Supplement of

Theoretical study of the reaction mechanisms and kinetics of acetyl and hydroperoxyl radicals: Implications for atmospheric chemistry

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Table of Contents

Contains six figures and twelve tables

Table S5. Isomerization and decomposition rate constants of the intermediate $CH_3C(O)O_4H$ in the temperature range of 200−310 K and 1 atm. Units of reaction rate constants: s^{-1}.

Table S6. Branching ratios for the reactions of $CH_3C(O)O_2$ radical with HO_2 radical in the temperature range of 200−310 K and 1 atm.

Table S7. The atmospheric lifetimes (τ, min) of $CH_3C(O)O_2$ radical at different concentrations of HO_2 radical ([HO_2], $1 \times 10^7 \sim 2 \times 10^7$ molecule cm^{-3}) in the temperature range of 200−310 K and 1 atm .

Table S8. The atmospheric lifetimes (τ, min) of $CH_3C(O)O_2$ radical at different concentrations of HO_2 radical ([HO_2], $0.2 \times 10^8 \sim 1.1 \times 10^8$ molecule cm^{-3}) in the temperature range of 200−310 K and 1 atm.

Table S9. The atmospheric lifetimes (τ, min) of $CH_3C(O)O_2$ radical at different concentrations of HO_2 radical ([HO_2], $1.1 \times 10^8 \sim 6.4 \times 10^8$ molecule cm^{-3}) in the temperature range of 200−310 K and 1 atm.

Table S10. The acute and chronic toxicity class. (Unit: mg L^{-1})

Table S11. Ecotoxicity (logLC50, logEC50 and LogChV) for $CH_3C(O)O_2$ radical precursors and its degradation products. (Unit: mg L^{-1})

Table S12. Cartesian coordinates of all the studied gaseous molecules optimized at the ωB97X-D/def2-TZVP level of theory.

Table S13. Calculated spin contamination values for open-shell key species involved in the reaction pathways.

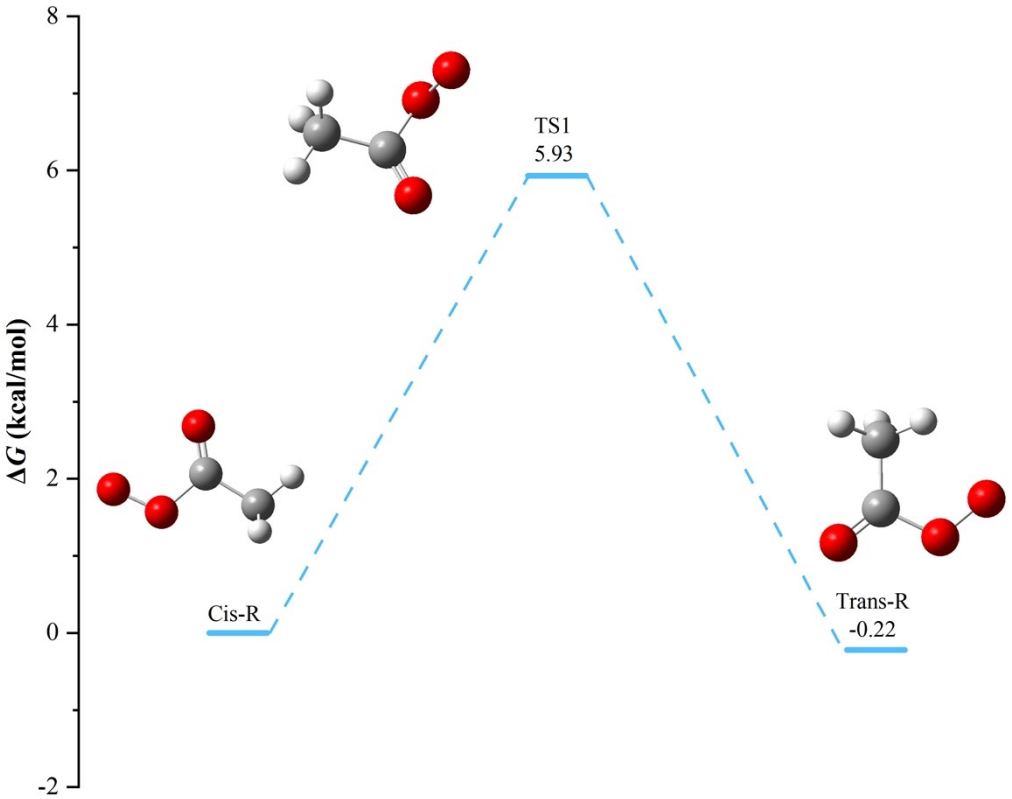


Figure S1. Potential energy surfaces for $CH_3C(O)O_2$ radical isomerization reactions. The relative Gibbs free energy (kcal mol^{-1} at 298.15 K) was calculated at the CCSD(T)-F12/cc-pVTZ-F12//ωB97X-D/def2-TZVP level of theory.

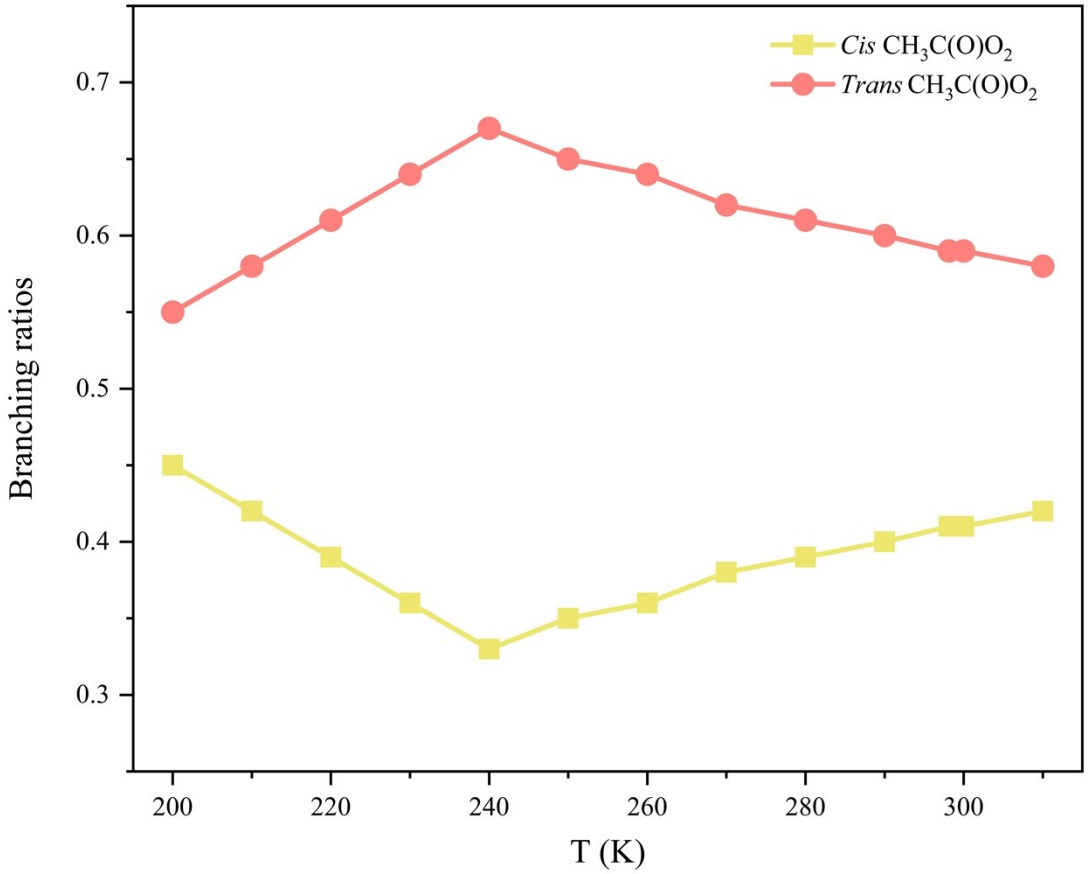
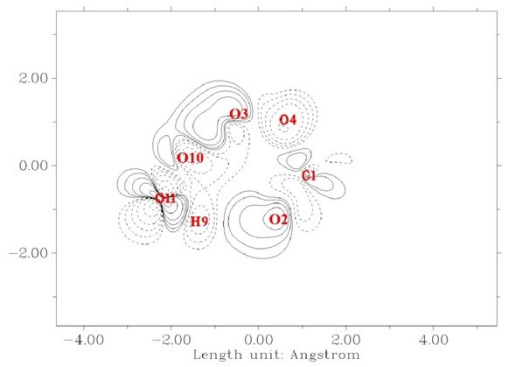
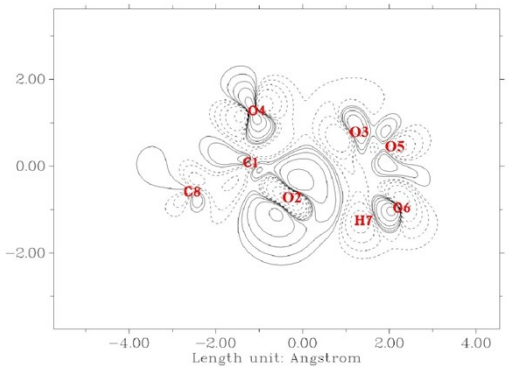


Figure S2. Branching ratios of *Cis*-$CH_3C(O)O_2$ radical and *Trans*-$CH_3C(O)O_2$ radical in the temperature range of 200−310 K at 1 atm.



TS2



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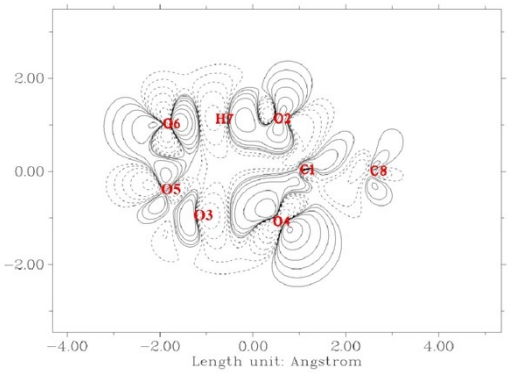

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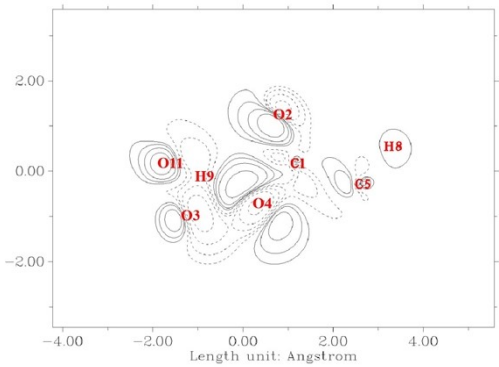

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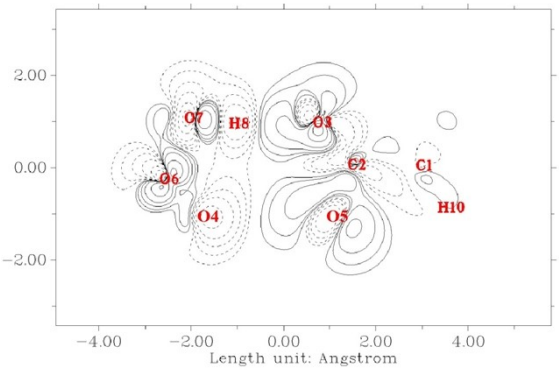

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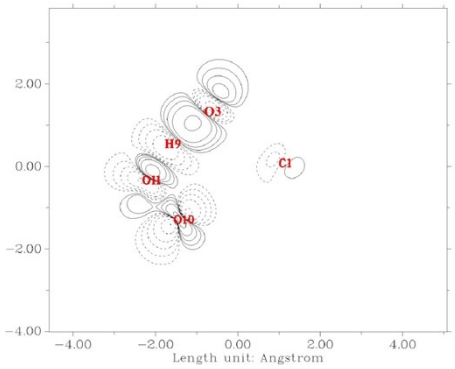

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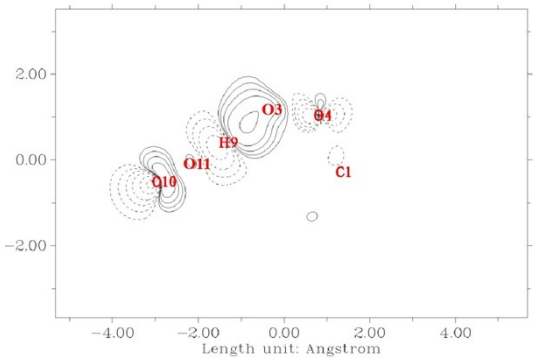

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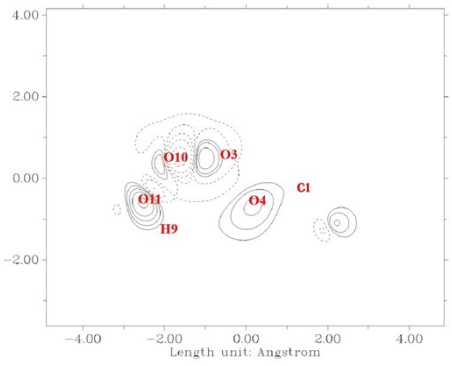

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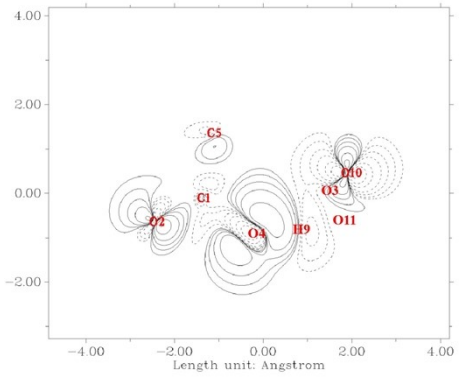

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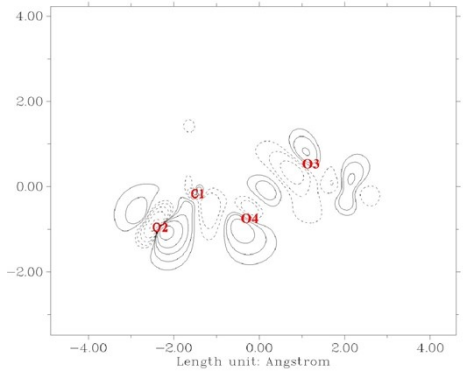

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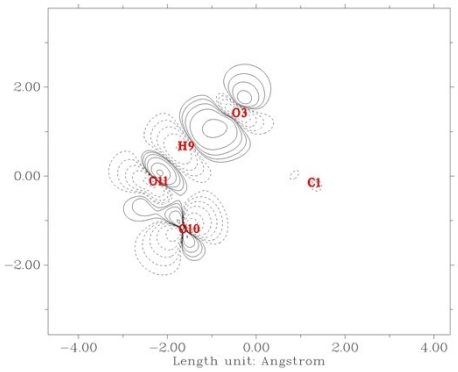

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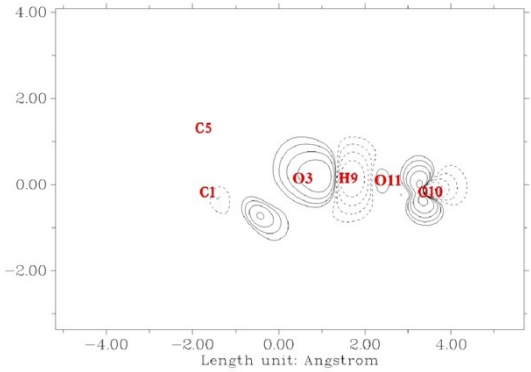

TS14

Figure S3. The contour maps of the electron density difference of key atoms in the transition states of the reaction of $CH_3C(O)O_2$ radical with HO_2 radical. Among them, *Cis*-$CH_3C(O)O_2$ related transition states include (TS2, TS4, TS5, TS6, TS7, TS8, TS9), and *Trans*-$CH_3C(O)O_2$ related transition states include (TS10, TS11, TS12, TS13, TS14). Solid and dash lines correspond to positive and negative parts, respectively.

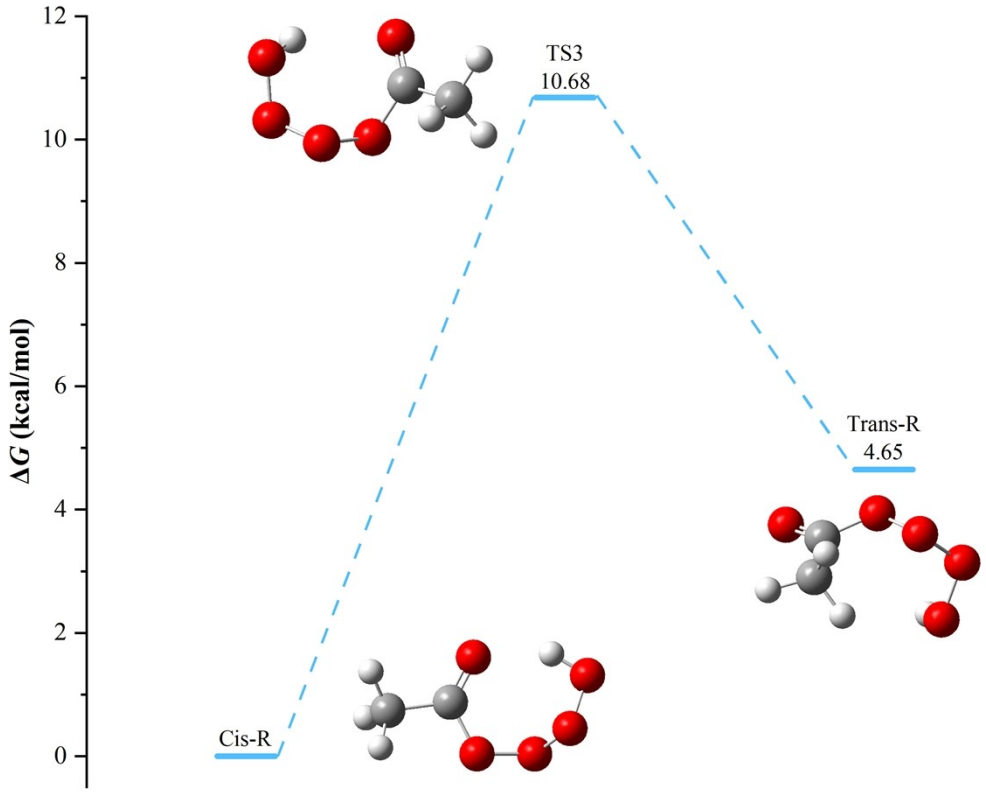

Figure S4. Potential energy surfaces for $CH_3C(O)O_4H$ isomerization reactions. The relative Gibbs free energy (kcal mol^{-1} at 298.15 K) was calculated at the CCSD(T)-F12/cc-pVTZ-F12//ωB97X-D/def2-TZVP level of theory.

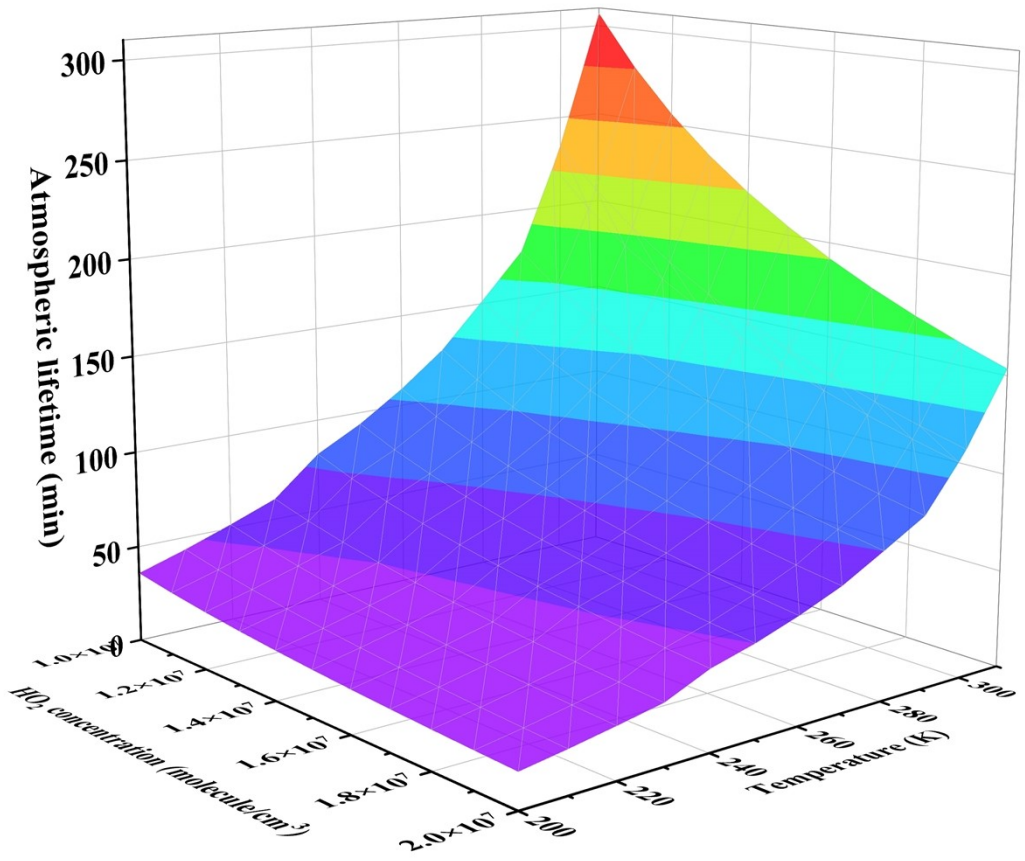

Figure S5. The atmospheric lifetime values (τ, min) of the $CH_3C(O)O_2$ radical determined from the HO_2 radical concentrations ([HO_2], $1 \times 10^7 \sim 2 \times 10^7$ molecules cm^{-3}) at different temperatures (200−310 K) in the atmosphere were calculated from apparent rate constants.

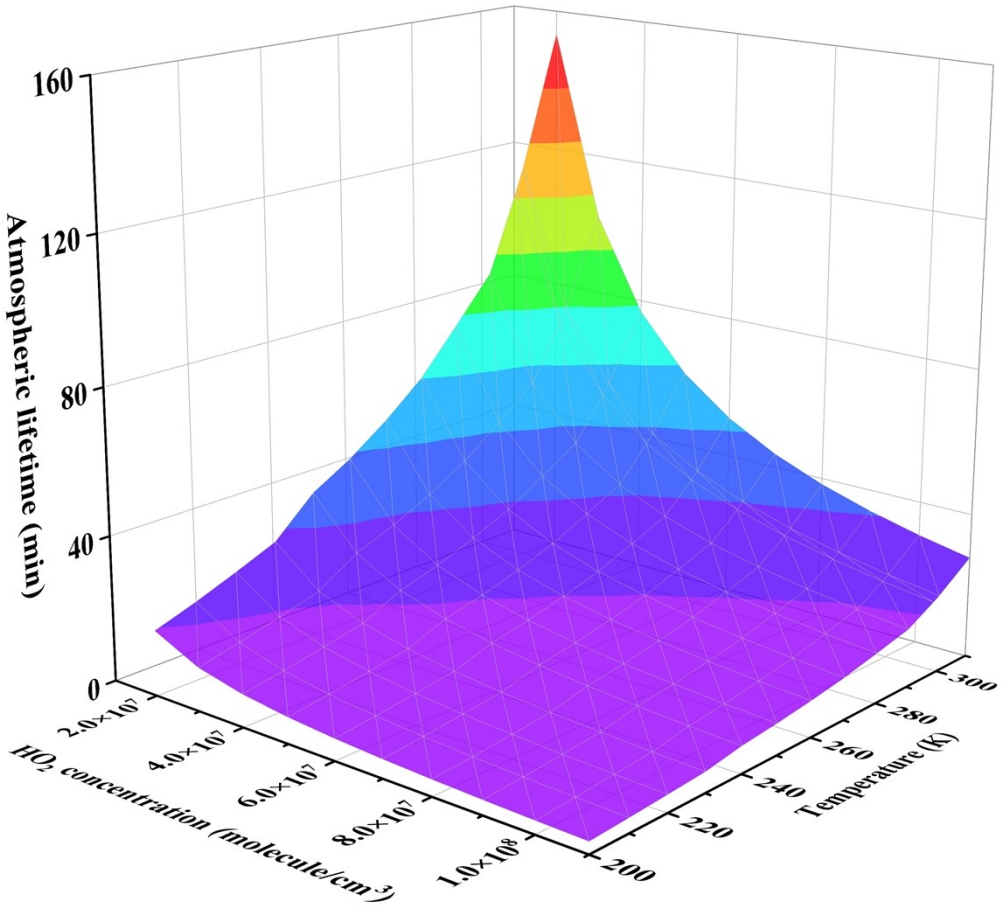

Figure S6. The atmospheric lifetime values (τ, min) of the $CH_3C(O)O_2$ radical determined from the HO_2 radical concentrations ([HO_2], 0.2 × 10^8 ~ 1.1 × 10^8 molecules cm^{-3}) at different temperatures (200−310 K) in the atmosphere were calculated from apparent rate constants.

Table S1. Imaginary frequencies (ν_{im}) of the transition states (TSs) at the ωB97X-D/def2-TZVP level of theory.

Transition States	Imaginary frequencies (ν_{im}) in cm^{-1}
TS1	126.95*i*
TS2	338.62*i*
TS3	109.66*i*
TS4	352.07*i*
TS5	947.41*i*
TS6	468.80*i*
TS7	86.09*i*
TS8	517.35*i*
TS9	971.64*i*
TS10	397.95*i*
TS11	785.85*i*
TS12	282.95*i*
TS13	579.58*i*
TS14	1159.66*i*

Table S2. Branching ratios of *Cis*-$CH_3C(O)O_2$ (*Cis*-R) radical, *Trans*-$CH_3C(O)O_2$ (*Trans*-R) radical and Complexes in the temperature range of 200−310 K and 1 atm.

Temperatures (K)	*Cis*-R	*Trans*-R	RC1	RC2	RC3	RC4	RC5	RC6	RC7	RC8	RC9
200	0.45	0.55	0.24	0.24	0.47	0.06	0.00	0.06	0.06	0.83	0.05
210	0.42	0.58	0.23	0.23	0.46	0.08	0.00	0.07	0.07	0.81	0.06
220	0.39	0.61	0.23	0.23	0.45	0.10	0.00	0.07	0.07	0.78	0.08
230	0.36	0.64	0.22	0.22	0.44	0.12	0.00	0.07	0.07	0.76	0.10
240	0.33	0.67	0.21	0.21	0.43	0.14	0.00	0.07	0.07	0.73	0.13
250	0.35	0.65	0.21	0.21	0.42	0.16	0.00	0.07	0.07	0.70	0.15
260	0.36	0.64	0.20	0.20	0.41	0.19	0.00	0.07	0.07	0.67	0.18
270	0.38	0.62	0.19	0.19	0.39	0.22	0.01	0.07	0.07	0.64	0.21
280	0.39	0.61	0.19	0.19	0.38	0.24	0.01	0.07	0.07	0.62	0.24
290	0.40	0.60	0.18	0.18	0.37	0.27	0.01	0.07	0.07	0.59	0.27
298.15	0.41	0.59	0.17	0.17	0.36	0.29	0.01	0.07	0.07	0.56	0.29
300	0.41	0.59	0.17	0.17	0.35	0.30	0.01	0.07	0.07	0.56	0.30
310	0.42	0.58	0.17	0.17	0.34	0.32	0.01	0.07	0.07	0.53	0.33

Table S3. Reaction rate constants for the isomerization of the $CH_3C(O)O_2$ radical in the temperature range of 200−310 K and 1 atm. Units of reaction rate constants: s^{-1}.

Temperatures (K)	k_1 *Cis*-$CH_3(O)O_2$ to *Trans*-$CH_3(O)O_2$	k_4 *Trans*-$CH_3(O)O_2$ to *Cis*-$CH_3(O)O_2$
200	3.40×10^6	2.76×10^6
210	6.41×10^6	4.60×10^6
220	1.14×10^7	7.25×10^6
230	1.94×10^7	1.09×10^7
240	3.15×10^7	1.58×10^7
250	4.91×10^7	2.62×10^7
260	7.41×10^7	4.21×10^7
270	1.09×10^8	6.52×10^7
280	1.55×10^8	9.79×10^7
290	2.15×10^8	1.43×10^8
298.15	2.77×10^8	1.91×10^8
300	2.93×10^8	2.04×10^8
310	3.91×10^8	2.84×10^8

Table S4. Rate constant of the favourable initial reaction of the $CH_3C(O)O_2$ radical with HO_2 radical in the temperature range of 200−310 K and 1 atm. Units of reaction rate constants: s^{-1}.

Temperatures (K)	k_8 (via TS2)	k_{10} (via TS8)	k_{12} (via TS10)	k_{14} (via TS13)
200	5.49×10^9	2.33×10^9	5.23×10^7	2.62×10^8
210	6.60×10^9	2.71×10^9	8.61×10^7	3.39×10^8
220	7.79×10^9	3.09×10^9	1.36×10^8	4.27×10^8
230	9.04×10^9	3.47×10^9	2.05×10^8	5.24×10^8
240	1.03×10^{10}	3.86×10^9	2.99×10^8	6.34×10^8
250	1.17×10^{10}	4.21×10^9	4.22×10^8	7.42×10^8
260	1.30×10^{10}	4.56×10^9	5.81×10^8	8.58×10^8
270	1.44×10^{10}	4.90×10^9	7.80×10^8	9.81×10^8
280	1.58×10^{10}	5.25×10^9	1.02×10^9	1.11×10^9
290	1.72×10^{10}	5.59×10^9	1.32×10^9	1.25×10^9
298.15	1.83×10^{10}	5.86×10^9	1.60×10^9	1.37×10^9
300	1.85×10^{10}	5.92×10^9	1.67×10^9	1.39×10^9
310	1.99×10^{10}	6.26×10^9	2.08×10^9	1.55×10^9

Table S5. Isomerisation and decomposition rate constants of the intermediate $CH_3C(O)O_4H$ in the temperature range of 200−310 K and 1 atm. Units of reaction rate constants: s^{-1}.

Temperatures (K)	k_{16} (Via TS11, IM1 to IM2)	k_{20} (Via TS11, IM2 to IM1)	k_{17} (via TS15)	k_{18} (via TS7)	k_{22} (via TS12)
200	9.57	1.11×10^6	10.2	0.91	7.04×10^3
210	35.9	2.39×10^6	38.4	5.03	2.22×10^4
220	1.19×10^2	4.83×10^6	1.28×10^2	24	6.34×10^4
230	3.59×10^2	9.18×10^6	3.87×10^2	1.01×10^2	1.66×10^5
240	9.85×10^2	1.66×10^7	1.07×10^3	3.78×10^2	4.04×10^5
250	2.50×10^3	2.86×107	2.71×10^3	1.28×10^3	9.18×10^5
260	5.91×10^3	4.74×107	6.45×10^3	3.99×10^3	1.97×10^6
270	1.31×10^4	7.58×107	1.44×10^4	1.15×10^4	4.01×10^6
280	2.76×10^4	1.17×10^8	3.03×10^4	3.07×10^4	7.78×10^6
290	5.53×10^4	1.76×10^8	6.09×10^4	7.72×10^4	1.45×10^7
298.15	9.40×10^4	2.41×10^8	1.04×10^5	1.57×10^5	2.34×10^7
300	1.06×10^5	2.58×10^8	1.17×10^5	1.83×10^5	2.60×10^7
310	1.94×10^5	3.70×10^8	2.15×10^5	4.13×10^5	4.49×10^7

Table S6. Branching ratios for the reactions of $CH_3C(O)O_2$ radical with HO_2 radical in the temperature range of 200−310 K and 1 atm.

Temperatures (K)	α_{IM1} $CH_3C(O)O_4H$	α_{R1a} $CH_3C(O)O_2H + O_2$	α_{R1b} $CH_3C(O)OH + O_3$	α_{R1c} $CH_3C(O)O + OH + O_2$	Total
200	0.585	0.17	0.22	0.02	0.99
210	0.209	0.22	0.49	0.07	0.99
220	1.58E-02	0.27	0.59	0.12	0.99
230	1.73E-03	0.30	0.54	0.15	0.99
240	4.39E-04	0.33	0.48	0.18	0.99
250	1.48E-04	0.33	0.45	0.21	0.99
260	5.29E-05	0.35	0.39	0.26	0.99
270	2.07E-05	0.36	0.34	0.29	0.99
280	8.32E-06	0.36	0.31	0.33	0.99
290	3.22E-06	0.35	0.27	0.37	0.99
298.15	1.41E-06	0.34	0.25	0.40	0.99
300	1.13E-06	0.34	0.25	0.41	0.99
310	5.02E-07	0.33	0.22	0.45	0.99

Table S7. The atmospheric lifetimes (τ, min) of $CH_3C(O)O_2$ radical at different concentrations of HO_2 radical ([HO_2], $1 \times 10^7 \sim 2 \times 10^7$ molecule cm^{-3}) in the temperature range of 200−310 K and 1 atm.

T / τ / [HO_2]	1×10^7	1.1×10^7	1.2×10^7	1.3×10^7	1.4×10^7	1.5×10^7	1.6×10^7	1.7×10^7	1.8×10^7	1.9×10^7	2.0×10^7
200 K	035.91	32.65	29.92	27.62	25.65	23.94	22.44	21.12	19.95	18.90	17.95
210 K	43.50	39.54	36.25	33.46	31.07	29.00	27.18	25.59	24.16	22.89	21.75
220 K	52.01	47.29	43.34	40.01	37.15	34.68	32.51	30.60	28.90	27.38	26.01
230 K	61.13	55.57	50.94	47.02	43.67	40.75	38.21	35.96	33.96	32.17	30.57
240 K	81.33	73.93	67.77	62.56	58.09	54.22	50.83	47.84	45.18	42.80	40.66
250 K	93.79	85.26	78.16	72.15	66.99	62.53	58.62	55.17	52.11	49.36	46.89
260 K	109.27	99.33	91.06	84.05	78.05	72.85	68.29	64.28	60.70	57.51	54.63
270 K	127.36	115.78	106.14	97.97	90.97	84.91	79.60	74.92	70.76	67.03	63.68
280 K	151.59	137.81	126.33	116.61	108.28	101.06	94.75	89.17	84.22	79.79	75.80
290 K	176.56	160.51	147.14	135.82	126.12	117.71	110.35	103.86	98.09	92.93	88.28
298.15 K	222.67	202.42	185.56	171.28	159.05	148.44	139.17	130.98	123.70	117.19	111.33
300 K	233.98	212.71	194.99	179.99	167.13	155.99	146.24	137.64	129.99	123.15	116.99

310 K	306.97	279.06	255.81	236.13	219.26	204.65	191.86	180.57	170.54	161.56	153.49

Table S8. The atmospheric lifetimes (τ, min) of $CH_3C(O)O_2$ radical at different concentrations of HO_2 radical ([HO_2], $0.2 \times 10^8 \sim 1.1 \times 10^8$ molecule cm^{-3}) in the temperature range of 200−310 K and 1 atm.

τ / [HO_2]	0.2×10^8	0.3×10^8	0.4×10^8	0.5×10^8	0.6×10^8	0.7×10^8	0.8×10^8	0.9×10^8	1.0×10^8	1.1×10^8
200 K	17.95	11.97	8.98	7.18	5.98	5.13	4.49	3.99	3.59	3.26
210 K	21.75	14.50	10.87	8.70	7.25	6.21	5.44	4.83	4.35	3.95
220 K	26.01	17.34	13.00	10.40	8.67	7.43	6.50	5.78	5.20	4.73
230 K	30.57	20.38	15.28	12.23	10.19	8.73	7.64	6.79	6.11	5.56
240 K	40.66	27.11	20.33	16.27	13.55	11.62	10.17	9.04	8.13	7.39
250 K	46.89	31.26	23.45	18.76	15.63	13.40	11.72	10.42	9.38	8.53
260 K	54.63	36.42	27.32	21.85	18.21	15.61	13.66	12.14	10.93	9.93
270 K	63.68	42.45	31.84	25.47	21.23	18.19	15.92	14.15	12.74	11.58
280 K	75.80	50.53	37.90	30.32	25.27	21.66	18.95	16.84	15.16	13.78
290 K	88.28	58.85	44.14	35.31	29.43	25.22	22.07	19.62	17.66	16.05
298.15 K	111.33	74.22	55.67	44.53	37.11	31.81	27.83	24.74	22.27	20.24
300 K	116.99	77.99	58.50	46.80	39.00	33.43	29.25	26.00	23.40	21.27
310 K	153.49	102.32	76.74	61.39	51.16	43.85	38.37	34.11	30.70	27.91

Table S9. The atmospheric lifetimes (τ, min) of $CH_3C(O)O_2$ radical at different concentrations of HO_2 radical ([HO_2], 1.1 × 10^8 ~ 6.4 × 10^8 molecule cm^{-3}) in the temperature range of 200−310 K and 1 atm.

T / τ / [HO_2]	1.1 × 10^8	1.5 × 10^8	2.0 × 10^8	2.5 × 10^8	3.0 × 10^8	3.5 × 10^8	4.0 × 10^8	4.5 × 10^8	5.0 × 10^8	5.5 × 10^8	6.0 × 10^8	6.4 × 10^8
200 K	3.26	2.39	1.80	1.44	1.20	1.03	0.90	0.80	0.72	0.65	0.60	0.56
210 K	3.95	2.90	2.17	1.74	1.45	1.24	1.09	0.97	0.87	0.79	0.72	0.68
220 K	4.73	3.47	2.60	2.08	1.73	1.49	1.30	1.16	1.04	0.95	0.87	0.81
230 K	5.56	4.08	3.06	2.45	2.04	1.75	1.53	1.36	1.22	1.11	1.02	0.96
240 K	7.39	5.42	4.07	3.25	2.71	2.32	2.03	1.81	1.63	1.48	1.36	1.27
250 K	8.53	6.25	4.69	3.75	3.13	2.68	2.34	2.08	1.88	1.71	1.56	1.47
260 K	9.93	7.28	5.46	4.37	3.64	3.12	2.73	2.43	2.19	1.99	1.82	1.71
270 K	11.58	8.49	6.37	5.09	4.25	3.64	3.18	2.83	2.55	2.32	2.12	1.99
280 K	13.78	10.11	7.58	6.06	5.05	4.33	3.79	3.37	3.03	2.76	2.53	2.37
290 K	16.05	11.77	8.83	7.06	5.89	5.04	4.41	3.92	3.53	3.21	2.94	2.76
298.15 K	20.24	14.84	11.13	8.91	7.42	6.36	5.57	4.95	4.45	4.05	3.71	3.48

300 K	21.27	15.60	11.70	9.36	7.80	6.69	5.85	5.20	4.68	4.25	3.90	3.66
310 K	27.91	20.46	15.35	12.28	10.23	8.77	7.67	6.82	6.14	5.58	5.12	4.80

Table S10. The acute and chronic toxicity class. (Unit: mg L^{-1})

Classification	Acute toxicity[1]	Chronic toxicity[2]
Not harmful	EC50 / LC50 > 100	ChV > 10
Harmful	10 < LC50 / EC50 < 100	1 < ChV < 10
Toxic	1 < LC50 / EC50 < 10	0.1 < ChV < 1
Very toxic	LC50 / EC50 < 1	ChV < 0.1

[1]Criteria set by the European Union (described in Annex VI of Directive 67/548/EEC);

[2]Criteria set by the Chinese hazard evaluation guidelines for new chemical substances (HJ/T 154–2004).

Table S11. Ecotoxicity (logLC50, logEC50 and logChV) for $CH_3C(O)O_2$ radical precursors and its degradation products. (Unit: mg L^{-1})

Toxicity	Species	Acetone	Methylglyoxal	Acetaldehyde	Isoprene	Peracetic acid	Oxygen	Acetic acid	Ozone
Acute Toxicity	Fish	3.69	2.31	1.46	1.23	4.56	2.63	4.41	4.17
	Daphnid	3.35	2.42	1.51	1.00	4.19	2.33	4.09	3.81
	Green algae	2.85	2.02	1.18	0.97	3.55	1.98	3.64	3.21
Chronic Toxicity	Fish	2.57	2.22	1.08	0.24	3.40	1.56	3.31	3.03
	Daphnid	2.09	0.18	-0.62	0.06	2.83	1.17	2.86	2.48
	Green algae	2.07	1.37	0.62	0.44	2.69	1.28	2.89	2.37

Table S12. Cartesian coordinates of all the studied gaseous molecules optimized at the ωB97X-D/def2-TZVP level of theory.

***Cis*-$CH_3C(O)O_2$:**

Atoms	X	Y	Z
C	0.40328900	0.22534200	0.00001300
O	0.22437900	1.38916900	0.00001200
O	-1.85524000	-0.15541500	-0.00012800
O	-0.67849900	-0.71519100	-0.00008300
C	1.68151700	-0.54538800	0.00014900
H	1.72448800	-1.18783200	0.88031200
H	1.72438600	-1.18840500	-0.87959500
H	2.51716100	0.14801300	-0.00010400

***Trans*-$CH_3C(O)O_2$:**

Atoms	X	Y	Z
C	-0.54418000	-0.13433400	-0.00000600
O	-1.46124600	-0.87890800	-0.00001500
O	1.74506600	0.07500300	0.00001700
O	0.74276500	-0.75836900	-0.00001300
C	-0.55046100	1.35698200	0.00001100
H	-0.02932100	1.73950100	0.87676700
H	-0.02921700	1.73953300	-0.87666800
H	-1.58628900	1.68327100	-0.00003900

HO_2 :

Atoms	X	Y	Z
H	-0.88041600	-0.86497600	0.00000000
O	0.05502600	0.70892500	0.00000000
O	0.05502600	-0.60080300	0.00000000

***Cis*-$CH_3C(O)O_4H$:**

Atoms	X	Y	Z
C	-1.08920400	0.20607600	-0.04281500
O	-0.54617300	1.25779100	-0.22833900
O	0.88761400	-0.99557000	-0.47204200
O	-0.46975700	-0.99759500	-0.01360300
O	1.68728300	-0.41124300	0.49416500
O	2.10869700	0.83141000	0.01475200
H	1.27045100	1.33481400	0.00067000
C	-2.55536200	0.00870900	0.19822700
H	-3.03864100	-0.14630400	-0.76810400
H	-2.74467600	-0.86308200	0.82041700
H	-2.96104600	0.90752600	0.65508500

***Trans*-$CH_3C(O)O_4H$:**

Atoms	X	Y	Z
C	-1.28623100	-0.11395200	0.06837400
O	-2.15555300	-0.63724100	0.68861400
O	0.81992000	-0.23264900	-0.93865800
O	-0.22866300	-0.93791000	-0.27656100
C	-1.24715100	1.31015800	-0.39113800
H	-0.39575500	1.82969700	0.04618700
H	-1.13864500	1.36013600	-1.47431800
H	-2.17704900	1.78009200	-0.08457000
H	1.50515100	0.06508600	1.62943200
O	1.92449200	-0.33230500	-0.14187600
O	1.81562700	0.61357500	0.89596200

***Cis*-$CH_3C(O)O_2H$:**

Atoms	X	Y	Z
C	-1.78341600	-0.42092400	-0.00006500
C	-0.40827100	0.16545000	-0.00021000
O	-0.12476100	1.33514600	0.00013300
O	0.53250700	-0.79113300	-0.00019500
H	-2.31419100	-0.05726000	-0.87936100
H	-1.75839700	-1.50764600	-0.00401100
H	-2.31108400	-0.06390900	0.88385400
O	1.83079200	-0.23876400	0.00021200
H	1.62548500	0.71967000	-0.00003000

***Trans*-$CH_3C(O)O_2H$:**

Atoms	X	Y	Z
C	0.58563729	-0.13473298	0.00288968
O	1.56025288	-0.82076863	0.01479145
O	-1.72190215	0.09053643	-0.06879865
O	-0.61084785	-0.79847651	-0.03340963
C	0.55365486	1.36264885	0.00956803
H	0.04021297	1.73800146	-0.87511198
H	0.01064641	1.73134785	0.87891911
H	1.58067120	1.71519366	0.02797413
H	-2.28730655	-0.32236851	0.59280714

O_2:

Atoms	X	Y	Z
O	0.00000000	0.00000000	0.59727200
O	0.00000000	0.00000000	-0.59727200

CH_3COOH :

Atoms	X	Y	Z
C	-0.09073000	0.12447700	-0.00003000
H	-1.72193300	-0.79065000	0.00006200
C	1.38850400	-0.12102000	0.00000000
H	1.66417800	-0.70416200	-0.87904200
H	1.91562500	0.82819500	-0.00039700
O	-0.78678500	-1.02841100	0.00002400
O	-0.62680500	1.19706900	-0.00002200
H	1.66421300	-0.70339500	0.87954400

O_3 :

Atoms	X	Y	Z
O	0.00000000	0.00000000	0.42425403
O	0.00000000	1.06179308	-0.21212702
O	0.00000000	-1.06179308	-0.21212702

$CH_3C(O)O$:

Atoms	X	Y	Z
C	-1.38562300	0.00005500	-0.00322400
C	0.10102700	-0.00026200	-0.00798400
O	0.80981400	-1.02833100	0.00149200
O	0.80981900	1.02844900	0.00152300
H	-1.72761300	0.00179200	1.03330200
H	-1.76077300	0.89534300	-0.49668200
H	-1.76110400	-0.89683200	-0.49349800

HO_3 :

Atoms	X	Y	Z
O	1.09085300	0.29615800	0.00012300
O	0.15993600	-0.53459000	-0.00018100
O	-1.14128100	0.10814900	0.00020700
H	-0.87606100	1.04226600	-0.00119600

OH:

Atoms	X	Y	Z
H	0.00000000	0.00000000	-0.86309200
O	0.00000000	0.00000000	0.10788700

Table S13. Calculated spin contamination $<S^2>$ values for open-shell key species involved in the reaction pathways.

Species	$<S^2>$ Before annihilation	$<S^2>$ After annihilation
Cis-$CH_3C(O)O_2$	0.754	0.750
Trans-$CH_3C(O)O_2$	0.755	0.750
HO_2	0.754	0.750
TS1	0.754	0.750
TS8	2.012	2.000
TS9	2.012	2.000
TS13	2.013	2.000
TS14	2.013	2.000
$CH_3C(O)O$	0.758	0.750
HO_3	0.755	0.750
OH	0.753	0.750
O_2	2.010	2.000