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Oxidation of $HOSO^{\bullet}$ by $Cl^{\bullet}$: A new source of SO_2 in the atmosphere ?

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Table S1: Optimized geometries in Cartesian coordinates and normal mode frequencies of all species calculate at MP2/aug-cc-pV(+d)TZ level of theory

Compound	Cartesian coordinate(Å)				Frequencies (cm^{-1}		
	S	0.137093	-0.477175	0.00	115.411	397.9768	787.086
$HOSO^{\bullet}$	O	1.241197	0.527636	0.00	1093.9523	1188.8807	3812.0452
	O	-1.26227	0.44581	0.00			
	H	-2.024901	-0.152764	-0.000001			
$Cl^{\bullet}$	Cl	0.00	0.00	0.00			
$OH^{\bullet}$	O	0.00	0.00	0.10772	3795.0583		
	H	0.00	0.00	-0.86172			
H_2O	O	0.00	0.00	0.11819	1627.7612	3824.705	3950.609
	H	0.00	0.75803	-0.47275			
	H	0.00	-0.75803	-0.47275			
SO_2	S	0.00	0.00	0.36419	535.298	1234.4436	1419.2614
	O	0.00	1.25431	-0.36419			
	O	0.00	-1.25431	-0.36419			
HCl	Cl	0.00	0.00	0.07067	3049.7398		
	H	0.00	0.00	-1.20138			
RC_{Cl}	S	0.52746	-0.13874	-0.4327	216.9845	294.4667	345.1948
	O	1.06675	-1.18215	0.41137	468.9399	489.0097	804.0112
	O	0.98803	1.2889	0.14482	1105.3615	1288.4892	3689.3776

	H	0.94258	1.27815	1.11855			
	Cl	-1.51884	0.00516	0.07971			
TS_{Cl}	S	-0.79632	-0.03138	0.39604	-1447.9079	111.389	349.2023
	O	-1.70871	-0.79213	-0.42534	463.0222	533.0092	813.8461
	O	-0.40677	1.29873	-0.23579	1071.944	1264.7298	1609.3846
	H	0.7434	1.00344	-0.25746			
	Cl	1.70127	-0.26789	-0.04648			
PC_{Cl}	S	1.52327	-0.34299	0.00161	13.5481	20.3147	95.1187
	O	2.87248	0.18317	-0.00415	294.7054	305.0543	505.0332
	O	0.40359	0.58472	0.00284	1119.8885	1333.5912	2979.6744
	H	-1.6532	0.30713	0.00209			
	Cl	-2.8781	-0.05662	-0.00103			
RC_{OH}	S	0.00	0.11073	-0.43303	119.5506	343.2882	414.0352
	O	-0.0001	1.36746	0.30678	450.7755	494.8956	780.8247
	O	1.24823	-0.74689	0.15139	790.6133	1075.9903	1108.9823
	H	1.46907	-0.3799	1.02608	1265.6144	3698.8941	3700.4182
	O	-1.24813	-0.74704	0.15138			
	H	-1.46913	-0.37994	1.02599			
TS_{OH}	S	0.34819	0.04037	0.41294	-1587.0632	236.5828	429.8697
	O	1.37815	-0.54914	-0.40577	497.7447	504.6002	664.2118
	O	-0.32801	1.26015	-0.24321	827.0747	1029.1588	1238.177
	H	-1.24415	0.50103	-0.43755	1307.7955	1940.5641	3748.5252

	O	-1.34936	-0.73947	-0.19255			
	H	-1.93309	-0.91929	0.56276			
PC_{OH}	S	0.64655	-0.00011	0.36915	28.6027	92.3635	105.4821
	O	0.74479	-1.24977	-0.36122	130.2642	216.4822	243.8289
	O	0.7463	1.24938	-0.36131	506.5475	1130.2826	1339.3725
	H	-2.42298	0.76168	-0.44179	1627.9239	3803.1789	3926.9203
	O	-2.17856	0.00047	0.09476			
	H	-2.42211	-0.76054	-0.44246			

Table S2: Pressure dependence bimolecular rate constants k(T) in cm^3 $molecule^{-1}$ s^{-1} for $HOSO^{\bullet}$ + $Cl^{\bullet}$ reaction at within temperature range of 213-400 K

Temp (K)	Pressure (atm)				
	0.1	0.5	1	5	10
213	5.61×10^{-13}	5.61×10^{-13}	5.61×10^{-13}	5.61×10^{-13}	5.61×10^{-13}
216	5.54×10^{-13}	5.54×10^{-13}	5.54×10^{-13}	5.54×10^{-13}	5.54×10^{-13}
219	5.48×10^{-13}	5.48×10^{-13}	5.48×10^{-13}	5.48×10^{-13}	5.48×10^{-13}
224	5.38×10^{-13}	5.38×10^{-13}	5.38×10^{-13}	5.38×10^{-13}	5.38×10^{-13}
235	5.18×10^{-13}	5.18×10^{-13}	5.18×10^{-13}	5.18×10^{-13}	5.18×10^{-13}
250	4.93×10^{-13}	4.93×10^{-13}	4.93×10^{-13}	4.93×10^{-13}	4.93×10^{-13}
259	4.79×10^{-13}	4.79×10^{-13}	4.79×10^{-13}	4.79×10^{-13}	4.79×10^{-13}
265	4.78×10^{-13}	4.78×10^{-13}	4.78×10^{-13}	4.78×10^{-13}	4.78×10^{-13}
270	4.64×10^{-13}	4.64×10^{-13}	4.64×10^{-13}	4.64×10^{-13}	4.64×10^{-13}
278	4.53×10^{-13}	4.53×10^{-13}	4.53×10^{-13}	4.53×10^{-13}	4.53×10^{-13}
280	4.51×10^{-13}	4.51×10^{-13}	4.51×10^{-13}	4.51×10^{-13}	4.51×10^{-13}
290	4.38×10^{-13}	4.38×10^{-13}	4.38×10^{-13}	4.38×10^{-13}	4.38×10^{-13}
298	4.29×10^{-13}	4.29×10^{-13}	4.29×10^{-13}	4.29×10^{-13}	4.29×10^{-13}
300	4.27×10^{-13}	4.27×10^{-13}	4.27×10^{-13}	4.27×10^{-13}	4.27×10^{-13}
310	4.16×10^{-13}	4.16×10^{-13}	4.16×10^{-13}	4.16×10^{-13}	4.16×10^{-13}
320	4.06×10^{-13}	4.06×10^{-13}	4.06×10^{-13}	4.06×10^{-13}	4.06×10^{-13}
350	3.80×10^{-13}	3.80×10^{-13}	3.80×10^{-13}	3.80×10^{-13}	3.80×10^{-13}
400	3.44×10^{-13}	3.44×10^{-13}	3.44×10^{-13}	3.44×10^{-13}	3.44×10^{-13}

Table S3: Bimolecular rate constant (in cm^3 $molecule^{-1}$ s^{-1}) for the association reaction along with the overall rate constant within the temperature range of 213-400 K

Temp (K)	$HOSO^{\bullet}+Cl^{\bullet}$		$HOSO^{\bullet}+OH^{\bullet}$	
	$k(T)_{association}$	$k(T)_{overall}$	$k(T)_{association}$	$k(T)_{overall}$
213	5.61×10^{-13}	5.61×10^{-13}	3.57×10^{-10}	3.57×10^{-10}
216	5.54×10^{-13}	5.54×10^{-13}	4.06×10^{-10}	4.06×10^{-10}
219	5.48×10^{-13}	5.48×10^{-13}	4.60×10^{-10}	4.60×10^{-10}
224	5.38×10^{-13}	5.38×10^{-13}	5.61×10^{-10}	5.61×10^{-10}
235	5.18×10^{-13}	5.18×10^{-13}	8.38×10^{-10}	8.38×10^{-10}
250	4.93×10^{-13}	4.93×10^{-13}	1.36×10^{-9}	1.36×10^{-9}
259	4.79×10^{-13}	4.79×10^{-13}	1.75×10^{-9}	1.75×10^{-9}
260	4.78×10^{-13}	4.78×10^{-13}	1.80×10^{-9}	1.80×10^{-9}
265	4.71×10^{-13}	4.71×10^{-13}	2.06×10^{-9}	2.06×10^{-9}
270	4.64×10^{-13}	4.64×10^{-13}	2.33×10^{-9}	2.33×10^{-9}
278	4.53×10^{-13}	4.53×10^{-13}	2.82×10^{-9}	2.82×10^{-9}
280	4.51×10^{-13}	4.51×10^{-13}	2.95×10^{-9}	2.95×10^{-9}
290	4.38×10^{-13}	4.38×10^{-13}	3.66×10^{-9}	3.66×10^{-9}
298	4.29×10^{-13}	4.29×10^{-13}	4.29×10^{-9}	4.29×10^{-9}
300	4.27×10^{-13}	4.27×10^{-13}	4.46×10^{-9}	4.46×10^{-9}
310	4.16×10^{-13}	4.16×10^{-13}	5.34×10^{-9}	5.34×10^{-9}
320	4.06×10^{-13}	4.06×10^{-13}	6.29×10^{-9}	6.29×10^{-9}
350	3.80×10^{-13}	3.80×10^{-13}	9.56×10^{-9}	9.56×10^{-9}
400	3.44×10^{-13}	3.44×10^{-13}	1.58×10^{-8}	1.58×10^{-8}

Table S4: Comparison of geometrical parameter of relevant molecules optimized at MP2/aug-cc-pV(+d)TZ level of theory and reaction energy obtained at CCSD(T)/aug-cc-pV(+d)TZ//MP2/aug-cc-pV(+d)TZ level of theory with the experimental and higher level of theory.

Molecule	Method	Bond length (Å)	Bond angle (deg)
HOSO$^{\bullet}$	MP2/aug-cc-pV(+d)TZ	S-0=1.45 O-H=0.97	H-O-S=107.9 O-S-O=105.9
	CCSD(T)/cc-pV(Q+d)Z [1]	S-0=1.46 O-H=0.96	H-O-S=107.9 O-S-O=105.4
HCl	MP2/aug-cc-pVT(+d)Z	H-Cl=1.28	-
	Experimental [2]	H-Cl=1.27	-
SO_2	MP2/aug-cc-pV(+d)TZ	S-O=1.45	O-S-O=119.7
	Experimental [2]	S-O=1.43	O-S-O=119.5
Reaction energy (298 K)	Experimental=$\sim$-65.6 kcal mol^{-1}	with SO=$\sim$-64.94 kcal mol^{-1}	without SO=$\sim$-66.1 kcal mol^{-1}

Table S5: Comparison of frequencies of relevant molecules optimized at MP2/aug-cc-pV(+d)TZ level of theory with the experimental value.

compound	frequencies (cm^{-1})	
	MP2/aug-cc-pV(+d)TZ	Experimental [2]
SO2	499	518
	1119	1151
	1339	1362
HCl	2886	3049

Table S6: Spin contamination value ($\langle S^2 \rangle$) for the relevant species obtained at MP2/aug-cc-pV(+d)TZ level of theory.

Species	HF Type	$\langle S^2 \rangle$	Ideal value
$HOSO^{\bullet}$	UHF	0.7836	0.7500
$Cl^{\bullet}$	UHF	0.7600	0.7500
RC	UHF	0.0000	0.0000
PC	UHF	0.0000	0.0000
TS	UHF	0.0000	0.0000
SO_2	UHF	0.0000	0.0000
HCl	UHF	0.0000	0.0000

Table S7: Comparison of L-J parameters for the species having similar size and composition.

Species	σ (Å)	ε/k_B (K)
CO	3.70	105
NO	3.49	117
C_2H_2	4.13	224
C_2H_4	4.23	217
C_3H_6	4.78	271
C_3H_8	4.94	275
Si_2H_3	4.49	318
Si_2H_2	4.36	323

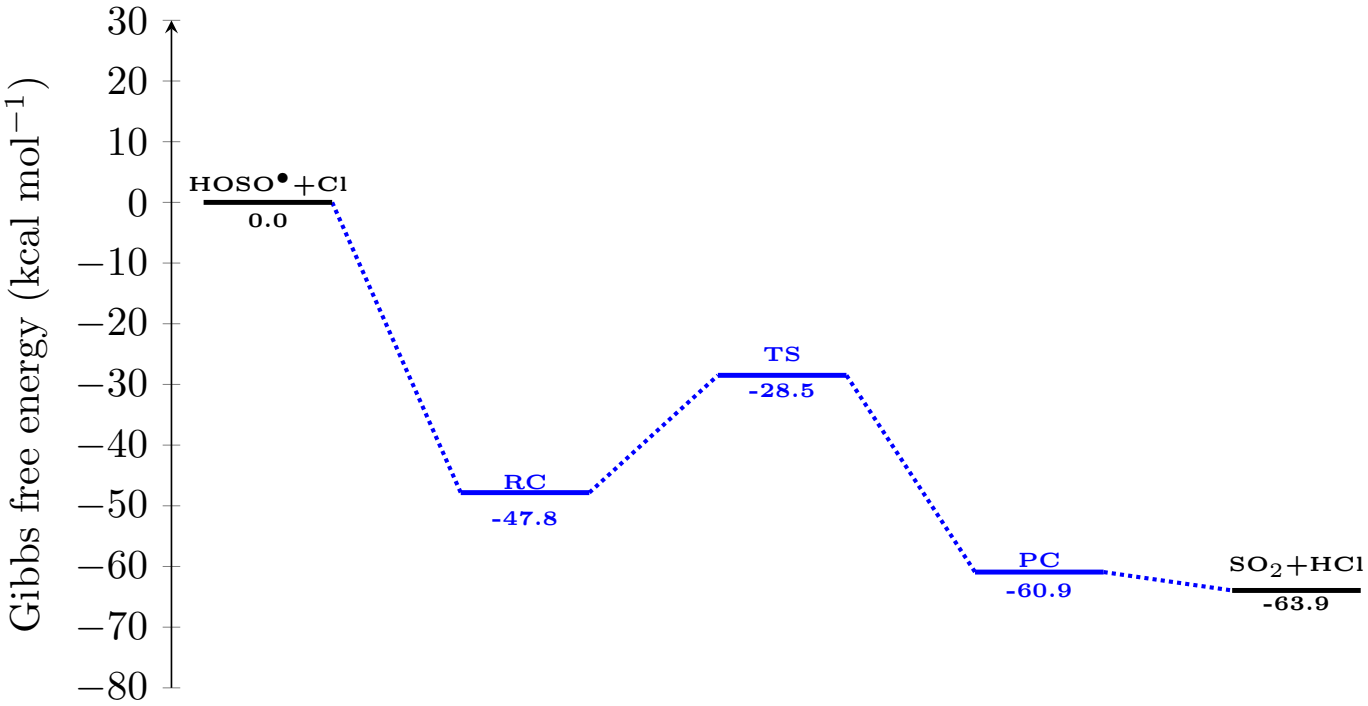

Figure S1: Gibbs free energy profile for the HOSO$^{\bullet}$ + Cl$^{\bullet}$ calculated at CCSD(T)/aug-cc-pV(+d)TZ//MP2/aug-cc-pV(+d)TZ level of theory.

References

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(2) Johnson III, R. D. *NIST 101. Computational chemistry comparison and benchmark database*; 1999.