Supplementary information

Mechanism and kinetics of the atmospheric reaction of 1,3,5-trimethylbenzene bicyclic peroxy radical with OH

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SUMMARY:

4 pages, including 2 Figures and 1 Table.

Figure Captions:

Fig. S1. Potential energy surface for CH_3O_2 + OH biradical reactions. The energies

(kcal mol^{-1}) relative to separated reactants CH_3O_2 and OH at M08-HX/6-311 + g(2df,2p) level of theory. RC, reactant complex; TS, transition state. The singlet reaction pathways are depicted in black, and the triplet reaction pathways are depicted in red for clarity.

Fig. S2. Structures of key species in the reaction of CH_3O_2 with OH radicals optimized at M08-HX/6-311 + g(2df,2p) level of theory. The singlet species are named in black, while the triplet ones are named in red for clarity. Bond distances are in angstrom.

Fig. S1.

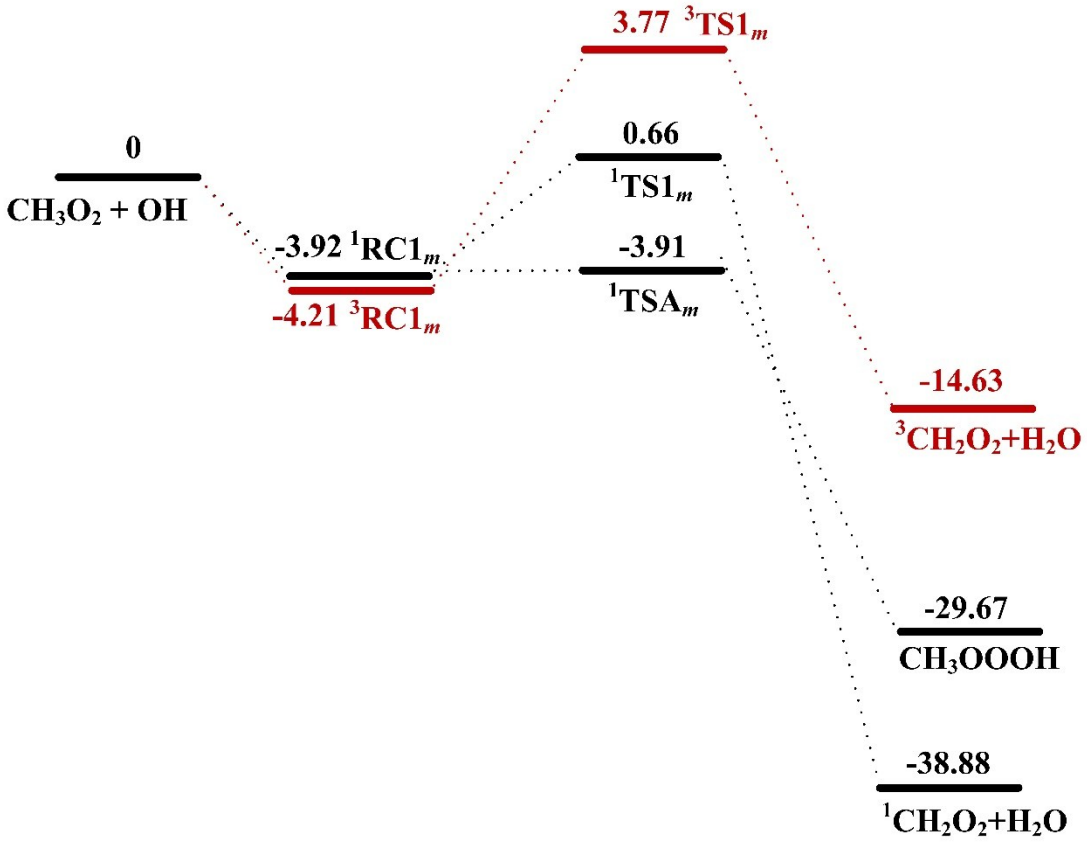
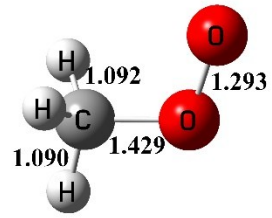
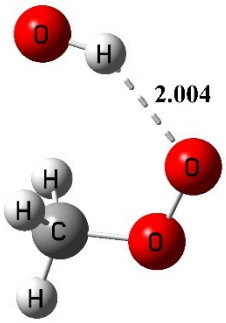

3.77 $^{3}TS1_{m}$
0
CH_3O_2 + OH
0.66
$^{1}TS1_{m}$
-3.92 $^{1}RC1_{m}$
-3.91
$^{1}TSA_{m}$
-4.21 $^{3}RC1_{m}$
-14.63
$^{3}CH_2O_2+H_2O$
-29.67
CH_3OOOH
-38.88
$^{1}CH_2O_2+H_2O$

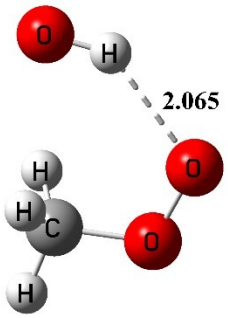
Fig. S2.



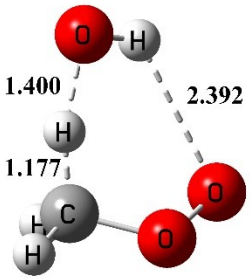
CH_3O_2



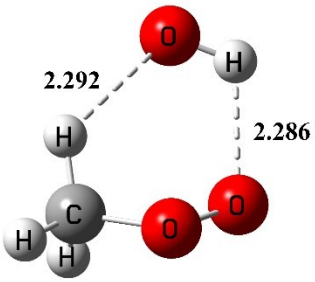
$^1RC1_m$



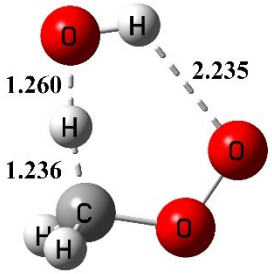
$^3RC1_m$



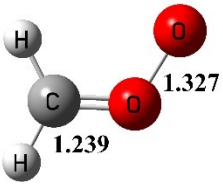
$^1TS1_m$



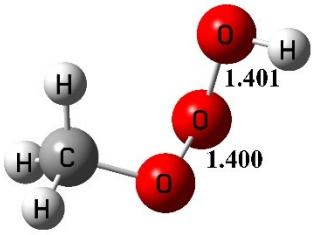
$^1TSA_m$



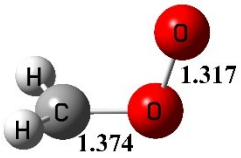
$^3TS1_m$



$^1CH_2O_2$



CH_3OOOH



$^3CH_2O_2$

Table S1. Calculated values at 298 K of equilibrium constants (K_{eq}, cm^3 $molecule^{-1}$),

the Eckart tunneling correction (κ), unimolecular rate constants (k_2, s^{-1}) including tunneling correction, rate constants (k_{TS}, cm^3 $molecule^{-1}$ s^{-1}), and the overall rate constant k_{Total} ($k_{Total} = k_{^1TS1_m} + k_{^1TSA_m} + k_{^3TS1_m}$, cm^3 $molecule^{-1}$ s^{-1}).

reaction pathways	K_{eq}	κ	k_2	k_{TS}	k_{Total}	*exptl.*
$^1TS1_m$	4.99×10^{-23}	3.87	1.43×10^{9}	7.14×10^{-14}		$(1.6 \pm 0.4) \times10^{-10}$
$^1TSA_m$	4.99×10^{-23}	1.01	2.93×10^{12}	1.46×10^{-10}	1.46×10^{-10}	(ref. 10)
$^3TS1_m$	1.54×10^{-22}	1.67×10^{1}	9.64×10^{7}	1.48×10^{-14}		$(8.21 \pm 1.39) \times10^{-11}$ (ref. 14)