Supporting information

Ab initio and DFT study of the molecular mechanisms of SO₃ and SOCl₂ reactions with water in the gas phase

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Cartesian coordinates of transition states and complexes optimized at the B3LYP/6-311++G(3df,3pd) level

Table S1. Transition state TS1a (Fig. 1a)

Atom	X	Y	Z
O1	0.539553	-0.460729	1.233942
S2	-0.282437	0.000021	0.057982
O3	1.390694	0.020439	-0.770423
H4	1.493562	-0.281226	0.420936
H5	1.644947	0.929518	-0.985722
O6	-1.047484	-0.998169	-0.596183
O7	-0.710202	1.357381	0.087297

Table S2. Transition state TS1b (Fig. 1b)

Atom	X	Y	Z
O1	-0.271173	-1.243578	-0.164933
S2	0.667124	-0.128493	0.044577
O3	-0.461453	1.200608	-0.428099
H4	-1.672207	0.709883	-0.195399
O5	-2.442718	-0.100548	-0.074935
H6	-1.695151	-0.833363	-0.056841
H7	-0.190278	1.987916	0.061270
H8	-2.868614	-0.061810	0.790537
O9	0.927065	0.204092	1.414817
O10	1.717312	-0.028916	-0.910950

Table S3. Transition state TS2a (Fig. 3a)

Atom	X	Y	Z
O1	-0.216234	1.478059	0.771117
S2	-0.202417	0.432966	-0.193704
Cl3	2.397384	-0.091193	-0.335613
Cl4	-2.268904	-0.277712	-0.317381
O5	0.222641	-1.175945	0.871001
H6	-0.227964	-1.947673	0.491776
H7	1.231220	-1.125309	0.571448

Table S4. Transition state TS2b (Fig. 3b)

Atom	X	Y	Z
O1	-0.448503	-0.681218	1.448505
S2	-0.502316	-0.545406	0.028096
Cl3	-2.635412	0.197345	-0.281720
Cl4	1.948390	-1.090219	-0.429068
H5	1.018105	1.535371	0.011023
H6	-0.774736	1.755476	-0.122410
O7	-0.009798	1.208284	-0.368040
H8	2.490370	0.723132	0.220250
H9	2.760050	2.222451	-0.215659
O10	2.236131	1.681548	0.387116

Table S5. Transition state TS3 (Fig. 3c)

Atom	X	Y	Z
O1	-1.823559	-0.709550	-0.427241
S2	-0.839221	-0.059654	0.383678
CL3	1.784314	-0.264088	-0.051003
O4	-0.384939	1.265920	-0.204765
H5	0.762177	0.992990	-0.215753

Table S6. Transition state TS5a (Fig. 3d)

Atom	X	Y	Z
O1	-0.284426	-1.263127	0.890288
S2	-0.107057	-0.368815	-0.363476
Cl3	-0.565490	1.589803	0.176356
Cl4	2.026340	-0.148815	-0.094069
O5	-2.098321	-0.876217	-0.391317
H6	-1.365343	-1.350817	0.688598
H7	-2.694228	-0.130201	-0.263643

Table S7. Transition state TS5b (Fig. 3e)

Atom	X	Y	Z
O1	0.397690	-1.161081	-0.455236
S2	-0.205161	-0.177014	0.524074
O3	1.601974	0.220858	1.211241
H4	2.613739	-0.203281	0.150931
O5	2.761924	-0.807473	-0.669086
H6	1.560357	-1.054588	-0.675708
H7	1.574760	1.067065	1.669407
H8	3.024708	-0.266288	-1.422118
Cl9	-0.256004	1.699638	-0.445917
Cl10	-2.307742	-0.683703	-0.071910

Table S8. Transition state TS7 (Fig. 3f)

Atom	X	Y	Z
O1	-0.358816	1.115116	0.687745
S2	0.503243	0.759924	-0.420364
Cl3	1.788521	-0.712887	0.120029
Cl4	-2.093307	-0.527096	-0.048037

Table S9. Transition state TS9 – Structure 1 (Fig. 4a)

Atom	X	Y	Z
O1	-0.126822	-1.260347	1.133150
S2	-0.126191	-0.450336	-0.041976
Cl3	-0.698495	1.512901	0.199620
Cl4	1.985041	0.004162	-0.272727
O5	-1.958131	-0.932326	-0.637383
H6	-2.595777	-0.212809	-0.728356
H7	-0.576830	-0.830509	-1.323354

Table S10. Transition state TS9 – Structure 2 (Fig. 4b)

Atom	X	Y	Z
O1	-0.000239	-1.642517	0.861829
S2	-0.000038	-0.239709	0.536177
Cl3	1.653446	-0.024706	-0.691782
Cl4	-1.653608	-0.024213	-0.691654
O5	0.000295	1.820559	0.760160
H6	0.002160	2.663245	0.286333
H7	0.000753	0.579389	1.677335

Table S11. Complex $\text{SOCl}_2\cdot\text{H}_2\text{O}$ – Structure 1 (Fig. 5a)

Atom	X	Y	Z
O1	-0.266883	-1.073081	1.140981
S2	0.015950	-0.426198	-0.112488
Cl3	-0.310529	1.657132	0.154093
Cl4	2.128999	-0.353019	-0.298248
O5	-2.832010	-0.724437	-0.566839
H6	-3.045690	-1.063244	0.308317
H7	-3.332367	0.092643	-0.651010

Table S12. Complex $\text{SOCl}_2 \cdot \text{H}_2\text{O}$ – Structure 2 (Fig. 5b)

Atom	X	Y	Z
O1	1.828597	-0.223864	1.011237
S2	0.448082	-0.046162	0.649466
Cl3	0.361005	1.586756	-0.705626
Cl4	-0.042935	-1.594830	-0.724811
O5	-2.663584	0.250839	0.684612
H6	-2.951767	1.083745	0.299910
H7	-2.944828	-0.423688	0.059255

Table S13. Complex $\text{SOCl}_2 \cdot 2\text{H}_2\text{O}$ – Structure 1 (Fig. 5c)

Atom	X	Y	Z
O1	-0.355519	-1.057856	-0.570814
S2	0.380718	-0.212645	0.340131
Cl3	0.601596	1.671318	-0.591501
Cl4	2.404531	-0.837927	0.184314
H5	-2.284814	1.575302	1.336097
H6	-2.685682	0.206995	0.746166
O7	-2.083369	0.636787	1.380343
H8	-2.424507	-1.120408	-0.939081
H9	-3.843161	-1.595837	-0.577509
O10	-3.305797	-0.807853	-0.695229

Table S14. Complex $\text{SOCl}_2 \cdot 2\text{H}_2\text{O}$ – Structure 2 (Fig. 5d)

Atom	X	Y	Z
O1	0.762933	1.253547	1.151253
S2	0.621876	0.506606	-0.066364
Cl3	-0.259500	-1.399360	0.449948
Cl4	2.554964	-0.242071	-0.536884
H5	-2.584924	1.000101	-0.389279
H6	-2.042973	2.232687	0.362327
O7	-1.881424	1.672847	-0.402374
H8	-4.024443	-0.939721	-1.052234
H9	-2.836260	-1.194578	-0.110214
O10	-3.567047	-0.588877	-0.282737

**Cartesian coordinates of transition states optimized
at the MP2/6-311++G(2df,2pd) level**

Table S15. Transition state TS1a (Fig. 1a)

Atom	X	Y	Z
O1	0.550657	-0.457891	1.236432
S2	-0.279260	0.001734	0.060865
O3	1.373228	0.004263	-0.791364
H4	1.479413	-0.292519	0.396929
H5	1.606081	0.931227	-0.954417
O6	-1.060546	-1.000172	-0.580518
O7	-0.690504	1.370494	0.083406

Table S16. Transition state TS1b (Fig. 1b)

Atom	X	Y	Z
O1	-0.237009	-1.215360	-0.425351
S2	0.646801	-0.134996	0.048351
O3	-0.423306	1.227993	-0.429215
H4	-1.613392	0.724199	-0.173104
O5	-2.382055	-0.084654	-0.074415
H6	-1.644988	-0.812412	-0.183260
H7	-0.144361	1.981028	0.109330
H8	-2.700024	-0.127614	0.835507
O9	0.680509	0.039808	1.477702
O10	1.831105	0.081554	-0.718982

Table S17. Transition state TS2a (Fig. 3a)

Atom	X	Y	Z
O1	-0.143877	1.449970	0.797810
S2	-0.156577	0.425907	-0.204272
Cl3	2.318282	-0.084763	-0.319886
Cl4	-2.234774	-0.226488	-0.299816
O5	0.172773	-1.243479	0.816036
H6	-0.312372	-1.957497	0.369219
H7	1.166809	-1.217680	0.523288

Table S18. Transition state TS2b (Fig. 3b)

Atom	X	Y	Z
O1	-0.367629	-0.589468	1.463522
S2	-0.470212	-0.568109	0.030618
Cl3	-2.585854	0.179189	-0.238196
Cl4	1.909656	-1.049135	-0.424223
H5	0.971357	1.509978	-0.043640
H6	-0.835850	1.633830	-0.321464
O7	-0.018611	1.137529	-0.517157
H8	2.389248	0.723212	0.274566
H9	2.667927	2.213528	-0.148504
O10	2.114499	1.676722	0.429922

**Cartesian coordinates of transition state TS2a optimized
at the MP2/6-311++G(3df,3pd) level**

Table S19. Transition state TS2a

Atom	X	Y	Z
O1	0.112326	-1.399753	0.859018
S2	0.126630	-0.429726	-0.190916
Cl3	-2.290476	0.057657	-0.325674
Cl4	2.230404	0.176770	-0.309373
O5	-0.144598	1.338887	0.773506
H6	0.366829	2.013322	0.296535
H7	-1.113494	1.363975	0.493722