinogenic nitrosamines were not produced in the indole oxidation reaction. This is most likely caused by the delocalized character of the formed C$_8$H$_6$N radicals due to the existence of the adjacent unsaturated bonds. Therefore, this study further confirms that the functional groups connected to the NH$_x$ ($x = 1, 2$) group highly affect the atmospheric fate of ONCs. Further studies should be performed to investigate the structure–activity relationship of •Cl initiated reactions of ONCs to comprehensively evaluate their atmospheric impacts.

**Data availability.** The data in this article are available from the corresponding author upon request (maff@dlut.edu.cn, hbxie@dlut.edu.cn).

**Supplement.** The supplement related to this article is available online at: https://doi.org/10.5194/acp-22-11543-2022-supplement.

**Author contributions.** FM and HBX designed the research model; JX, FM and HBX performed the research; JX, FM and HBX analyzed the data; JX, FM, JE, HBX and JC wrote the paper; and FM, HBX, JE and JC reviewed and revised the paper.

**Competing interests.** The contact author has declared that none of the authors has any competing interests.

**Disclaimer.** Publisher’s note: Copernicus Publications remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

**Acknowledgements.** We thank Struan H. Robertson (Dassault Systèmes) for the discussion on the MESMER simulations. The study was supported by National Natural Science Foundation of China (grant nos. 22176022, 21876024), the LiaoNing Revitalization Talents Program (grant no. XLYC1907194), the Major International (Regional) Joint Research Project (grant no. 21661142001) and the Supercomputing Center of Dalian University of Technology.

**Financial support.** This research has been supported by the National Natural Science Foundation of China (grant nos. 22176022, 21876024), the LiaoNing Revitalization Talents Program (grant no. XLYC1907194) and the Major International (Regional) Joint Research Project (grant no. 21661142001).

**Review statement.** This paper was edited by John Liggio and reviewed by two anonymous referees.

**References**


J. Xue et al.: Atmospheric oxidation mechanism and kinetics of indole initiated by •OH and •Cl

11555


https://doi.org/10.5194/acp-22-11543-2022
Atmos. Chem. Phys., 22, 11543–11555, 2022