Supplementary Information (SI) for Physical Chemistry Chemical Physics.

ESI of

Role of Non-Statistical Effect in Deciding the Fate of $HO_3^\bullet$ in the Atmosphere

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Table S1: Cartesian coordinates and all normal mode frequencies of the optimized geometries calculated at LC-ωHPBE/cc-pVDZ level of theory.

Species	Cartesian coordinate (Å)				Frequencies (cm^{-1})		
cis-$HO_3^\bullet$	O	0.152582	-0.538694	-0.000001			
	O	1.079890	0.294943	0.000000	296.9	568.7	853.1
	O	-1.128462	0.112995	0.000001	1317.3	1481.3	3694.2
	H	-0.832086	1.046048	-0.000004			
trans-$HO_3^\bullet$	O	-0.160126	0.499124	0.000085			
	O	-1.130875	-0.263503	-0.000074	158.2	559.8	799.1
	O	1.075844	-0.290507	0.000078	1305.5	1453.3	3775.4
	H	1.721250	0.439091	-0.000716			
$TS_{cis-trans}$	O	-0.166861	0.510454	-0.00593			
	O	-1.114004	-0.294954	0.017251	-148.4	584.1	809.8
	O	1.104854	-0.197994	-0.112681	1304.1	1358.7	3772.4
	H	1.408088	-0.140048	0.810879			
cis-TS_{Diss}	O	0.320823	-0.535216	-0.000003			
	O	1.134003	0.344931	0.000001	-528.5	86.2	431.3
	O	-1.321387	0.064246	0.000002	1045.8	1623.7	3740.1
	H	-1.067514	1.008313	0.000005			
trans-TS_{Diss}	O	0.300913	0.509088	0.000000			
	O	1.167767	-0.311347	0.000000	-525.9	123.3	439.6
	O	-1.247618	-0.267464	0.000000	1017.9	1643.0	3765.6
	H	-1.768494	0.557776	-0.000001			
$OH^\bullet$	O	0.000000	0.000000	0.108864		3725.2	
	H	0.000000	0.000000	-0.870911			
O_2	O	0.000000	0.000000	0.595835		1781.0	
	O	0.000000	0.000000	-0.595835			

Table S2: The relative energies of $HO_3^\bullet$ with respect to $OH^\bullet$ and O_2, calculated using various DFT functionals with the cc-pVDZ basis set, alongside higher-level theories, are provided. All DFT and CCSD(T) calculations exclude ZPE, while the post-CCSD(T) method includes ZPE.

Level of Theory	*cis*-$HO_3^\bullet$	*trans*-$HO_3^\bullet$	$TS_{cis-trans}$
Post-CCSD(T)[1]	-2.96	-3.11	-2.12
LC-ωHPBE	-2.82	-1.36	-0.75
ωB97XD	-3.52	-2.53	-1.64
M08HX	-3.89	-2.08	-1.55
CAM-B3LYP	-5.12	-3.73	-2.98
M06	-5.53	-4.59	-3.52
B3LYP	-6.04	-5.30	-4.03
M11	-6.30	-4.57	-4.03
MN15L	-7.61	-6.89	-5.36
LC-BLYP	-8.36	-6.22	-5.83
TPPSh	-8.38	-7.99	-6.43
tHCTHhyb	-8.85	-8.37	-6.81
BHandHLYP	8.99	10.08	13.01
BLYP	-18.25	-18.08	-15.41
PW91	-21.78	-21.57	-18.76
CCSD(T)/aug-cc-pVDZ[1]	1.63	2.06	2.37
CCSD(T)/aug-cc-pVTZ[1]	-2.09	-1.18	-0.86
CCSD(T)/aug-cc-pVQZ[1]	-2.73	-1.77	-1.36
CCSD(T)/CBS[1]	-3.24	-2.22	-1.78

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Figure S1: Comparison of energetics and geometrical parameters obtained at LC-wHPBE/cc-pVDZ level of theory with the post-CCSD(T) corrected potential energy surface. The geometrical parameters, i.e., bond lengths (Å) and angles (degree) in paranthesis are depicted for CCSD(T)/aug-cc-pVDZ optimized level of theory. Similarly, the energetics at post-CCSD(T) method are shown in paranthesis.

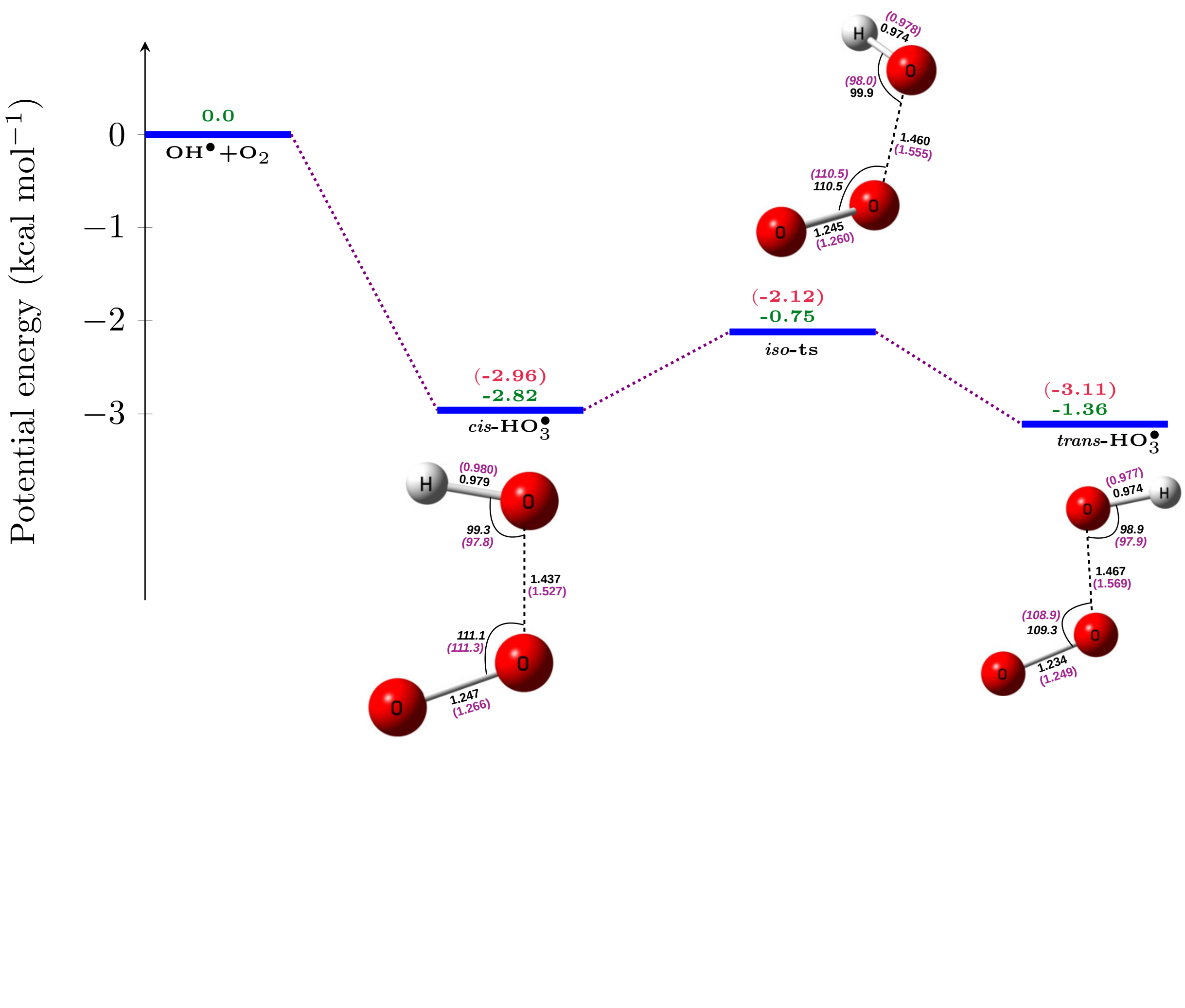
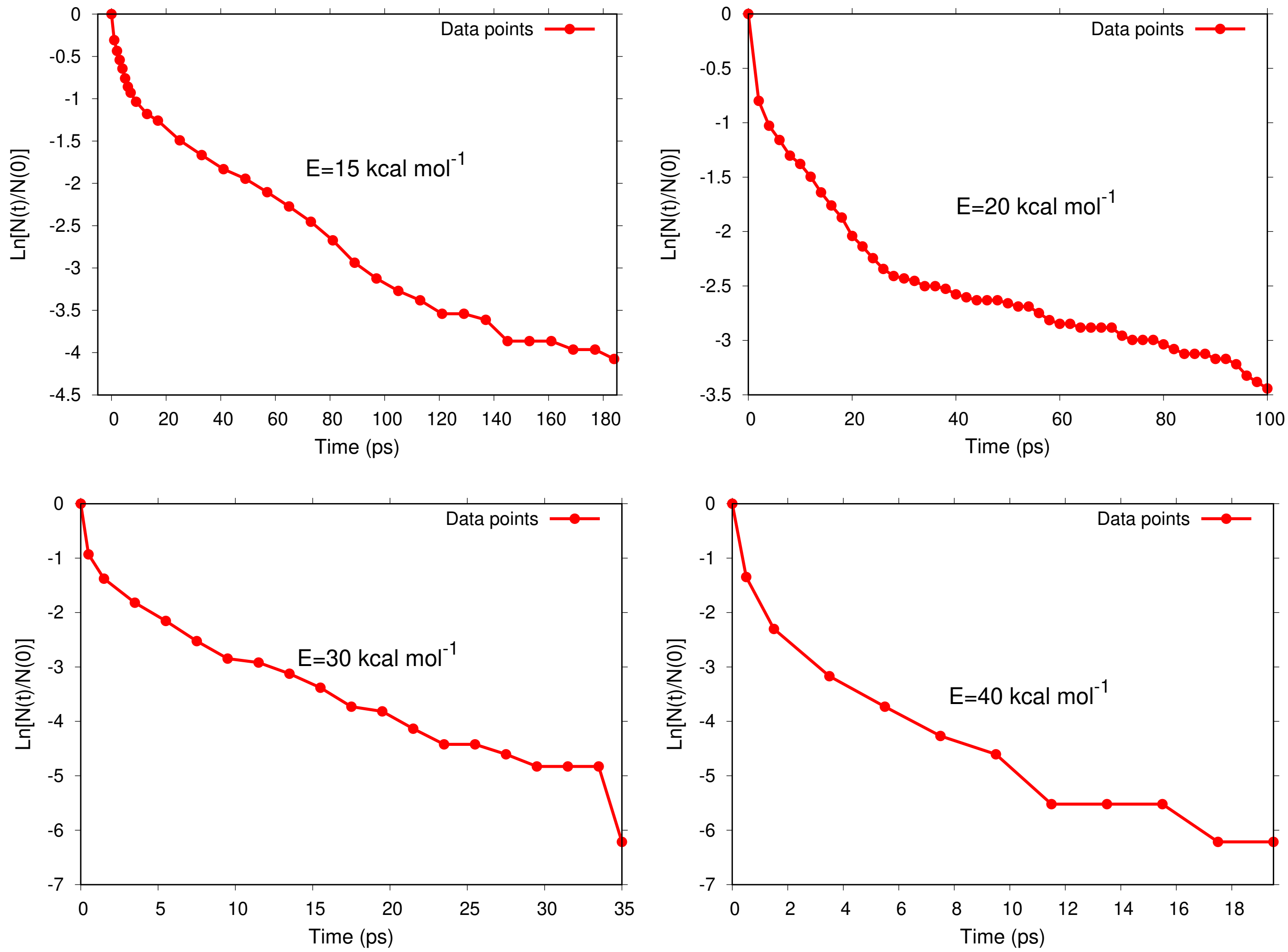


Figure S2: Ln[N(t)/N(0)] vs. time (in picosecond) excited using microcanonical sampling at total energies of E = 15, 20, 30, and 40 kcal mol^{-1}.



Details of kinetics calculations

If N(t) is exponential, unimolecular rate constant equals the RRKM rate constant, whereas if N(t) is non-exponential, unimolecular rate constant varies with pressure. Therefore, we have calculated the rate constant in three regions; i.e., high pressure limiting rate constant (k^∞), low pressure limiting rate constant (k^0) and finite pressure unimolecular rate constant (k) using following expressions:

$$\mathrm{k} = \omega \frac{\sum_\mathrm{i} \mathrm{f_i k_i}/(\omega + \mathrm{k_i})}{1 - \sum_\mathrm{i} \mathrm{f_i k_i}/(\omega + \mathrm{k_i})}$$

Here, ω is the collision frequency, which is proportional to the pressure.

$$\mathrm{k}^\infty = \sum_\mathrm{i} \mathrm{f_i k_i}$$

$$\mathrm{k}^0 = \frac{1}{\sum_\mathrm{i} \mathrm{f_i/k_i}}$$

(*f_i and k_i are the fitting parameters for N(t)/N(0) distributions. These values are listed in table 1 of the main manuscript.*)

Table S3: Rate constants (ps^{-1}) at different pressures and corresponding half-life in ps (0.693/rate constant) for the different microcanonical excitation energies (kcal mol^{-1}).

	E = 15	E = 20	E = 30	E = 40
k^0	0.05	0.07	0.47	1.48
k	0.06	0.10	0.52	1.56
k^∞	1.29	1.18	2.39	3.23
$\tau^0_{1/2}$	13.86	9.90	1.49	0.47
$\tau_{1/2}$	11.55	6.93	1.34	0.44
$\tau^\infty_{1/2}$	0.54	0.59	0.29	0.21