

*Supplement of*

# **Atmospheric Oxidation Mechanism and Kinetics of Indole Initiated by $\cdot\text{OH}$ and $\cdot\text{Cl}$ : A Computational Study**

Jingwen Xue<sup>1#</sup>, Fangfang Ma<sup>1\*</sup>, Jonas Elm<sup>2</sup>, Jingwen Chen<sup>1</sup>, Hong-Bin Xie<sup>1\*</sup>

5 <sup>1</sup>Key Laboratory of Industrial Ecology and Environmental Engineering (Ministry of Education), School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China

<sup>2</sup>Department of Chemistry and iClimate, Aarhus University, Langelandsgade 140, DK-8000 Aarhus C, Denmark

*Correspondence to:* Fang-Fang Ma (maff@dlut.edu.cn); Hong-Bin Xie (hbxie@dlut.edu.cn)

	1. Tunneling effects.....	S3
	2. Table S2.....	S4
	3. Table S3.....	S5
	4. Table S4.....	S5
15	5. Table S5.....	S6
	6. Table S6.....	S12
	7. Figure S1 .....	S15
	8. Figure S2 .....	S16
	9. References .....	S17
20		

## 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 (IM<sub>1-7</sub>, IM<sub>2-5</sub> and IM<sub>2-6</sub>), products (P<sub>2-10</sub>, P<sub>1-7-4-1</sub>), organonitrates (and alkoxy radicals, NO-P<sub>3</sub> and NO-P<sub>4</sub>), hydroperoxide (HO<sub>2</sub>-P<sub>3</sub>, and HO<sub>2</sub>-P<sub>4</sub>)) 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 P<sub>2-10</sub>, and P<sub>1-7-4-1</sub>, almost have no effect on the yields of IM<sub>1-7</sub>, IM<sub>2-6</sub>, NO-P<sub>4</sub> and HO<sub>2</sub>-P<sub>4</sub> and reduce the yields of IM<sub>2-5</sub>, NO-P<sub>3</sub> and HO<sub>2</sub>-P<sub>3</sub>.

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 1 atm and 298 K

Pathways	$k$		Species	$I$	
	Tun*	NoTun <sup>#</sup>		Tun*	NoTun <sup>#</sup>
R <sub>1</sub> → P <sub>1-10</sub>	$1.7 \times 10^{-15}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	$1.1 \times 10^{-16}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	IM <sub>1-7</sub>	77.4%	77.9%
			IM <sub>2-5</sub>	31.4%	34.3%
R <sub>2</sub> → P <sub>2-10</sub>	$4.5 \times 10^{-11}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	$8.7 \times 10^{-12}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	IM <sub>2-6</sub>	45.5%	50.1%
			P <sub>2-10</sub>	23.1%	15.6%
			P <sub>1-7-4-1</sub>	6.4%	3.1%
IM <sub>1-7</sub> -4OO- <i>s</i> → IM <sub>1-7</sub> -4OO-OH- <i>s</i>	$1.2 \times 10^{-2}$ s <sup>-1</sup>	$5.5 \times 10^{-3}$ s <sup>-1</sup>	NO-P <sub>3</sub>	67.3%	70.6%
IM <sub>2-5</sub> -6OO- <i>a</i> → IM <sub>2-5</sub> -6OO-C5H- <i>a</i>	$7.6 \times 10^{-4}$ s <sup>-1</sup>	$2.3 \times 10^{-7}$ s <sup>-1</sup>	HO <sub>2</sub> -P <sub>3</sub>	24.9%	26.1%
			NO-P <sub>4</sub>	72.4%	73.0%
			HO <sub>2</sub> -P <sub>4</sub>	26.8%	27.0%

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

<sup>#</sup>Tunneling effects were not taken into account when calculating the reaction rate constants.

40 **Table S2. Values of T<sub>1</sub> 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 <sub>1</sub> diagnostics	Species	T <sub>1</sub> diagnostics
TS <sub>1-7</sub>	0.039	IM <sub>1-7</sub>	0.033
TS <sub>2-5</sub>	0.033	IM <sub>2-5</sub>	0.031
TS <sub>2-6</sub>	0.034	IM <sub>2-6</sub>	0.031
TS <sub>2-10</sub>	0.028	C <sub>8</sub> H <sub>6</sub> N	0.039
TS <sub>3-2</sub>	0.038	IM <sub>1-7-4OO-s</sub>	0.020
TS <sub>3-2'</sub>	0.037	IM <sub>1-7-4OO-a</sub>	0.020
TS <sub>3-2-4</sub>	0.037	IM <sub>1-7-4OO-NH-s</sub>	0.031
TS <sub>3-2-7</sub>	0.027	IM <sub>1-7-4OO-OH-s</sub>	0.035
TS <sub>4-3</sub>	0.035	IM <sub>2-5-6OO-s</sub>	0.020
TS <sub>4-3'</sub>	0.036	IM <sub>2-5-6OO-a</sub>	0.020
TS <sub>4-3'-7</sub>	0.032	IM <sub>2-5-6OO-C5H-a</sub>	0.029
TS <sub>5-2</sub>	0.037	IM <sub>2-6-5OO-s</sub>	0.020
TS <sub>5-2'</sub>	0.038	IM <sub>2-6-5OO-a</sub>	0.020
TS <sub>5-2'-1</sub>	0.031	IM <sub>2-6-52OO-a</sub>	0.023
TS <sub>6-2</sub>	0.036	C <sub>8</sub> H <sub>6</sub> N-4OO-s	0.021
TS <sub>6-2'</sub>	0.036	C <sub>8</sub> H <sub>6</sub> N-4OO-a	0.021
TS <sub>6-2-3</sub>	0.043	C <sub>8</sub> H <sub>6</sub> N-43OO-s	0.036
TS <sub>6-2'-3</sub>	0.043	C <sub>8</sub> H <sub>6</sub> N-43OO-a	0.036

**Table S3. Polarizabilities ( $\alpha$ ) and the first ionization potentials ( $I$ ) used in the long-range transition state theory.**

Species	$\alpha/a_0^3$	$I$ (eV)
C <sub>8</sub> H <sub>7</sub> N (indole)	105.62*	7.74*
·C <sub>8</sub> H <sub>6</sub> N (P <sub>1-10</sub> /P <sub>2-10</sub> )	106.58*	8.08*
·C <sub>8</sub> H <sub>6</sub> N (P <sub>1-11</sub> /P <sub>2-11</sub> )	104.79*	8.29*
·C <sub>8</sub> H <sub>6</sub> N (P <sub>1-12</sub> /P <sub>2-12</sub> )	104.90*	8.04*
·C <sub>8</sub> H <sub>6</sub> N (P <sub>1-13</sub> /P <sub>2-13</sub> )	104.49*	7.68*
·C <sub>8</sub> H <sub>6</sub> N (P <sub>1-14</sub> /P <sub>2-14</sub> )	103.25*	8.13*
·C <sub>8</sub> H <sub>6</sub> N (P <sub>1-15</sub> /P <sub>2-15</sub> )	103.47*	7.80*
·C <sub>8</sub> H <sub>6</sub> N (P <sub>1-16</sub> /P <sub>2-16</sub> )	104.00*	7.62*
·OH	8.26 <sup>#</sup>	15.24 <sup>#</sup>
H <sub>2</sub> O·	10.60 <sup>#</sup>	14.71 <sup>#</sup>
·Cl	14.71 <sup>#</sup>	12.97 <sup>#</sup>
HCl	16.97 <sup>#</sup>	12.74 <sup>#</sup>

45

\*  $\alpha$  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.<sup>1-4</sup>

<sup>#</sup> Obtained from the NIST database<sup>5</sup>

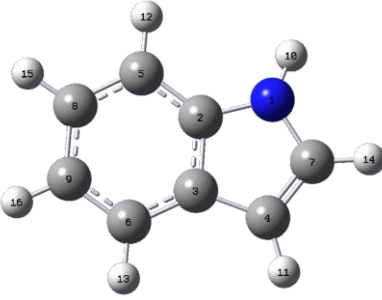
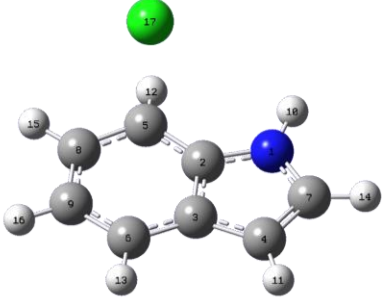
50

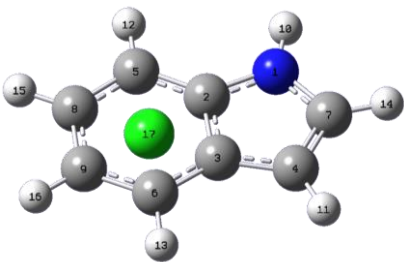
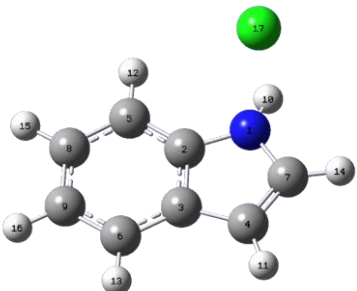
**Table S4. Lennard-Jones parameters of the intermediates for various reactions used in the MultiWell or MESMER simulations.**

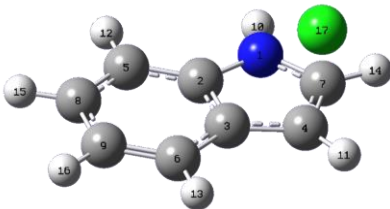
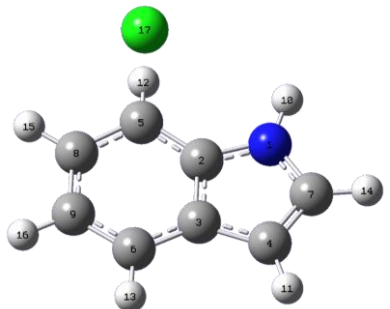
Reactions	$\sigma$ /(Å)	$\epsilon$ /(K)
Indole + ·OH	6.4	685
Indole + ·Cl	6.5	619
IM <sub>1-7</sub> + O <sub>2</sub>	6.6	739
IM <sub>2-5</sub> + O <sub>2</sub>	6.7	673
IM <sub>2-6</sub> + O <sub>2</sub>	6.7	673
C <sub>8</sub> H <sub>6</sub> N + O <sub>2</sub>	6.4	635

55

Table S5. NBO charge distribution for all the pre-reactive complexes of the indole +  $\cdot\text{Cl}$  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
RC <sub>2-5</sub> 	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

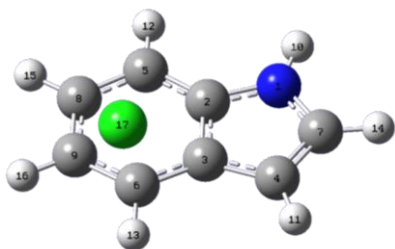
	H	16	0.261
	Cl	17	-0.350
<hr/>			
 <p>RC<sub>2-6</sub></p>	N	1	-0.576
	C	2	0.126
	C	3	-0.087
	C	4	-0.302
	C	5	-0.201
	C	6	-0.199
	C	7	-0.020
	C	8	-0.273
	C	9	-0.193
	H	10	0.459
	H	11	0.270
	H	12	0.254
	H	13	0.293
	H	14	0.255
	H	15	0.260
	H	16	0.267
	Cl	17	-0.334
<hr/>			
 <p>RC<sub>2-10</sub></p>	N	1	-0.524
	C	2	0.140
	C	3	-0.099
	C	4	-0.260
	C	5	-0.240
	C	6	-0.215
	C	7	-0.042
	C	8	-0.246
	C	9	-0.252
	H	10	0.484
	H	11	0.267
	H	12	0.263
	H	13	0.257
	H	14	0.265

	H	15	0.257
	H	16	0.256
	Cl	17	-0.310
<hr/>			
RC <sub>2</sub> -11			
	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
	H	13	0.260
	H	14	0.281
	H	15	0.257
	H	16	0.257
	Cl	17	-0.391
<hr/>			
RC <sub>2</sub> -12			
	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



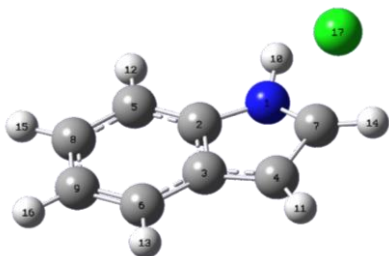
H	14	0.256
H	15	0.266
H	16	0.261
Cl	17	-0.350

RC<sub>2</sub>-13



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

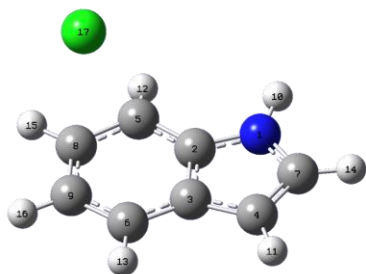
RC<sub>2</sub>-14



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

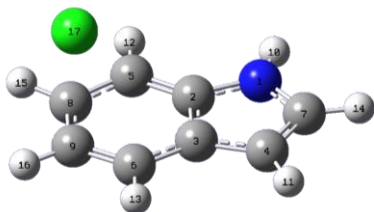
H	13	0.260
H	14	0.281
H	15	0.257
H	16	0.257
Cl	17	-0.391

RC<sub>2-15</sub>



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

RC<sub>2-16</sub>

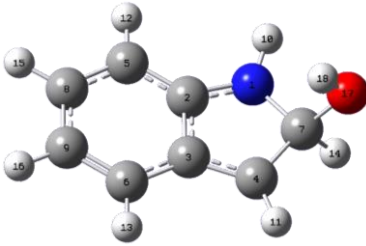
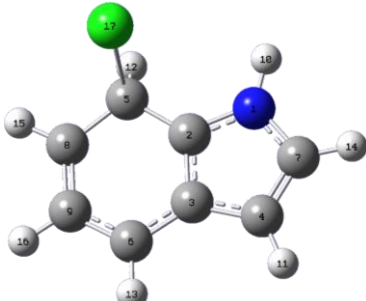


N	1	-0.579
C	2	0.123
C	3	-0.068
C	4	-0.323
C	5	-0.197
C	6	-0.213
C	7	-0.006
C	8	-0.226
C	9	-0.242
H	10	0.462
H	11	0.266

H	12	0.267
H	13	0.258
H	14	0.255
H	15	0.289
H	16	0.264
Cl	17	-0.331

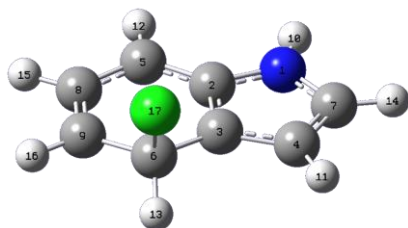
---

60 **Table S6.** Calculated spin distribution based on the Mulliken population analysis for main intermediates involved in the indole +  $\cdot\text{OH}/\cdot\text{Cl}$  reactions.

Species	Atoms	Number	Mulliken atomic spin densities
 IM <sub>1-7</sub>	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
 IM <sub>2-5</sub>	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

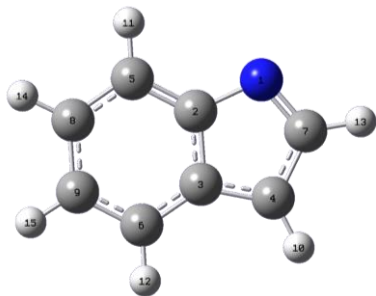
H	13	-0.024
H	14	0.002
H	15	-0.022
H	16	0.005
Cl	17	0.171

IM<sub>2-6</sub>



N	1	0.037
C	2	-0.217
C	3	0.235
C	4	-0.041
C	5	0.612
C	6	-0.098
C	7	0.146
C	8	-0.261
C	9	0.481
H	10	-0.002
H	11	0.001
H	12	-0.025
H	13	0.024
H	14	-0.007
H	15	0.006
H	16	-0.022
Cl	17	0.130

C<sub>8</sub>H<sub>6</sub>N



N	1	0.256
C	2	-0.021
C	3	-0.147
C	4	0.690
C	5	-0.018
C	6	0.270
C	7	-0.101
C	8	0.187
C	9	-0.072
H	10	-0.027
H	11	0.000

H	12	-0.009
H	13	0.000
H	14	-0.009
H	15	0.001

---

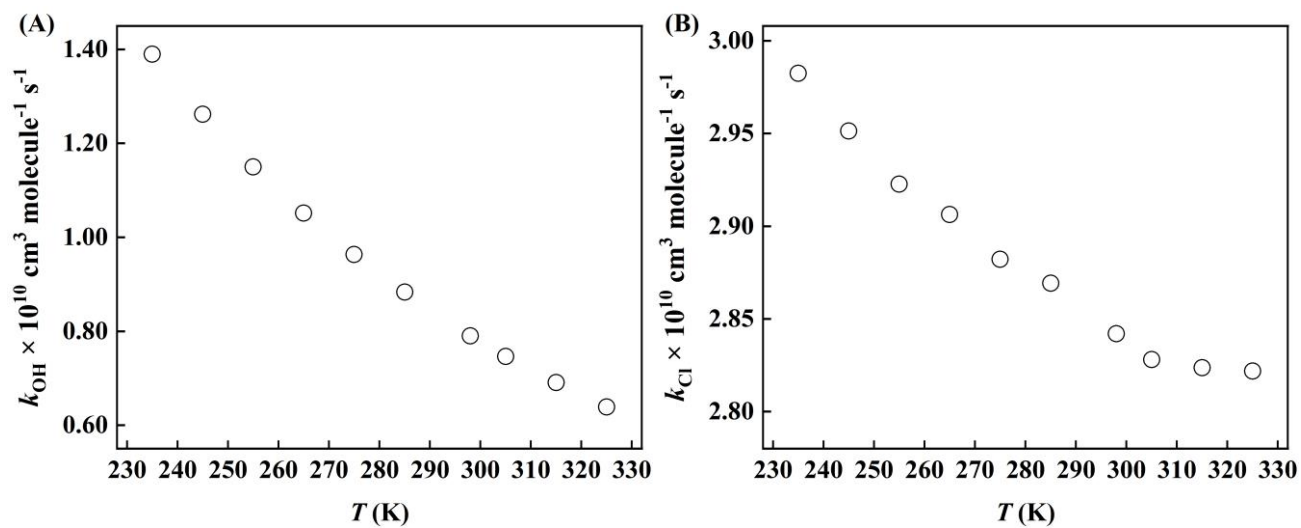
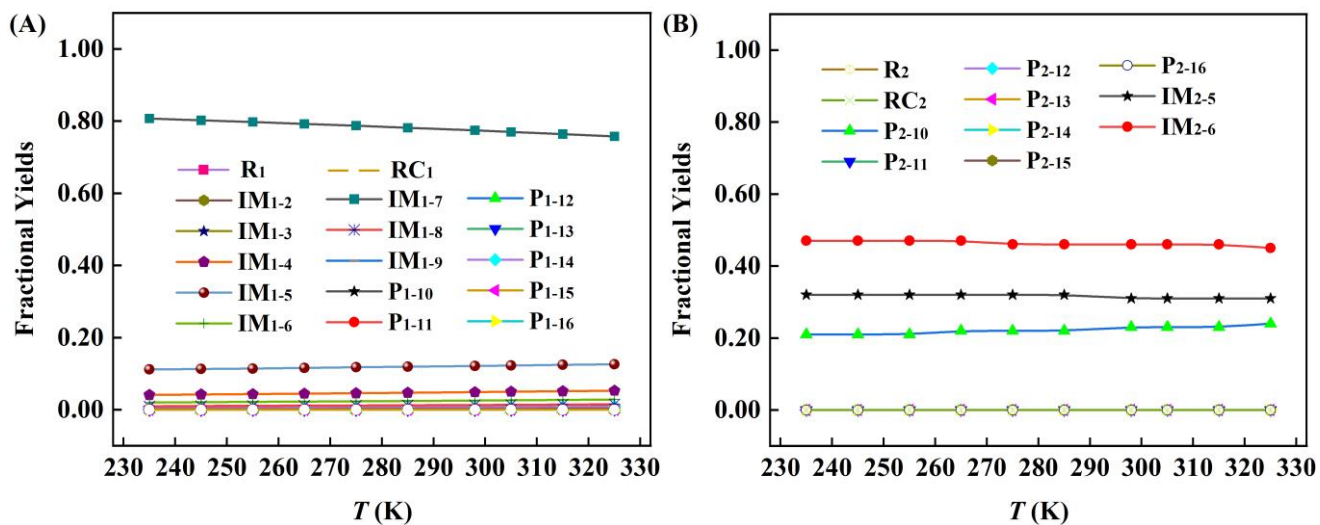


Figure S1. Calculated reaction rate constants ( $k$ ) over the temperature range from 230 to 330 K for the indole +  $\cdot\text{OH}$  (A) and indole +  $\cdot\text{Cl}$  (B) reactions.



65

Figure S2. Calculated branching ratios ( $F$  values) over the temperature range from 230 to 330 K for the indole +  $\cdot\text{OH}$  (A) and indole +  $\cdot\text{Cl}$  (B) reactions.



## References

- 70 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.
- 75 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 NH<sub>x</sub>-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/>.