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ESI of

Accurate determination of reaction energetics and kinetics of $HO_2^{\bullet}+O_3 \rightarrow OH^{\bullet}+2O_2$ reaction

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Table S1: Cartesian coordinates and all normal mode frequencies of the optimized geometries calculated at CCSD(T)/6-311++G** level of theory.

Species	Cartesian coordinate (Å)				Frequencies (cm^{-1})		
	O	0.000000	0.000000	0.000000			
$HO_2^\bullet$	O	0.000000	0.000000	1.334705	1129.04	1428.41	3675.13
	H	0.941318	0.000000	-0.246989			
	O	0.000000	0.000000	0.000000			
O_3	O	0.000000	0.000000	1.276127	717.24	1014.31	1139.99
	O	1.135784	0.000000	-0.582218			
	O	0.000000	0.000000	0.000000			
	O	0.000000	0.000000	1.278584	76.78	95.03	110.76
RC	H	1.955899	0.000000	1.942882	167.56	189.06	365.36
	O	2.759814	0.551893	1.950201	729.56	1060.69	1116.05
	O	2.522015	1.473292	1.016889	1138.80	1468.36	3651.87
	O	1.000411	-0.527031	-0.571230			
	O	1.600142	-0.719797	-0.433836			
	O	1.005564	-0.050578	0.463970	-2062.76	87.84	135.47
TS_H	O	0.559127	1.152499	0.065909	205.47	392.20	634.47
	H	-0.732216	0.868261	-0.260560	702.88	831.54	1028.48
	O	-1.643709	0.297655	-0.355927	1138.99	1373.05	1705.07
	O	-1.429598	-0.788312	0.292454			
	O	0.000000	0.000000	0.000000			
	O	0.000000	0.000000	1.267932	-2075.44	87.09	134.46

TS_{Iso}	O	1.220117	0.000000	1.830238	205.01	392.59	632.23
	H	1.410077	-1.324923	2.077084	703.47	831.35	1028.78
	O	1.182321	-2.378302	2.148246	1138.57	1371.75	1706.30
	O	-0.076682	-2.464872	1.918972			
	O	0.000000	0.000000	0.000000			
	O	0.000000	0.000000	1.288007	-571.09	74.07	132.15
TS_O	O	1.245748	0.000000	1.821167	289.95	337.51	532.36
	O	1.848161	-1.733234	1.527554	653.18	770.77	1043.71
	O	2.778188	-1.665882	0.558501	1092.02	1451.32	3674.32
	H	2.261195	-1.656527	-0.267059			
	O	-0.177560	-0.543580	0.001715			
$HO_3^\bullet$	O	-1.108059	0.306054	-0.001192	252.45	486.00	738.91
	O	1.173668	0.107445	-0.001973	1208.45	1391.76	3715.73
	H	0.895617	1.040647	0.011603			
O_2	O	0.000000	0.000000	0.000000		1590.93	
	O	0.000000	0.000000	1.211348			
$HO^\bullet$	O	0.000000	0.000000	0.000000		3753.95	
	H	0.000000	0.000000	0.972610			

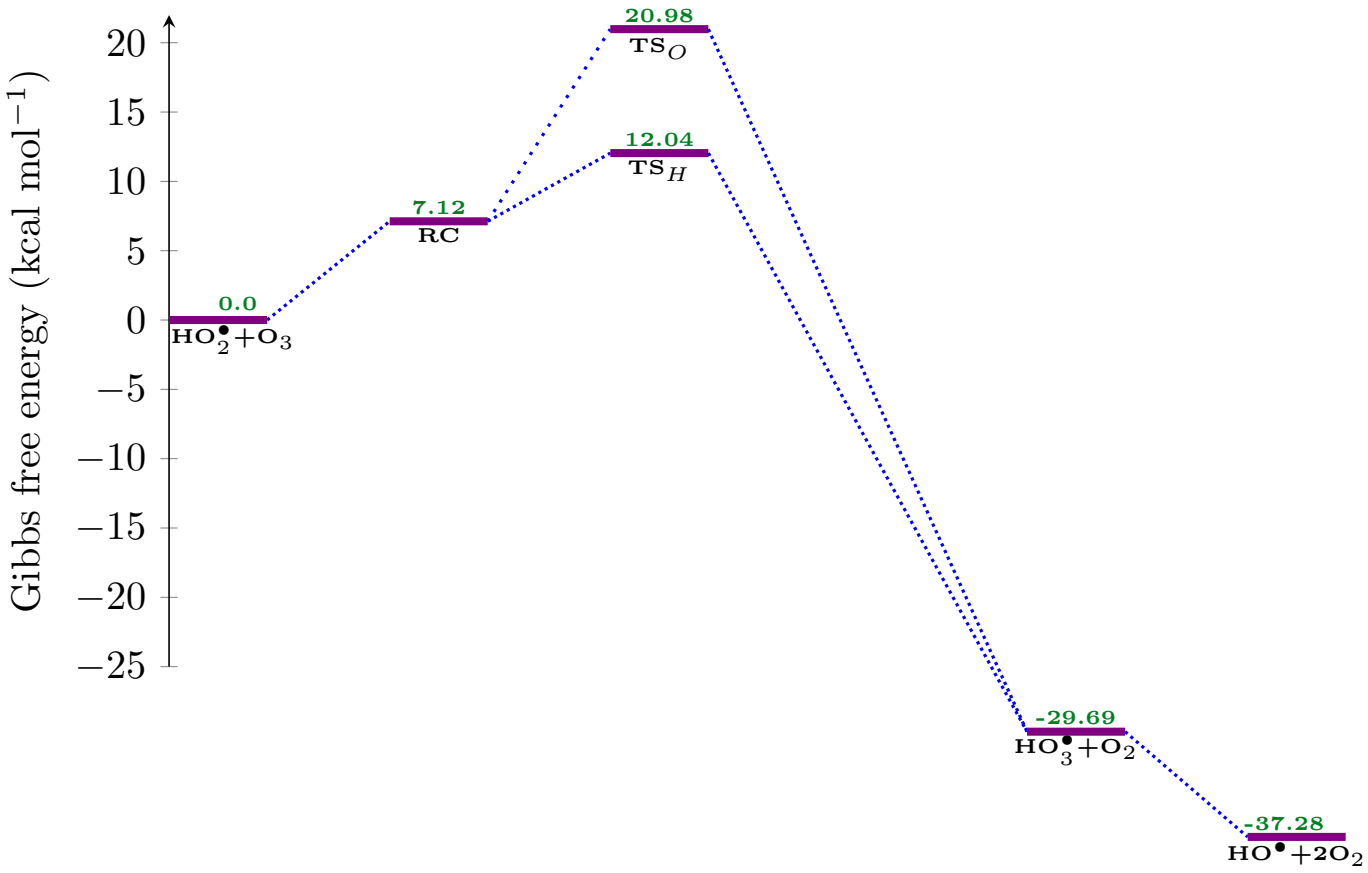

Figure S1: Gibbs free energy profile for the $HO_2^\bullet+O_3$ reaction at 298 K including post-CCSD(T) corrections.

Figure S2: Optical isomers of TS_H with bond lengths (in Angstrom) and (angle in degree).

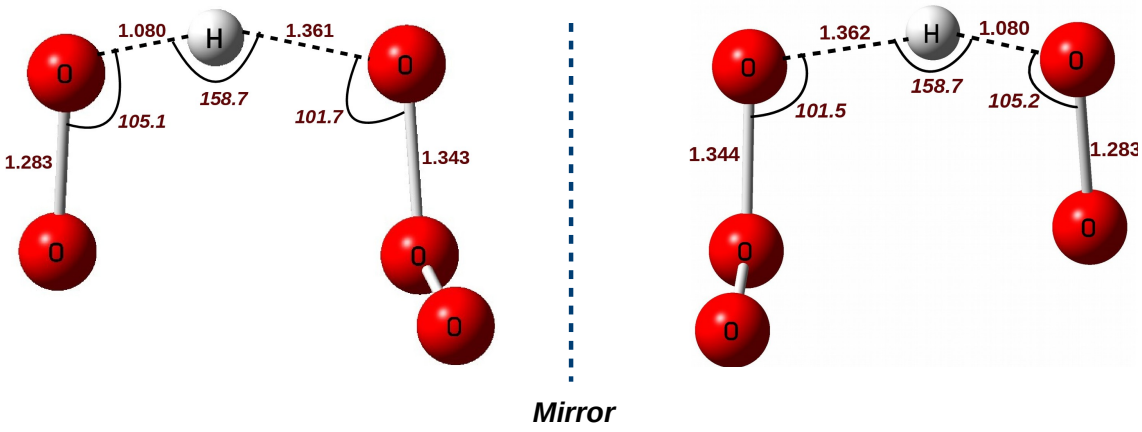

Table S2: Comparison of frequencies (in cm^{-1}) and geometrical parameters of the isolated species, obtained in present work (CCSD(T)/6-311++G**) with the experimental[1] and higher-level theoretical data (CCSD(T)/aug-cc-pVTZ)[1] available in the literature.

Methods	Species	Frequencies			Bond lengths ($\AA$)		Angles (°)	
					R_{O-H}	R_{O-O}	A_{H-O-O}	A_{O-O-O}
Experiment	$HO_2^\bullet$	1098	1392	3436	0.97	1.33	104.3	
	O_3	716	1089	1135		1.28		116.8
	$HO^\bullet$		3738		0.97			
	O_2		1580			1.21		
CCSD(T)/aug-cc-pVTZ	$HO_2^\bullet$	1125	1429	3641	0.97	1.34	104.2	
	O_3	714	1038	1147		1.28		117.1
	$HO^\bullet$		3713		0.97			
	O_2		1574			1.21		
CCSD(T)/6-311++G**	$HO_2^\bullet$	1129	1428	3675	0.97	1.33	104.7	
	O_3	717	1014	1139		1.28		117.1
	$HO^\bullet$		3753		0.97			
	O_2		1590			1.21		

1. Johnson III, R. D. NIST computational chemistry comparison and benchmark database, NIST standard reference database number 101. Release 16a http://cccbdb.nist.gov/ (accessed Jan 10, 2023) **2013**.

Table S3: Rate constant values obtained at TST (k_{TST}) and CVT (k_{CVT}) level along with ZCT, SCT and Eckart tunneling coefficients. The rate constants are in $cm^3 \cdot molecule^{-1} \cdot s^{-1}$.

T(K)	TST	CVT	ZCT	SCT	Eckart
197	9.32×10^{-18}	5.61×10^{-18}	55.47	119.35	98.97
202	1.15×10^{-17}	6.93×10^{-18}	47.10	99.47	83.45
204	1.24×10^{-17}	7.53×10^{-18}	44.24	92.73	78.14
208	1.45×10^{-17}	8.83×10^{-18}	39.19	80.93	68.86
211	1.63×10^{-17}	9.92×10^{-18}	35.92	73.35	62.83
219	2.17×10^{-17}	1.33×10^{-17}	28.88	57.23	49.91
225	2.67×10^{-17}	1.64×10^{-17}	24.83	48.12	42.54
230	3.14×10^{-17}	1.94×10^{-17}	22.05	41.97	37.54
232	3.35×10^{-17}	2.07×10^{-17}	21.07	39.81	35.77
233	3.45×10^{-17}	2.14×10^{-17}	20.60	38.79	34.92
238	4.03×10^{-17}	2.51×10^{-17}	18.47	34.18	31.08
243	4.68×10^{-17}	2.92×10^{-17}	16.66	30.30	27.85
245	4.95×10^{-17}	3.10×10^{-17}	16.01	28.92	26.69
250	5.71×10^{-17}	3.58×10^{-17}	14.55	25.84	24.07
253	6.20×10^{-17}	3.89×10^{-17}	13.76	24.20	22.69
265	8.48×10^{-17}	5.36×10^{-17}	11.21	18.98	18.17
267	8.92×10^{-17}	5.64×10^{-17}	10.85	18.27	17.56
270	9.60×10^{-17}	6.08×10^{-17}	10.36	17.28	16.69
273	1.03×10^{-16}	6.54×10^{-17}	9.90	16.37	15.89
274	1.06×10^{-16}	6.70×10^{-17}	9.75	16.08	15.63
280	1.22×10^{-16}	7.73×10^{-17}	8.95	14.50	14.23
283	1.30×10^{-16}	8.29×10^{-17}	8.58	13.80	13.60
296	1.73×10^{-16}	1.10×10^{-16}	7.26	11.29	11.32
297	1.76×10^{-16}	1.13×10^{-16}	7.18	11.13	11.17
298	1.80×10^{-16}	1.15×10^{-16}	7.09	10.97	11.03
320	2.77×10^{-16}	1.78×10^{-16}	5.59	8.23	8.47
323	2.93×10^{-16}	1.89×10^{-16}	5.43	7.94	8.20
333	3.50×10^{-16}	2.26×10^{-16}	4.95	7.10	7.39
334	3.56×10^{-16}	2.30×10^{-16}	4.91	7.03	7.32
342	4.07×10^{-16}	2.64×10^{-16}	4.59	6.47	6.78
343	4.14×10^{-16}	2.68×10^{-16}	4.55	6.40	6.72
345	4.28×10^{-16}	2.77×10^{-16}	4.47	6.28	6.60
350	4.64×10^{-16}	3.01×10^{-16}	4.30	5.98	6.31
360	5.43×10^{-16}	3.53×10^{-16}	3.99	5.47	5.80
365	5.86×10^{-16}	3.81×10^{-16}	3.86	5.24	5.57
373	6.60×10^{-16}	4.30×10^{-16}	3.66	4.91	5.24
380	7.30×10^{-16}	4.76×10^{-16}	3.50	4.65	4.98
400	9.58×10^{-16}	6.26×10^{-16}	3.12	4.04	4.36
413	1.13×10^{-15}	7.41×10^{-16}	2.92	3.72	4.03
450	1.75×10^{-15}	1.15×10^{-15}	2.48	3.06	3.33

Table S4: The rate constant values for $HO_2^{\bullet}+O_3$ reaction with rigid rotor harmonic approximation (k_{WTHR}) along with hindered rotor approximation (k_{HR}). The values are given in $cm^3 \cdot molecule^{-1} \cdot s^{-1}$.

T (K)	k_{WTHR}	k_{HR}
197	2.37×10^{-15}	1.51×10^{-15}
202	2.30×10^{-15}	1.52×10^{-15}
204	2.28×10^{-15}	1.52×10^{-15}
208	2.24×10^{-15}	1.52×10^{-15}
211	2.20×10^{-15}	1.52×10^{-15}
219	2.13×10^{-15}	1.53×10^{-15}
225	2.08×10^{-15}	1.53×10^{-15}
230	2.05×10^{-15}	1.53×10^{-15}
232	2.03×10^{-15}	1.53×10^{-15}
233	2.03×10^{-15}	1.53×10^{-15}
238	2.00×10^{-15}	1.54×10^{-15}
243	1.97×10^{-15}	1.54×10^{-15}
245	1.96×10^{-15}	1.54×10^{-15}
250	1.94×10^{-15}	1.54×10^{-15}
253	1.93×10^{-15}	1.54×10^{-15}
265	1.90×10^{-15}	1.56×10^{-15}
267	1.89×10^{-15}	1.56×10^{-15}
270	1.88×10^{-15}	1.56×10^{-15}
273	1.88×10^{-15}	1.57×10^{-15}
274	1.88×10^{-15}	1.57×10^{-15}
280	1.87×10^{-15}	1.58×10^{-15}
283	1.87×10^{-15}	1.58×10^{-15}
296	1.86×10^{-15}	1.61×10^{-15}
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298	1.86×10^{-15}	1.61×10^{-15}
320	1.89×10^{-15}	1.68×10^{-15}
323	1.89×10^{-15}	1.69×10^{-15}
333	1.91×10^{-15}	1.72×10^{-15}
334	1.92×10^{-15}	1.73×10^{-15}
342	1.94×10^{-15}	1.76×10^{-15}
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345	1.95×10^{-15}	1.77×10^{-15}
350	1.97×10^{-15}	1.79×10^{-15}
360	2.00×10^{-15}	1.84×10^{-15}
365	2.03×10^{-15}	1.87×10^{-15}
373	2.06×10^{-15}	1.91×10^{-15}
380	2.10×10^{-15}	1.95×10^{-15}
400	2.21×10^{-15}	2.08×10^{-15}
413	2.30×10^{-15}	2.18×10^{-15}
450	2.60×10^{-15}	2.49×10^{-15}

Figure S3: IRC for the hydrogen abstraction transition state (bond lengths are in $\mathring{A}$) obtained at M11/6-311++G(2df,2p) level of theory.

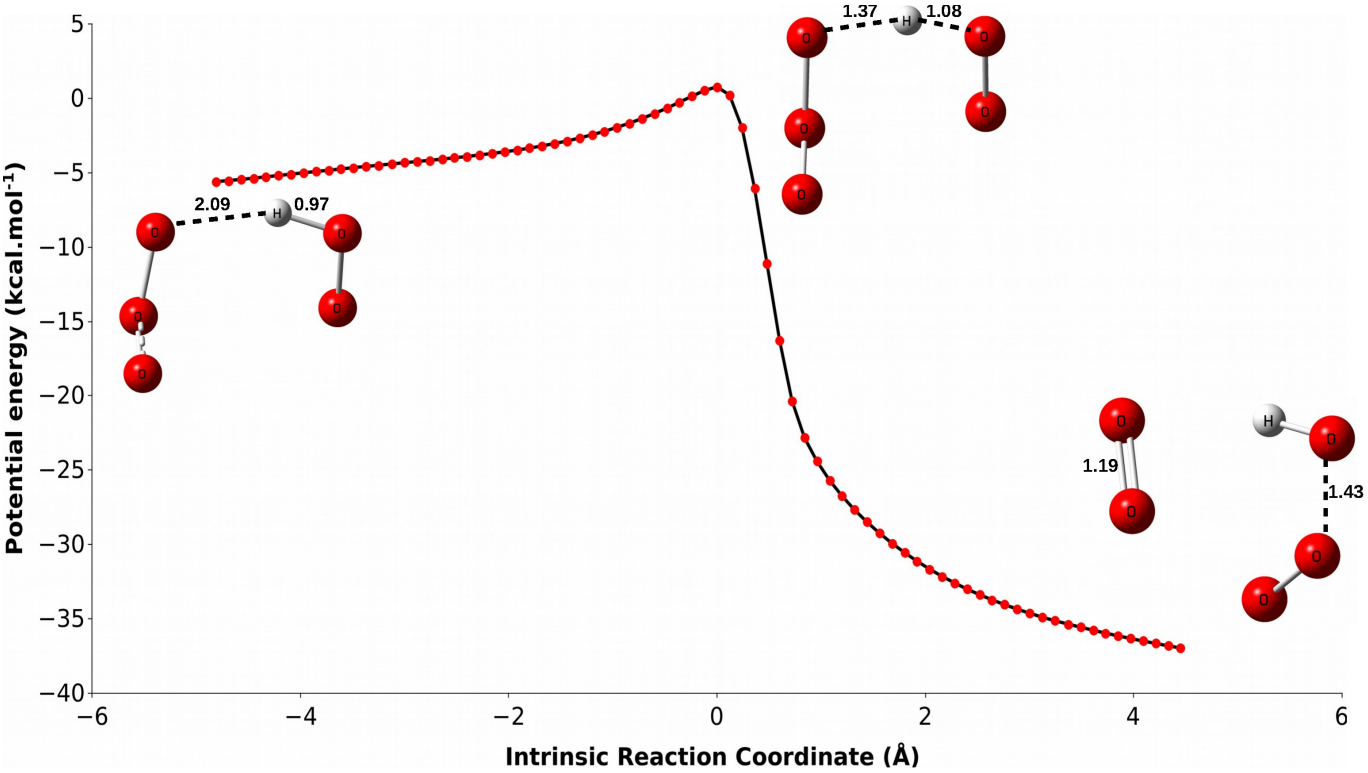

Figure S4: IRC for the oxygen abstraction transition state (bond lengths are in $\mathring{A}$) obtained at M11/6-311++G(2df,2p) level of theory.