Supplementary Information

Mechanisms and Kinetic Parameters for the Gas-phase Reactions of 3-methyl-3-buten-2-one and 3-methyl-3-penten-2-one with Ozone

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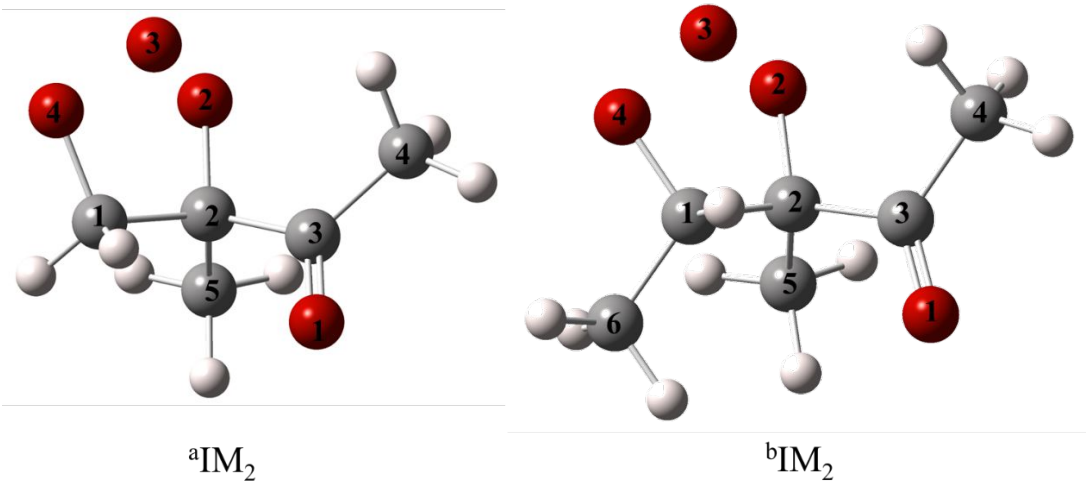


Figure S1. The chemical structure for POZs with atom numbers.

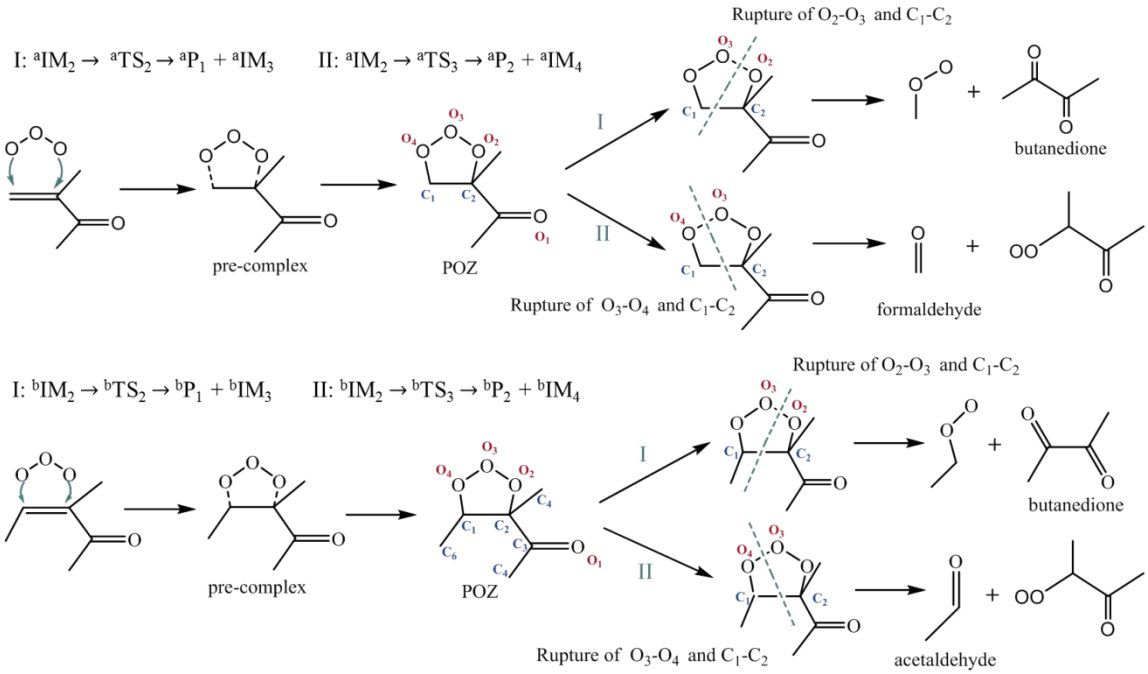


Figure S2. The mechanism for the formation and decomposition of POZs through two possible pathways.

The decomposition of POZs

$^{a}IM_2 \rightarrow {}^{a}TS_2 \rightarrow {}^{a}P_1 + {}^{a}IM_3$

ΔE = 23.55 kcal mol^{-1} $\Delta_r E$ = 2.99 kcal mol^{-1} (R1)

$^{a}IM_2 \rightarrow {}^{a}TS_3 \rightarrow {}^{a}P_2 + {}^{a}IM_4$

ΔE = 25.65 kcal mol^{-1} $\Delta_r E$ = -1.69kcal mol^{-1} (R2)

$^{b}IM_2 \rightarrow {}^{b}TS_2 \rightarrow {}^{b}P_1 + {}^{b}IM_3$

ΔE = 20.16 kcal mol^{-1} $\Delta_r E$ = -1.66 kcal mol^{-1} (R3)

$^{b}IM_2 \rightarrow {}^{b}TS_3 \rightarrow {}^{b}P_2 + {}^{b}IM_4$

ΔE = 24.75 kcal mol^{-1} $\Delta_r E$ = -5.97 kcal mol^{-1} (R4)

The reaction scheme of $^{a}IM_3$ can be described as follows:

$^{a}IM_3 + NO \rightarrow {}^{a}TS_4 \rightarrow NO_2 + {}^{a}P_2$

ΔE = 13.13 kcal mol^{-1} $\Delta_r E$ = -66.37 kcal mol^{-1} (R5)

$^{a}IM_3 + HCHO \rightarrow {}^{a}TS_5 \rightarrow {}^{a}P_3 + {}^{a}P_2$

ΔE = 15.49 kcal mol^{-1} $\Delta_r E$ = -120.73 kcal mol^{-1} (R6)

$^{a}IM_3 + H_2O \rightarrow {}^{a}IM_5$ (HMHP) $\Delta_r E$ = -48.78 kcal mol^{-1}

$^{a}IM_5 \rightarrow {}^{a}TS_7 \rightarrow {}^{a}P_3 + H_2O$

ΔE = 59.46 kcal mol^{-1} $\Delta_r E$ = -71.94 kcal mol^{-1} (R7)

$^{a}IM_3 + HCOOH \rightarrow {}^{a}IM_6$ (HPMF) $\Delta_r E$ = -46.72 kcal mol^{-1}

$^{a}IM_6 \rightarrow {}^{a}TS_9 \rightarrow {}^{a}P_4$ (FAN)+ H_2O

ΔE = 76.02 kcal mol^{-1} $\Delta_r E$ = -64.91 kcal mol^{-1} (R8)

$^{a}IM_3 \rightarrow {}^{a}TS_{10} \rightarrow {}^{a}IM_7$

ΔE = 21.99 kcal mol^{-1} $\Delta_r E$ = -29.09 kcal mol^{-1}

$^{a}IM_7 \rightarrow {}^{a}TS_{11} \rightarrow CO_2 + H_2$

ΔE = 93.98 kcal mol^{-1} $\Delta_r E$ = -96.26 kcal mol^{-1} (R9)

Further reactions of $^{a}IM_4$

$^{a}IM_4 + NO \rightarrow {}^{a}TS_{12} \rightarrow NO_2 + {}^{a}P_1$

ΔE = 17.07 kcal mol^{-1} $\Delta_r E$ = -61.69 kcal mol^{-1} (R10)

$^{a}IM_4 + HCHO \rightarrow {}^{a}TS_{13} \rightarrow {}^{a}P_3 + {}^{a}P_1$

ΔE = 19.22 kcal mol^{-1} $\Delta_r E$ = -116.05 kcal mol^{-1} (R11)

$^{a}IM_4 + H_2O \rightarrow {}^{a}TS_{14} \rightarrow {}^{a}IM_7$

ΔE = 1.63 kcal mol^{-1} $\Delta_r E$ = -43.94 kcal mol^{-1}

$^{a}IM_7 \rightarrow {}^{a}TS_{15} \rightarrow {}^{a}P_5 + {}^{a}P_5$

ΔE = 54.64 kcal mol^{-1} $\Delta_r E$ = -79.10 kcal mol^{-1} (R12)

$^{a}IM_4 + HCOOH \rightarrow {}^{a}TS_{16} \rightarrow {}^{a}IM_8$
(232-HPBF)

ΔE = 0.91 kcal mol^{-1} $\Delta_r E$ = -33.09 kcal mol^{-1}

$^{a}IM_8 \rightarrow {}^{a}TS_{17} \rightarrow {}^{a}P_6 + {}^{a}P_8$

ΔE = 81.09 kcal mol^{-1} $\Delta_r E$ = -47.76 kcal mol^{-1} (R13)

$^{a}IM_4 \rightarrow {}^{a}TS_{18} \rightarrow {}^{a}IM_9$

$^{a}IM_4 \rightarrow {}^{a}TS_{18} \rightarrow {}^{a}IM_9$

ΔE = 26.98 kcal mol^{-1} $\Delta_r E$ = -24.26 kcal mol^{-1}

$^{a}IM_9 \rightarrow {}^{a}TS_{19} \rightarrow CO_2 + {}^{a}P_9$

ΔE = 81.37 kcal mol^{-1} $\Delta_r E$ = -94.67 kcal mol^{-1} (R14)

Further reactions of $^{b}IM_3$

$^{b}IM_3 + NO \rightarrow {}^{b}TS_4 \rightarrow NO_2 + {}^{b}P_2$

ΔE = 11.84 kcal mol^{-1} $\Delta_r E$ = -66.00 kcal mol^{-1} (R15)

$^{b}IM_3 + HCHO \rightarrow {}^{b}TS_5 \rightarrow {}^{b}P_3 + {}^{b}P_2$

ΔE = 13.78 kcal mol^{-1} $\Delta_r E$ = -120.36 kcal mol^{-1} (R16)

$^{b}IM_3 + H_2O \rightarrow {}^{b}TS_6 \rightarrow {}^{b}IM_5$ (1-HEHP) $\Delta_r E$ = -45.42 kcal mol^{-1}

$^{b}IM_5 \rightarrow {}^{b}TS_4 \rightarrow {}^{b}P_7 + H_2O$

ΔE = 60.47 kcal mol^{-1} $\Delta_r E$ = -74.18 kcal mol^{-1} (R17)

$^{b}IM_3 + HCOOH \rightarrow {}^{b}IM_6$ $\Delta_r E$ = -43.96 kcal mol^{-1}

$^{b}IM_6 \rightarrow {}^{b}TS_9 \rightarrow {}^{b}P_5 + H_2O$

ΔE = 62.24 kcal mol^{-1} $\Delta_r E$ = -64.91 kcal mol^{-1} (R18)

$^{b}IM_3 \rightarrow {}^{b}TS_{10} \rightarrow {}^{b}IM_7$

ΔE = 18.74 kcal mol^{-1} $\Delta_r E$ = -28.21 kcal mol^{-1}

$^{b}IM_7 \rightarrow {}^{b}TS_{11} \rightarrow CO_2 + CH_4$

ΔE = 94.01 kcal mol^{-1} $\Delta_r E$ = -99.93 kcal mol^{-1} (R19)

Table S1. The rate constants (k_i/cm^3 molecule^{-1} s^{-1}) of MBO332 + O_3 → $^aIM_2$ at different pressures and temperatures

k_a P / T/K	MBO332 + O_3 → $^aIM_2$			
	0.76Torr	7.6Torr	76Torr	760Torr
200	6.76×10^{-18}	4.08×10^{-17}	1.79×10^{-16}	4.81×10^{-16}
225	2.74×10^{-18}	2.63×10^{-17}	1.28×10^{-16}	4.04×10^{-16}
250	1.06×10^{-18}	1.06×10^{-17}	9.70×10^{-17}	3.45×10^{-16}
275	4.80×10^{-19}	4.80×10^{-18}	4.80×10^{-17}	2.98×10^{-16}
298	2.59×10^{-19}	2.59×10^{-18}	2.59×10^{-17}	2.59×10^{-16}
325	1.40×10^{-19}	1.40×10^{-18}	1.40×10^{-17}	1.40×10^{-16}
350	8.65×10^{-20}	8.65×10^{-19}	8.65×10^{-18}	8.65×10^{-17}
375	5.64×10^{-20}	5.64×10^{-19}	5.64×10^{-18}	5.64×10^{-17}
400	3.89×10^{-20}	3.89×10^{-19}	3.89×10^{-18}	3.89×10^{-17}

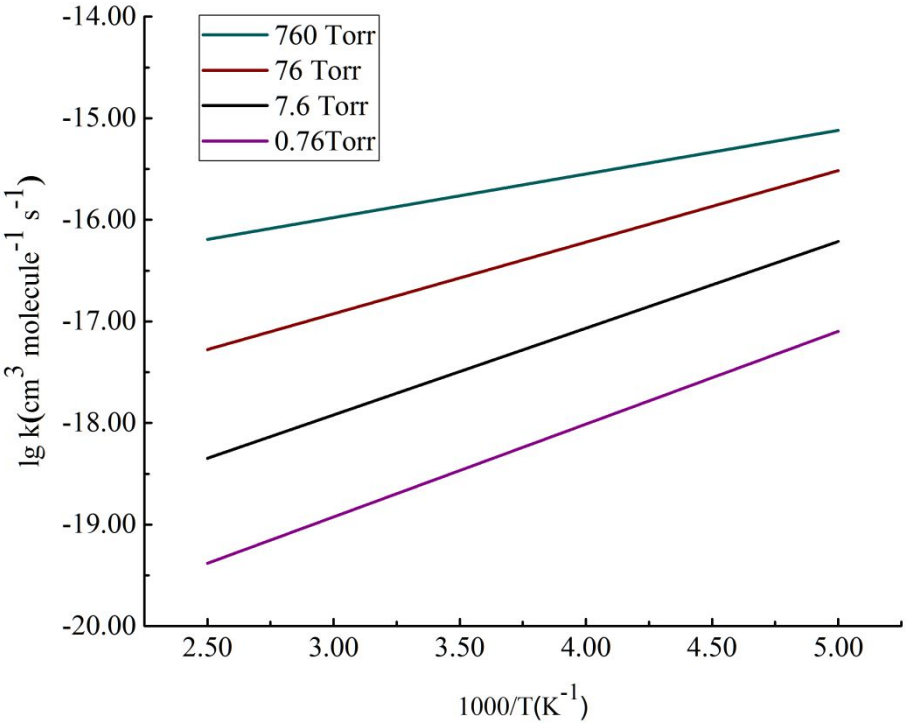


Figure S3. Changes of k_a under different temperatures and pressures.

Table S2. The rate constants (k_i/cm^3 molecule^{-1} s^{-1}) of MPO332 + O_3 → $^bIM_2$ at different pressures and temperatures

k_b P / T/K	MPO332 + O_3 → $^bIM_2$			
	0.76Torr	7.6Torr	76Torr	760Torr
200	1.50×10^{-17}	1.50×10^{-16}	1.50×10^{-15}	1.50×10^{-14}
225	3.69×10^{-18}	3.69×10^{-17}	3.69×10^{-16}	3.69×10^{-15}
250	1.20×10^{-18}	1.20×10^{-17}	1.20×10^{-16}	1.20×10^{-15}
275	4.74×10^{-19}	4.74×10^{-18}	4.74×10^{-17}	4.74×10^{-16}
298	2.29×10^{-19}	2.29×10^{-18}	2.29×10^{-17}	2.29×10^{-16}
325	1.11×10^{-19}	1.11×10^{-18}	1.11×10^{-17}	1.11×10^{-16}
350	6.20×10^{-20}	6.20×10^{-19}	6.20×10^{-18}	6.20×10^{-17}
375	3.77×10^{-20}	3.77×10^{-19}	3.77×10^{-18}	3.77×10^{-17}
400	2.42×10^{-20}	2.42×10^{-19}	2.42×10^{-18}	2.42×10^{-17}

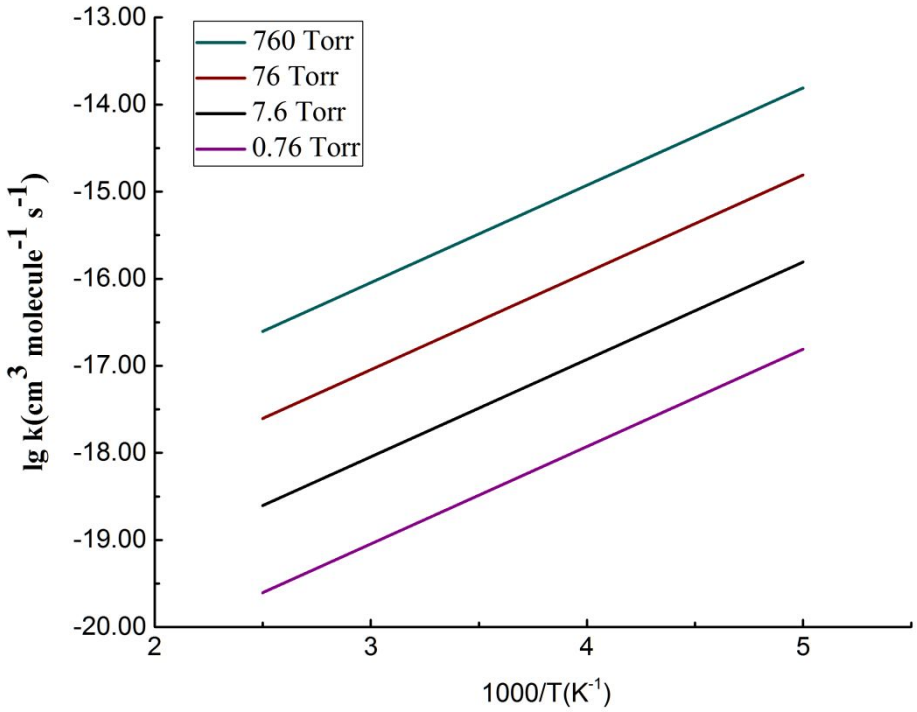


Figure S4. Changes of k_b under different temperatures and pressures.

Table S3. Branching ratios (Ri) at different temperatures.

Branching ratios				
P	MBO332 + O_3 → $^{a}IM_2$		MPO332 + O_3 → $^{b}IM_2$	
T/K	R1	R2	R3	R4
200	56.65%	43.35%	42.91%	57.09%
225	57.01%	42.99%	42.80%	57.20%
250	57.27%	42.73%	42.71%	57.29%
275	57.51%	42.49%	42.64%	57.36%
298	57.73%	42.27%	42.58%	57.42%
325	57.98%	42.02%	42.51%	57.49%
350	58.16%	41.84%	42.47%	57.53%
375	58.38%	41.62%	42.42%	57.58%
400	58.54%	41.46%	42.38%	57.62%

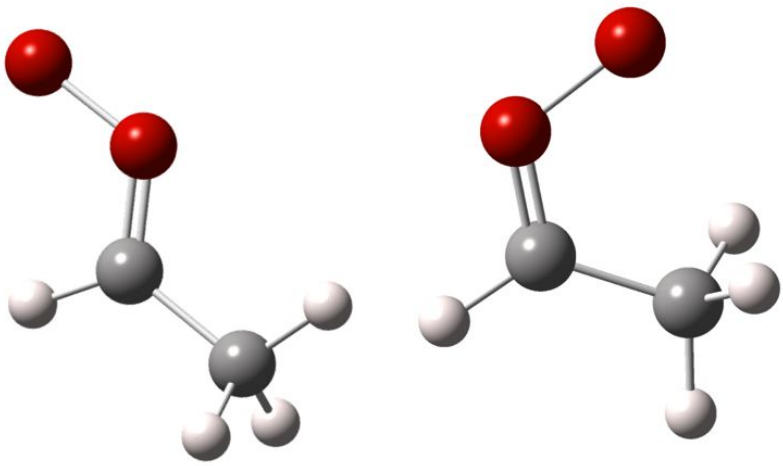


Figure S5. The configuration of syn-CH_3CHOO and anti-CH_3CHOO.

Table S4. A comparison of the energies for the reactions of syn-CH3CHOO and anti-CH3CHOO with some small molecules.

Reaction partner	anti-CH_3CHOO				syn- CH_3CHOO			
	NO	H_2O	HCHO	HCOOH	NO	H_2O	HCHO	HCOOH
ΔE	11.84	barrierless	13.78	barrierless	14.15	4.85	barrierless	barrierless
ΔrE	-66.00	-45.42	-120.36	-43.96	-62.80	-41.02	-117.16	-36.65

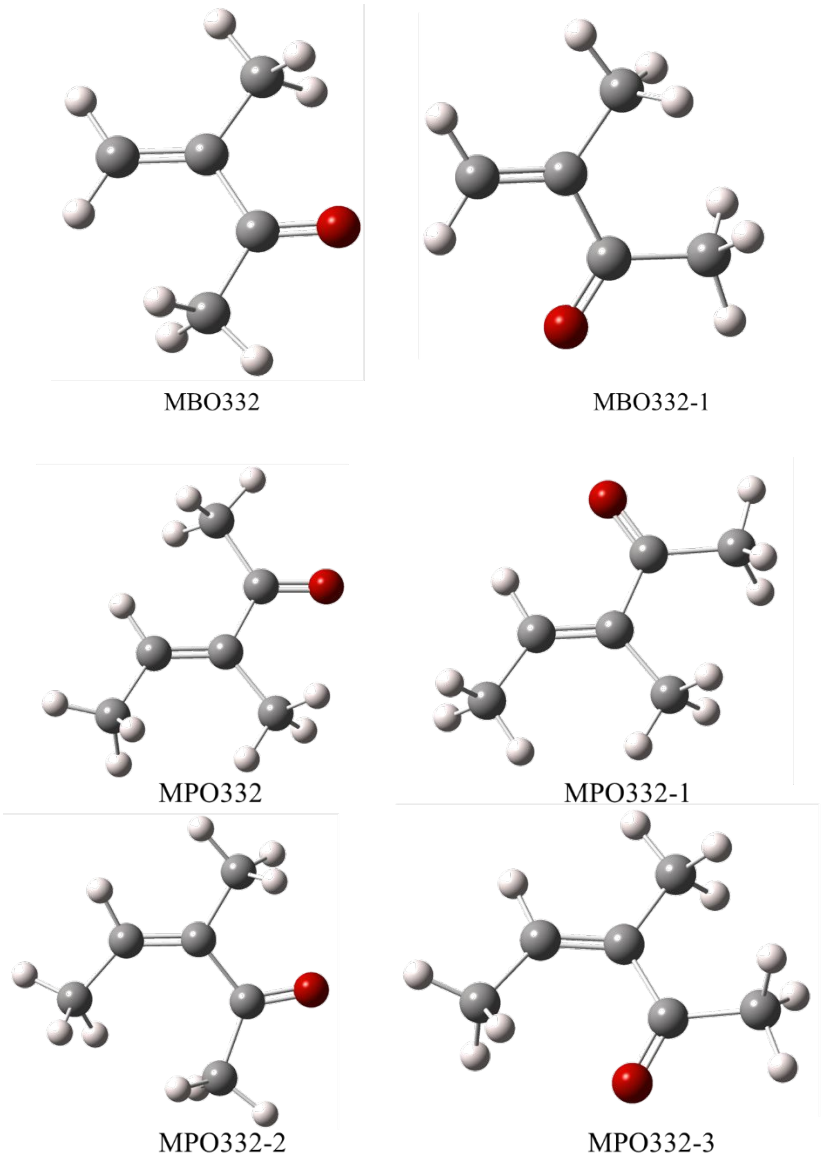
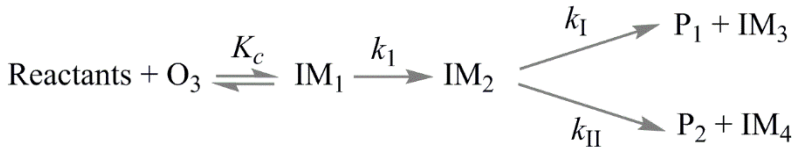


Figure S6. The main energy configurations of MBO332 and MPO332.

Table S5. Data comparison of several main energy configurations of MBO332 and MPO332.

	SP (KJ·mol^{-1})	ZPE (KJ·mol^{-1})	SP+ZPE (KJ·mol^{-1})	ΔE (Kcal·mol^{-1})	ΔrE (Kcal·mol^{-1})	k/298K, 1atm (cm^3 molecule^{-1} s^{-1})
MBO332	-270.52164	0.11884	-270.403	3.48	-65.03	2.59×10^{-16}
MBO332-1	-270.51797	0.11853	-270.399	2.86	-65.14	1.86×10^{-15}
MPO332	-309.83011	0.14689	-309.683	2.00	-66.81	2.28×10^{-16}
MPO332-1	-309.82762	0.14692	-309.681	1.62	-65.99	1.52×10^{-14}
MPO332-2	-309.82438	0.14722	-309.677	--	--	--
MPO332-3	-309.82692	0.14706	-309.679	--	--	--

The calculation of total rate constants (k_a and k_b)



The formation of IM_2 occurs according to a two-step mechanism[1], involving first a fast pre-equilibrium between the reactants (MBO332, MPO332) and a pre-reactive complex ($^{a}IM_1$, $^{b}IM_1$), followed by the irreversible formation of POZs. In this step, k_c is the equilibrium constant for the pre-equilibrium, and the rate constants can be calculated as follows:

$$k_0 = K_c k_1$$

The total rate constants k_{tot} (k_a, k_b) for the reaction of O_3 with MBO332 and MPO332 can be calculated by the follow equation[2]:

$$\frac{1}{k_{tot}} = \frac{1}{k_0} + \frac{1}{k_I + k_{II}}$$

Equation for calculating atmospheric half-life

In order to estimate the atmospheric effects of MBO332 and MPO332 emission, the half-life ($t_{1/2}$) for the ozonolysis of considered unsaturated ketones is calculated by the following formula:

$$t_{1/2} = \frac{\ln 2}{k[X]}$$

Wherein, $[X]$ is the concentration of typical atmospheric oxidants (OH, NO_3, Cl and O_3) and k represent the rate constant k_a or k_b.

Reference

(1) Abolfazl, S.; Deleuze, M. S. Theoretical study of the oxidation mechanisms of naphthalene initiated by hydroxyl radicals: the H abstraction pathway. *J. Phys. Chem. A* **2014**, *118* (20), 4593-4610.

(2) Ramírez-Anguita, J. M.; àngels, G.-L.; Lluch, J. M. Variational transition-state theory study of the rate constant of the DMS·OH scavenging reaction by O_2. *J. Comput. Chem.* **2011**, *32* (10), 2104-2118.