Supplement of

Atmospheric oxidation mechanism and kinetics of indole initiated by ·OH and ·Cl: a computational study

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1. Tunneling effects ........................................................................................................... S3
2. Table S2 ....................................................................................................................... S4
3. Table S3 ....................................................................................................................... S5
4. Table S4 ....................................................................................................................... S5
5. Table S5 ....................................................................................................................... S6
6. Table S6 ....................................................................................................................... S12
7. Table S7 ....................................................................................................................... S13
8. Table S8 ....................................................................................................................... S14
9. Table S9 ....................................................................................................................... S15
10. Table S10 ................................................................................................................... S16
11. Figure S1 .................................................................................................................. S19
12. Figure S2 .................................................................................................................. S20
13. References ............................................................................................................... S21
Tunneling effects

For the reactions involving H-abstraction or H-shift, tunneling effects could influence their reaction rate constants and branching ratios of products. To probe the tunneling effects, reaction rate constants \( (k) \) of bimolecular H-abstraction pathways and unimolecular H-shift pathways involved in the key reaction pathways and branching ratios \( (I) \) of important species (intermediates \( \text{IM}_{1-7} \), \( \text{IM}_{2-5} \) and \( \text{IM}_{2-6} \)), products \( (\text{P}_{2-10}, \text{P}_{1-7-4-1}) \), organonitrates (and alkoxy radicals, \( \text{NO-P}_3 \) and \( \text{NO-P}_4 \)), hydroperoxide \( (\text{HO}_2\text{-P}_3, \text{HO}_2\text{-P}_4) \)) without tunneling effects were calculated at 298 K and 1 atm. The calculated data are shown in Table S1. It can be noted that all the values of \( k \) without the tunneling effects are at least one (up to three) order of magnitude lower than the corresponding values with tunneling effects, indicating that tunneling effects can significantly increase \( k \) values of the important reaction pathways. In addition, the tunneling effects have various effects on the branching ratios of important species. The tunneling effects increase the yields of \( \text{P}_{2-10} \), and \( \text{P}_{1-7-4-1} \), almost have no effect on the yields of \( \text{IM}_{1-7} \), \( \text{IM}_{2-6} \), \( \text{NO-P}_4 \) and \( \text{HO}_2\text{-P}_4 \) and reduce the yields of \( \text{IM}_{2-5} \), \( \text{NO-P}_3 \) and \( \text{HO}_2\text{-P}_3 \).

Table S1. Calculated reaction rate constants \( (k) \) of important unimolecular H-shift/bimolecular H-abstraction pathways and branching ratios \( (I) \) of main products with and without considering tunneling effects at 298 K and 1 atm .

| Pathways                      | \( k \)                          | Species     | \( I \)   |
|-------------------------------|----------------------------------|-------------|-----------|
| \( \text{R}_1 \rightarrow \text{P}_{1-10} \) | Tun\(^*\) \( 1.7 \times 10^{-15} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) | \( \text{IM}_{1-7} \) | 77.4% 77.9% |
|                               | NoTun\(^\#\) \( 1.1 \times 10^{-16} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) | \( \text{IM}_{2-5} \) | 31.4% 34.3% |
| \( \text{R}_2 \rightarrow \text{P}_{2-10} \) | Tun\(^*\) \( 4.5 \times 10^{-11} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) | \( \text{IM}_{2-6} \) | 45.5% 50.1% |
|                               | NoTun\(^\#\) \( 8.7 \times 10^{-12} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) | \( \text{P}_{2-10} \) | 23.1% 15.6% |
| \( \text{IM}_{1-7}4\text{OO-s} \rightarrow \text{IM}_{1-7}4\text{OO-OH-s} \) | Tun\(^*\) \( 1.2 \times 10^{-2} \) s\(^{-1}\) | \( \text{P}_{1-7-4-1} \) | 6.4% 3.1% |
|                               | NoTun\(^\#\) \( 5.5 \times 10^{-3} \) s\(^{-1}\) | \( \text{NO-P}_3 \) | 67.3% 70.6% |
| \( \text{IM}_{2-5}6\text{OO-a} \rightarrow \text{IM}_{2-5}6\text{OO-C5H-a} \) | Tun\(^*\) \( 7.6 \times 10^{-4} \) s\(^{-1}\) | \( \text{HO}_2\text{-P}_3 \) | 24.9% 26.1% |
|                               | NoTun\(^\#\) \( 2.3 \times 10^{-7} \) s\(^{-1}\) | \( \text{NO-P}_4 \) | 72.4% 73.0% |
|                               |                                  | \( \text{HO}_2\text{-P}_4 \) | 26.8% 27.0% |

\(^*\)Tunneling effects were taken into account when calculating the reaction rate constants.

\(^\#\)Tunneling effects were not taken into account when calculating the reaction rate constants.
Table S2. Values of $T_1$ diagnostics for the intermediates and transition states involved in the key reaction pathways in the CCSD(T)/6-31+G(d') calculations within the CBS-QB3 scheme.

| Species       | $T_1$ diagnostics | Species            | $T_1$ diagnostics |
|---------------|-------------------|--------------------|-------------------|
| TS$_{1,7}$    | 0.039             | IM$_{1,7}$         | 0.033             |
| TS$_{2,5}$    | 0.033             | IM$_{2,5}$         | 0.031             |
| TS$_{2,6}$    | 0.034             | IM$_{2,6}$         | 0.031             |
| TS$_{2,10}$   | 0.028             | C$_8$H$_6$N        | 0.039             |
| TS$_{3,2}$    | 0.038             | IM$_{1,7}$-4OO-s  | 0.020             |
| TS$_{3,2'}$   | 0.037             | IM$_{1,7}$-4OO-a  | 0.020             |
| TS$_{3,2-4}$  | 0.037             | IM$_{1,7}$-4OO-NH-s | 0.031          |
| TS$_{3,2-7}$  | 0.027             | IM$_{1,7}$-4OO-OH-s | 0.035          |
| TS$_{4,3}$    | 0.035             | IM$_{2,5}$-6OO-s  | 0.020             |
| TS$_{4,3'}$   | 0.036             | IM$_{2,5}$-6OO-a  | 0.020             |
| TS$_{4,3-7}$  | 0.032             | IM$_{2,5}$-6OO-C5H-a | 0.029        |
| TS$_{5,2}$    | 0.037             | IM$_{2,6}$-5OO-s  | 0.020             |
| TS$_{5,2'}$   | 0.038             | IM$_{2,6}$-5OO-a  | 0.020             |
| TS$_{5,2-1}$  | 0.031             | IM$_{2,6}$-52OO-a | 0.023             |
| TS$_{6,2}$    | 0.036             | C$_8$H$_6$N-4OO-s | 0.021             |
| TS$_{6,2'}$   | 0.036             | C$_8$H$_6$N-4OO-a | 0.021             |
| TS$_{6,2-3}$  | 0.043             | C$_8$H$_6$N-43OO-s | 0.036          |
| TS$_{6,2-3}$  | 0.043             | C$_8$H$_6$N-43OO-a | 0.036          |
Table S3. Polarizabilities ($\alpha$) and the first ionization potentials ($I$) used in the long-range transition state theory.

| Species                  | $\alpha/ao^3$ | $I$/eV   |
|--------------------------|---------------|---------|
| C$_8$H$_7$N (indole)     | 105.62$^*$    | 7.74$^*$|
| $\cdot$C$_8$H$_6$N (P$_{1-10}$/P$_{2-10}$) | 106.58$^*$    | 8.08$^*$|
| $\cdot$C$_8$H$_6$N (P$_{1-11}$/P$_{2-11}$) | 104.79$^*$    | 8.29$^*$|
| $\cdot$C$_8$H$_6$N (P$_{1-12}$/P$_{2-12}$) | 104.90$^*$    | 8.04$^*$|
| $\cdot$C$_8$H$_6$N (P$_{1-13}$/P$_{2-13}$) | 103.47$^*$    | 7.80$^*$|
| $\cdot$C$_8$H$_6$N (P$_{1-14}$/P$_{2-14}$) | 103.25$^*$    | 8.13$^*$|
| $\cdot$C$_8$H$_6$N (P$_{1-15}$/P$_{2-15}$) | 104.00$^*$    | 7.62$^*$|
| $\cdot$C$_8$H$_6$N (P$_{1-16}$/P$_{2-16}$) | 8.26$^#$      | 15.24$^#$|
| OH                       | 10.60$^#$     | 14.71$^#$|
| Cl                       | 14.71$^#$     | 12.97$^#$|
| HCl                      | 16.97$^#$     | 12.74$^#$|

$^*$ $\alpha$ and $I$ were calculated at BLYP/def2-QZVPD and CBS-QB3//M06-2X/6-31+G(d,p) level of theory, respectively, which have been used in our previous studies.1-4

# Obtained from the NIST database 5

Table S4. Lennard-Jones parameters of the intermediates for various reactions used in the MultiWell or MESMER simulations.

| Reactions     | $\sigma$/\AA | $\varepsilon$/K |
|---------------|---------------|-----------------|
| Indole + $\cdot$OH | 6.4           | 685             |
| Indole + $\cdot$Cl    | 6.5           | 619             |
| IM$_{1-7}$ + O$_2$     | 6.6           | 739             |
| IM$_{2-5}$ + O$_2$     | 6.7           | 673             |
| IM$_{2-6}$ + O$_2$     | 6.7           | 673             |
| C$_8$H$_6$N + O$_2$    | 6.4           | 635             |
Table S5. NBO charge distribution for all the pre-reactive complexes of the indole + ·Cl reaction.

| Species | Atoms | Number | Natural Charge |
|---------|-------|--------|----------------|
| Indole  | N     | 1      | -0.596         |
|         | C     | 2      | 0.143          |
|         | C     | 3      | -0.109         |
|         | C     | 4      | -0.327         |
|         | C     | 5      | -0.274         |
|         | C     | 6      | -0.222         |
|         | C     | 7      | -0.043         |
|         | C     | 8      | -0.255         |
|         | C     | 9      | -0.276         |
|         | H     | 10     | 0.453          |
|         | H     | 11     | 0.259          |
|         | H     | 12     | 0.249          |
|         | H     | 13     | 0.250          |
|         | H     | 14     | 0.248          |
|         | H     | 15     | 0.250          |
|         | H     | 16     | 0.250          |
| RC₂₋₅  | N     | 1      | -0.563         |
|         | C     | 2      | 0.173          |
|         | C     | 3      | -0.127         |
|         | C     | 4      | -0.304         |
|         | C     | 5      | -0.241         |
|         | C     | 6      | -0.141         |
|         | C     | 7      | -0.040         |
|         | C     | 8      | -0.185         |
|         | C     | 9      | -0.286         |
|         | H     | 10     | 0.466          |
|         | H     | 11     | 0.265          |
|         | H     | 12     | 0.294          |
|         | H     | 13     | 0.256          |
|         | H     | 14     | 0.256          |
|         | H     | 15     | 0.266          |
| Atm   | Num | Value |
|-------|-----|-------|
| H     | 14  | 0.256 |
| H     | 15  | 0.266 |
| H     | 16  | 0.261 |
| Cl    | 17  | -0.350|

**RC\textsubscript{2-13}**  

| Atm   | Num | Value |
|-------|-----|-------|
| N     | 1   | -0.576|
| C     | 2   | 0.126 |
| C     | 3   | -0.087|
| C     | 4   | -0.302|
| C     | 5   | -0.201|
| C     | 6   | -0.199|
| C     | 7   | -0.020|
| C     | 8   | -0.273|
| C     | 9   | -0.193|
| H     | 10  | 0.459 |
| H     | 11  | 0.270 |
| H     | 12  | 0.254 |
| H     | 13  | 0.293 |
| H     | 14  | 0.255 |
| H     | 15  | 0.260 |
| H     | 16  | 0.267 |
| Cl    | 17  | -0.334|

**RC\textsubscript{2-14}**  

| Atm   | Num | Value |
|-------|-----|-------|
| N     | 1   | -0.578|
| C     | 2   | 0.165 |
| C     | 3   | -0.122|
| C     | 4   | -0.221|
| C     | 5   | -0.269|
| C     | 6   | -0.193|
| C     | 7   | 0.041 |
| C     | 8   | -0.228|
| C     | 9   | -0.268|
| H     | 10  | 0.465 |
| H     | 11  | 0.288 |
| H     | 12  | 0.257 |
| Atom | Number | Charge |
|------|--------|--------|
| H    | 10     | 0.260  |
| H    | 14     | 0.281  |
| H    | 15     | 0.257  |
| H    | 16     | 0.257  |
| Cl   | 17     | -0.391 |

**RC2-15**

| Atom | Number | Charge |
|------|--------|--------|
| N    | 1      | -0.563 |
| C    | 2      | 0.173  |
| C    | 3      | -0.127 |
| C    | 4      | -0.304 |
| C    | 5      | -0.241 |
| C    | 6      | -0.141 |
| C    | 7      | -0.040 |
| C    | 8      | -0.185 |
| C    | 9      | -0.286 |
| H    | 10     | 0.466  |
| H    | 11     | 0.265  |
| H    | 12     | 0.294  |
| H    | 13     | 0.256  |
| H    | 14     | 0.256  |
| H    | 15     | 0.266  |
| H    | 16     | 0.261  |
| Cl   | 17     | -0.350 |

**RC2-16**

| Atom | Number | Charge |
|------|--------|--------|
| N    | 1      | -0.579 |
| C    | 2      | 0.123  |
| C    | 3      | -0.068 |
| C    | 4      | -0.323 |
| C    | 5      | -0.197 |
| C    | 6      | -0.213 |
| C    | 7      | -0.006 |
| C    | 8      | -0.226 |
| C    | 9      | -0.242 |
| H    | 10     | 0.462  |
| H    | 11     | 0.266  |
| Element | Position | Distance |
|---------|----------|----------|
| H       | 12       | 0.267    |
| H       | 13       | 0.258    |
| H       | 14       | 0.255    |
| H       | 15       | 0.289    |
| H       | 16       | 0.264    |
| Cl      | 17       | -0.331   |
| Pathways | 0.1 atm | 0.4 atm | 0.7 atm | 1.0 atm |
|----------|---------|---------|---------|--------|
| Indole + ·OH | $7.90 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $7.90 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $7.90 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $7.90 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ |
| Indole + ·Cl | $2.91 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.91 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.91 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.91 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ |
| IM$_{1.7}$ + O$_2$ | $6.12 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.12 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.12 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.12 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ |
| IM$_{2.5}$ + O$_2$ | $6.15 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.15 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.15 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.15 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ |
| IM$_{2.6}$ + O$_2$ | $6.10 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.10 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.10 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.10 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ |
| CsH$_6$N + O$_2$ | $6.13 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.13 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.13 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.13 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ |
| IM$_{1.7}$-4OO $\rightarrow$ IM$_{1.7}$-4OO-OH | $1.22 \times 10^{-2}$ s$^{-1}$ | $1.22 \times 10^{-2}$ s$^{-1}$ | $1.22 \times 10^{-2}$ s$^{-1}$ | $1.22 \times 10^{-2}$ s$^{-1}$ |
| IM$_{2.5}$-6OO $\rightarrow$ IM$_{2.5}$-6OO-C5H | $2.94 \times 10^{-4}$ s$^{-1}$ | $2.94 \times 10^{-4}$ s$^{-1}$ | $2.94 \times 10^{-4}$ s$^{-1}$ | $2.94 \times 10^{-4}$ s$^{-1}$ |
| IM$_{2.6}$-5OO $\rightarrow$ IM$_{2.6}$-5OO-a | $3.60 \times 10^{-7}$ s$^{-1}$ | $3.60 \times 10^{-7}$ s$^{-1}$ | $3.60 \times 10^{-7}$ s$^{-1}$ | $3.60 \times 10^{-7}$ s$^{-1}$ |
| CsH$_6$N-4OO $\rightarrow$ CsH$_6$N-4OO-a | $8.77 \times 10^{-9}$ s$^{-1}$ | $8.77 \times 10^{-9}$ s$^{-1}$ | $8.77 \times 10^{-9}$ s$^{-1}$ | $8.77 \times 10^{-9}$ s$^{-1}$ |

Table S6. Calculated reaction rate constants ($k$) at 298 K and over the pressure range from 0.1 to 1.0 atm of the main reaction pathways for the indole + ·OH/Cl reactions.
Table S7. Calculated reaction rate constants ($k$) at 298 K and over the energy transfer parameters from 50 to 250 cm$^{-1}$ of the main reaction pathways for the indole + ·OH/Cl reactions

| Pathways                  | $\Delta E_d = 50$ cm$^{-1}$ | $\Delta E_d = 100$ cm$^{-1}$ | $\Delta E_d = 150$ cm$^{-1}$ | $\Delta E_d = 200$ cm$^{-1}$ | $\Delta E_d = 250$ cm$^{-1}$ |
|---------------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|
| Indole+OH                 | $7.89 \times 10^{11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $2.90 \times 10^{10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $7.90 \times 10^{11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $7.90 \times 10^{11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $7.90 \times 10^{11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ |
| Indole+Cl                 | $2.90 \times 10^{10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.12 \times 10^{12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.12 \times 10^{12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.12 \times 10^{12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.12 \times 10^{12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ |
| IM$_{1.7}$ + O$_2$        | $6.15 \times 10^{12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.15 \times 10^{12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.15 \times 10^{12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.15 \times 10^{12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.15 \times 10^{12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ |
| IM$_{2.5}$ + O$_2$        | $6.10 \times 10^{12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.10 \times 10^{12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.10 \times 10^{12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.10 \times 10^{12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.10 \times 10^{12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ |
| IM$_{2.6}$ + O$_2$        | $6.13 \times 10^{12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.13 \times 10^{12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.13 \times 10^{12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.13 \times 10^{12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.13 \times 10^{12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ |
| C$_{5}$H$_{5}$N + O$_2$  | $6.13 \times 10^{12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.13 \times 10^{12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.13 \times 10^{12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.13 \times 10^{12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ | $6.13 \times 10^{12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ |
| IM$_{1.7}$-4OO-s $\rightarrow$ IM$_{1.7}$-4OO-Cl $\rightarrow$ | $1.22 \times 10^{-2}$ s$^{-1}$ | $1.22 \times 10^{-2}$ s$^{-1}$ | $1.22 \times 10^{-2}$ s$^{-1}$ | $1.22 \times 10^{-2}$ s$^{-1}$ | $1.22 \times 10^{-2}$ s$^{-1}$ |
| IM$_{2.5}$-6OO-a $\rightarrow$ IM$_{2.5}$-6OO-C5H-a | $7.65 \times 10^{-4}$ s$^{-1}$ | $7.65 \times 10^{-4}$ s$^{-1}$ | $7.65 \times 10^{-4}$ s$^{-1}$ | $7.65 \times 10^{-4}$ s$^{-1}$ | $7.65 \times 10^{-4}$ s$^{-1}$ |
| IM$_{2.6}$-5OO-a $\rightarrow$ IM$_{2.6}$-5OO-C5H-a | $3.60 \times 10^{-7}$ s$^{-1}$ | $3.60 \times 10^{-7}$ s$^{-1}$ | $3.60 \times 10^{-7}$ s$^{-1}$ | $3.60 \times 10^{-7}$ s$^{-1}$ | $3.60 \times 10^{-7}$ s$^{-1}$ |
| C$_{5}$H$_{5}$N-4OO-a/s $\rightarrow$ C$_{5}$H$_{5}$N-43OO-a/s | $8.77 \times 10^{-9}$ s$^{-1}$ | $8.77 \times 10^{-9}$ s$^{-1}$ | $8.77 \times 10^{-9}$ s$^{-1}$ | $8.77 \times 10^{-9}$ s$^{-1}$ | $8.77 \times 10^{-9}$ s$^{-1}$ |
Table S8. Calculated branching ratios ($\Gamma$) at 298 K and over the pressure range from 0.1 to 1.0 atm of the main reaction pathways for the indole + \textbf{ -OH/-Cl reactions}

| Species | $\Gamma$ 0.1 atm | $\Gamma$ 0.4 atm | $\Gamma$ 0.7 atm | $\Gamma$ 1.0 atm |
|---------|-----------------|-----------------|-----------------|-----------------|
| IM$_{1-7}$ | 77.4% | 77.4% | 77.4% | 77.4% |
| IM$_{2-5}$ | 31.4% | 31.4% | 31.4% | 31.4% |
| IM$_{2-6}$ | 45.5% | 45.5% | 45.5% | 45.5% |
| P$_{2-10}$ | 23.1% | 23.1% | 23.1% | 23.1% |
| P$_{1-7-4-1}$ | 6.6% | 6.5% | 6.5% | 6.5% |
| NO-P$_{3}$ | 67.3% | 67.3% | 67.3% | 67.3% |
| HO$_{2}$-P$_{3}$ | 24.9% | 24.9% | 24.9% | 24.9% |
| NO-P$_{4}$ | 72.4% | 72.4% | 72.4% | 72.4% |
| HO$_{2}$-P$_{4}$ | 26.8% | 26.8% | 26.8% | 26.8% |
| NO-P$_{5}$ | 72.7% | 72.7% | 72.7% | 72.7% |
| HO$_{2}$-P$_{5}$ | 26.9% | 26.9% | 26.9% | 26.9% |
| NO-P$_{6}$ | 73.0% | 73.0% | 73.0% | 73.0% |
| HO$_{2}$-P$_{6}$ | 27.0% | 27.0% | 27.0% | 27.0% |
Table S9. Calculated branching ratios ($\Gamma$) at 298 K and over the energy transfer parameters range from 50 to 250 cm$^{-1}$ of the main reaction pathways for the indole + -OH/-Cl reactions

| Species | $\Delta E_d = 50$ cm$^{-1}$ | $\Delta E_d = 100$ cm$^{-1}$ | $\Delta E_d = 150$ cm$^{-1}$ | $\Delta E_d = 200$ cm$^{-1}$ | $\Delta E_d = 250$ cm$^{-1}$ |
|---------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| IM1-7   | 77.4%                      | 77.4%                      | 77.4%                      | 77.4%                      | 77.4%                      |
| IM2-5   | 31.4%                      | 31.4%                      | 31.4%                      | 31.4%                      | 31.4%                      |
| IM2-6   | 45.5%                      | 45.5%                      | 45.5%                      | 45.5%                      | 45.5%                      |
| P2-10   | 23.1%                      | 23.1%                      | 23.1%                      | 23.1%                      | 23.1%                      |
| P1-7-4-1| 6.5%                       | 6.5%                       | 6.5%                       | 6.5%                       | 6.5%                       |
| NO-P3   | 67.3%                      | 67.3%                      | 67.3%                      | 67.3%                      | 67.3%                      |
| HO2-P3  | 24.9%                      | 24.9%                      | 24.9%                      | 24.9%                      | 24.9%                      |
| NO-P4   | 72.4%                      | 72.4%                      | 72.4%                      | 72.4%                      | 72.4%                      |
| HO2-P4  | 26.8%                      | 26.8%                      | 26.8%                      | 26.8%                      | 26.8%                      |
| NO-P5   | 72.7%                      | 72.7%                      | 72.7%                      | 72.7%                      | 72.7%                      |
| HO2-P5  | 26.9%                      | 26.9%                      | 26.9%                      | 26.9%                      | 26.9%                      |
| NO-P6   | 73.0%                      | 73.0%                      | 73.0%                      | 73.0%                      | 73.0%                      |
| HO2-P6  | 27.0%                      | 27.0%                      | 27.0%                      | 27.0%                      | 27.0%                      |
Table S10. Calculated spin distribution based on the Mulliken population analysis for main intermediates involved in the indole + ·OH/·Cl reactions.

| Species | Atoms | Number | Mulliken atomic spin densities |
|---------|-------|--------|-------------------------------|
| IM1.7   | N     | 1      | 0.038                         |
| C       | 2     | 0.146  |
| C       | 3     | -0.222 |
| C       | 4     | 0.729  |
| C       | 5     | -0.111 |
| C       | 6     | 0.287  |
| C       | 7     | -0.039 |
| C       | 8     | 0.278  |
| C       | 9     | -0.107 |
| H       | 10    | -0.002 |
| H       | 11    | -0.031 |
| H       | 12    | 0.003  |
| H       | 13    | -0.011 |
| H       | 14    | 0.027  |
| H       | 15    | -0.013 |
| H       | 16    | 0.003  |
| O       | 17    | 0.021  |
| H       | 18    | 0.003  |

| IM2.5   | N     | 1      | 0.044  |
| C       | 2     | 0.200  |
| C       | 3     | -0.186 |
| C       | 4     | 0.103  |
| C       | 5     | -0.061 |
| C       | 6     | 0.573  |
| C       | 7     | -0.055 |
| C       | 8     | 0.461  |
| C       | 9     | -0.230 |
| H       | 10    | -0.003 |
| H       | 11    | -0.003 |
| H       | 12    | 0.023  |
| H | 12 | -0.009 |
|---|----|--------|
| H | 13 | 0.000  |
| H | 14 | -0.009 |
| H | 15 | 0.001  |
Figure S1. Calculated reaction rate constants ($k$) at 1 atm and over the temperature range from 230 to 330 K for the indole + ·OH (A) and indole + ·Cl (B) reactions.
Figure S2. Calculated branching ratios ($\Gamma$ values) at 1 atm and over the temperature range from 230 to 330 K for the indole + ·OH (A) and indole + ·Cl (B) reactions.
References

1. Guo, X. R.; Ma, F. F.; Liu, C., Niu, J., He, N., Chen, J. W.; Xie, H. B.: Atmospheric Oxidation Mechanism and Kinetics of Isoprene Initiated by Chlorine Radicals: A Computational Study, *Sci. Total Environ.*, 2020, 712, 136330.

2. Ma, F.F.; Xie, H. B.; Li, M.; Wang, S.; Zhang, R. Y.; Chen, J. W.: Autoxidation Mechanism for Atmospheric Oxidation of Tertiary Amines: Implications for Secondary Organic Aerosol Formation, *Chemosphere*, 2021, 273, 129207.

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

4. Xie, H. B.; Ma, F. F.; Yu, Q.; He, N.; Chen, J. W. Computational Study of the Reactions of Chlorine Radicals with Atmospheric Organic Compounds Featuring NHx-pi-Bond (x=1, 2) Structures. *J. Phys. Chem. A* 2017, 121, 1657-1665.

5. NIST Computational Chemistry Comparison and Benchmark Database. NIST Standard Reference Database Number 101, R. D. Johnson III, Release 16a, August 2013. http://cccbdb.nist.gov/.