Supplementary information for the manuscript "Nitrate radical addition-elimination reactions of atmospherically relevant sulfur – containing molecules" by Theo Kurtén, Joseph R. Lane, Solvejg Jørgensen and Henrik G. Kjaergaard

S1. Spin contamination and multireference effects

Reasonably large spin contamination values were observed in the unrestricted Hartree-Fock steps of the CBS-QB3 calculations. The $<S^2>$ values for the transition states containing the reduced sulfur species (H_2S, DMS and DMSO) were in the 0.99-1.05 range before annihilation, and 0.77-0.81 after. As each CBS-QB3 calculation contains three separate UHF steps, using three different basis sets, there are three values for each structure. For the $SO_2 - NO_3$ transition states, values were even higher; 1.18-1.21 before and 0.83-0.86 after annihilation. The various reactant and product complexes mostly had lower spin contamination, with $<S^2>$ values below 0.79 before and below 0.76 after annihilation. The exceptions to this were the H_2S-NO_3 reactant complex, with values in the range 0.90-0.95 before and around 0.76 after annihilation, and the non-reactive SO_2-NO_3 complex with values in the range 0.84-1.07 before and 0.76-0.81 after annihilation.

In the B3LYP calculations, spin contamination values were significantly lower; under 0.78 before and under 0.7503 after annihilation in the worst cases. The geometries are thus likely not much affected by spin contamination. B2-PLYP displayed somewhat larger but still fairly small spin contamination. $<S^2>$ values for the transition states were between 0.80-0.83 and 0.7508-0.7517 after annihilation, while those for the reactant and product complexes were around or under 0.77 before and 0.7501-0.7502 after annihilation.

The UCCSD(T)-F12 calculations were based on ROHF reference wavefunctions. The ROHF wavefunction has no spin contamination per definition. The spin contamination of the UCCSD(T) calculation was less than 0.04 for the transition states and less than 0.007 for the reactant and product complexes. Test calculations indicate that the difference between RCCSD(T)-F12 and UCCSD(T)-F12 energies of the transition states, both with ROHF references, is around 1 kcal/mol.

The T1 indicators computed in the CCSD(T)-F12 calculations for the transition states were between 0.02 and 0.03, indicating that these systems have a non-negligible, but probably not overwhelmingly large, multireference character. We attempted to assess the sign and magnitude of the multireference effects with CASSCF, CASPT2 and MRCI calculations. As it is not possible to carry out consistent multireference calculations for transition states and separated reactants, we focused on computing the energy differences between the reactant complexes and transition states. These could then be compared to the corresponding values given by the best single-reference methods in order to assess their reliability. Unfortunately, carrying out the multireference calculations proved to be complicated for the studied systems. Specifically, it was extremely challenging to define an active space that would be small enough for both static and dynamic correlation to be included, but large enough to describe well all the stationary points of the studied systems, or even just the lowest-energy reactant complex and highest-energy transition state. The problem was especially pronounced for the $SO_2 + NO_3$ system, where the rate-determining energy difference is that between the RCa and TS1 stationary points. As these have different symmetry, defining a common active space for them proved especially complicated, and it was not possible to select the correct orbitals via visual inspection of the orbital shapes and energies. We thus ended up forcing the RCa complex to have C_s symmetry in order to keep track of the orbitals. Another complicating issue was that for the augmented basis sets such as aug-cc-pV(D+d)Z or aug-cc-pV(T+d)Z, the lowest-energy UHF and, to a lesser extent, ROHF, virtual orbitals were unphysically diffuse, and did not correspond to any chemical bonding patterns. Therefore, we adopted the cc-pV(T+d)Z basis set for all multireference calculations, which led to more reasonably shaped orbitals and also decreased the computational effort, allowing for somewhat larger active spaces to be used. Test calculations indicate that differences between cc-pV(T+d)Z and aug-cc-pV(T+d)Z results are in any case fairly small, on the order of 1 kcal/mol in terms of the MR-CISD relative energies.

The multireference calculations were carried out as follows. First, a ROHF/cc-pV(T+d)Z calculation was done. This was followed by a CISD calculation, which yielded natural CISD orbitals and their (fractional) occupation numbers. The active space for the CASSCF or MR-CISD calculations was then constructed with use of the natural CISD orbitals, which were ordered by occupation number, and was centered around the singly occupied orbital. We then added either 3 or 7 occupied orbitals with increasing occupation numbers. The same number of virtual orbitals were choosen with decreasing occupation numbers. If the system had more than one symmetry group, the virtual orbitals were picked for each symmetry group to match the number of doubly occupied orbitals of that symmetry. For the SO_2-NO_3 system, the RCa reactant complex was forced to have C_s symmetry in order to keep track of the different orbitals and reduce the computational effort. This changed the ROHF/cc-pV(T+d)Z and CISD/cc-pV(T+d)Z energies by less than 0.1 kcal/mol. The H_2S-NO_3 system was not forced to have any symmetry as none of the stationary points was symmetric in the first place.

As CASPT2 and CIPT2 calculations almost invariably failed to converge for either the reactant complex or the transition state of at least one of the studied systems for any given number of electrons and orbitals, dynamic correlation could only be included with the computationally very costly MR-CISD method. This in turn severely limited the size of the active space that could be used. We thus performed two types of multireference calculations: CASSCF calculations with a large active space (and no dynamic correlation) and MR-CISD calculations with a small active space. With the computational resources available, the "large" and "small" active spaces turned out to correspond to 15 electrons/orbitals and 7 electrons/orbitals, respectively. The MR-CISD calculations correlated all valence electrons up to single and double excitations in each of the CASSCF configurations formed from the active space with 7 electrons in 7 orbitals. For the systems studied here this CAS included all occupied obitals with occupation numbers less than about 1.974 and virtual orbitals with occupation numbers larger than about 0.02. Even the 15 – electron active space was still somewhat smaller than ideal, since in the SO_2-NO_3 and H_2S-NO_3 systems there were no fewer than 19 electrons in orbitals with occupation numbers below 1.980, which is often quoted as a "rule-of-thumb" threshold for inclusion in the active space. For these two systems, all occupied orbitals with occupation numbers less than about 1.978 were included. For the DMS-NO_3 and DMSO-NO_3 systems, the 15 electron / 15 orbital CAS corresponded precisely to the active space obtained by including the singly occupied orbital and all doubly occupied orbitals with occupation numbers below 1.980. For all systems, the largest occupation number of a virtual orbital not included in the (15,15) CAS was below 0.015.

For DMS-NO_3 and DMSO-NO_3, the choice of active space for the CASSCF and MR-CISD calculations was unambiguous, as the orbitals of the reactant complexes and transition states had similar ordering with respect to the CI occupation numbers. For these systems, the (15,15) space consisted of 9 orbitals with A' and 7 orbitals with A'' symmetry, while the (7,7) space consisted of 5 orbitals with A' and 2 orbitals with A'' symmetry. For H_2S-NO_3, the lack of symmetry prevented any tracking of the orbitals in first place, so no additional problems arose with the active space selection. For SO_2-NO_3, the (7,7) space was also easy to select based on the CI occupation numbers; it contained 3 orbitals with A' and 4 orbitals with A'' symmetry. However, there was no unambiguous way to select a CAS space with precisely 15 orbitals. Based on the CI occupation numbers of the reactant complex RCa, the active space would contain 9 orbitals with A' and 7 orbitals with A'' symmetry. In contrast, using the CI occupation numbers of the transition state TS1 would lead to an active space containing 7 orbitals with A' and 8 orbitals with A'' symmetry. We thus performed the calculation with both the "9+6" and "7+8" – type active spaces. We also attempted to perform a 17-electron CASSCF calculation for the SO_2-NO_3 system (with 9 electrons in A' orbitals and 8 electrons in A'' orbitals), but this failed to converge. A 19-electron CASSCF, on the other hand, required more memory than we had available.

The energy differences between the transition states and the reactant complexes computed by various methods are given in Table S1. It can be seen that the MR-CISD values, at least after either the Davidson or Pople corrections for higher-order correlation, are qualitatively similar to the best (CBS-QB3 and CCSD(T)-F12) single-reference values. MR-CISD and CCSD(T)-F12 both predict that the TS – RC energy difference for the SO_2-NO_3 system is few kcal/mol larger than that of the DMSO-NO_3 system, while that of the DMS-NO_3 system is 8-10 kcal/mol larger, and that of the H_2S-NO_3 system over 10 kcal/mol larger. After the Davidson or Pople corrections, the MR-CISD(7,7) values agree very well with the CCSD(T)-F12 and CBS-QB3 values, especially for the DMS-NO_3 and DMSO-NO_3 systems.

Another interesting feature is that the overall effect of electron correlation (as demonstrated e.g. by the ROHF – CISD differences) on the reaction is very different for SO_2 and the other three species. Before electron correlation is accounted for, the potential energy surface of the SO_2-NO_3 reaction is relatively flat, with both reactant complexes and transition states lying slightly below the reactants in energy (see also Table S2 for ROHF-VDZ energies), and the RCa – TS1 difference is only a few kcal/mol. When dynamic correlation is included, the barrier height increases notably. For the reactions of H_2S, DMS and DMSO, the opposite occurs: including dynamic correlation lowers the relative energies of the transition states by roughly 10-20 kcal/mol. The large difference between CISD and CCSD(T)-F12 relative energies, as well as the large effect of the Davidson or Pople corrections on the relative MR-CISD energies, further indicate that higher-order (i.e. beyond second-order) dynamic correlation plays a major role in stabilizing the transition states for H_2S, DMS and DMSO.

The CASSCF(15,15) energy difference values for DMS-NO_3 and DMSO-NO_3 are in the same order as the other values, but their absolute magnitudes are much larger. This likely is due to the lack of dynamic correlation which stabilizes the transition states, as indicated by the ROHF – CISD energy differences discussed above. Specifically, the CASSCF calculation is unlikely to account for the stabilizing H···O interactions, which are primarily related to nonlocal dynamic correlation (dispersion), and likely involve CISD orbitals with non-fractional occupation numbers. For the H_2S-NO_3 system, the CASSCF energy difference is smaller than that of the methods including dynamic correlation, though within a few kcal/mol of the CCSD(T)-F12 or corrected MR-CISD values. The probable explanation is that unlike the DMS-NO_3 and DMSO-NO_3 systems, the 15-electron active space is sufficient to fully describe the H_2S – NO_3 bonding, and the CASSCF calculation thus captures also the relevant dynamic electron correlation.

For the SO_2-NO_3 system, the CASSCF value depends on the choice of active space. Unsurprisingly, the TS1-RCa energy difference is small for the "7+8" active space that describes the transition state better, and large for the "9+6" active space that describes the reactant complex better. The average of these two values (24.7 kcal/mol) is reasonably close, and slightly larger than, the value for DMSO-NO_3. This is in qualitative agreement with the MR-CISD(7,7) and single-reference results.

Table S1. Transition state – reactant complex energy differences (in kcal/mol) for the SO_2–NO_3, H_2S-NO_3, DMS-NO_3 and DMSO-NO_3 systems, using various methods. For SO_2-NO_3, the RCa-TS1 energy difference is given. In the multireference calculations the SO_2-NO_3 RCa complex has been forced to have C_s symmetry.

	SO_2-NO_3	H_2S-NO_3	DMS-NO_3	DMSO-NO_3
B2-PLYP	10.7	22.3	18.3	11.0
CBS-QB3	8.4[a]	23.0	15.5	7.0
CCSD(T)-F12/VDZ-F12	10.2	20.8	15.5	6.1
ROHF/cc-pV(T+d)Z	3.2	49.3	37.1	25.8
CISD/cc-pV(T+d)Z	9.8	36.9	27.8	17.1
CASSCF(15,15)/ cc-pV(T+d)Z	39.4[b] / 9.9[c]	16.7	34.0	21.8
MR-CISD(7,7)/ cc-pV(T+d)Z	12.3	30.4	19.9	9.3
MR-CISD(7,7)/ cc-pV(T+d)Z +Davidson correction, relaxed reference	8.5	22.9	16.6	7.2
MR-CISD(7,7)/ cc-pV(T+d)Z +Pople correction, relaxed reference	7.3	21.4	15.3	6.3

a)No reactant complex found for SO_2-NO_3 with CBS-QB3; this value is energy difference between TS and free reactants.

b) 9 orbitals with A' symmetry and 6 orbitals with A'' symmetry

c) 7 electrons with A' symmetry and 8 orbitals with A'' symmetry

S2. Energetic and Geometric data.

The absolute electronic energies are given in Table S2. Absolute enthalpies and Gibbs free energies are given in Table S3. Cartesian co-ordinates at the UB3LYP/aug-cc-pV(T+d)Z level, as reported by Gaussian 09, are given in Table S4. Note that for some of the structures, the strict symmetry specification of MolPro meant that a lower point group was identified compared to Gaussian. In these cases, the structures were reoptimized using z-matrix geometry specification to ensure the correct point group symmetry.

Table S2. Absolute energies (in hartree).

species	B3LYP[a]	B2-PLYP[b]	CBS-QB3	CCSD(T)-F12[c]	ROHF[d]
NO_3	-280.33634	-280.17377	-279.93139	-279.94065	-278.85939
H_2S	-399.43414	-399.28410	-398.94976	-398.95427	-398.71372
DMS	-478.08685	-477.85712	-477.45111	-477.45504	-476.80038
DMSO	-553.31588	-553.04548	-552.57775	-552.58916	-551.64967
SO_2	-548.72679	-548.50682	-548.04446	-548.06395	-547.28956
NO_2	-205.16047	-205.03842	-204.86128	-204.87085	-204.09539
H_2SO	-474.63461	-474.44208	-474.04537	-474.05723	-473.53300
$DMSO_2$	-628.58222	-628.27363	-627.74887	-627.76762	-626.54861
SO_3	-623.94994	-623.68909	-623.16734	-623.19410	-622.14403
H_2S-NO_3, RC	-679.77659	-679.45332	-678.88211	-678.89603	-677.60632
H_2S-NO_3, TS	-679.73773	-679.41760	-678.84555	-678.86290	-677.52865
H_2S-NO_3, PC	-679.79813	-679.48468	-678.91296	-678.93376	-677.63249
$DMS-NO_3$, RC	-758.44572	-758.04610	-757.40106	-757.41690	-755.70060
$DMS-NO_3$, TS	-758.41359	-758.01697	-757.37635	-757.39220	-755.64047
$DMS-NO_3$, PC	-758.47945	-758.08816	-757.44605	-757.46585	-755.74946
$DMSO-NO_3$, RC	-833.67005	-833.22830	-832.52235	-832.54207	-830.53817
$DMSO-NO_3$, TS	-833.64631	-833.21084	-832.51115	-832.53238	-830.49496
$DMSO-NO_3$, PC	-833.74511	-833.31583	-832.61664	-832.64377	-830.64751
SO_2-NO_3, RCa	-829.06366	-828.67545	Not found	-828.00735	-826.15840
SO_2-NO_3, RCb	-829.06444	-828.67076	-827.98961	-828.00822	-826.15290
SO_2-NO_3, TS1	-829.05120	-828.65841	-827.96251	-827.99099	-826.15227
SO_2-NO_3, RA	-829.06512	-828.67579	-827.98126	-828.00915	-826.15167
SO_2-NO_3, TS2	-829.06451	-828.67698	-827.97938	-828.01057	-826.15061
SO_2-NO_3, PC	-829.11303	-828.73145	Not found	-828.07024	-826.24221

a)B3LYP/aug-cc-pV(T+d)Z

b)B2-PLYP/aug-cc-pV(T+d)Z energies at the B3LYP/aug-cc-pV(T+d)Z geometries.

c)UCCSD(T)-F12a/VDZ-F12 energies with ROHF reference wavefunctions at the B3LYP/aug-cc-pV(T+d)Z geometries.

d)ROHF/VDZ-F12 energies at the B3LYP/aug-cc-pV(T+d)Z geometries.

Table S3. Absolute enthalpies and free energies (in hartree), at 298.15 K and 1 atm reference pressure.

species	H, B3LYP[a]	H, CBS-QB3	G, B3LYP[a]	G, CBS-QB3
NO$_3$	-280.32094	-279.91591	-280.35107	-279.94579
H$_2$S	-399.41530	-398.93111	-399.43864	-398.95446
DMS	-478.00571	-477.37061	-478.03796	-477.40291
DMSO	-553.23029	-552.49307	-553.26511	-552.52818
SO$_2$	-548.71578	-548.03363	-548.74396	-548.06184
NO$_2$	-205.14784	-204.84867	-205.17507	-204.87590
H$_2$SO	-474.60996	-474.02124	-474.63716	-474.04846
DMSO$_2$	-628.49019	-627.65780	-628.52590	-627.69381
SO$_3$	-623.93316	-623.15090	-623.96232	-623.18011
H$_2$S-NO$_3$, RC	-679.73803	-678.84384	-679.77815	-678.88414
H$_2$S-NO$_3$, TS	-679.70045	-678.80862	-679.74064	-678.84889
H$_2$S-NO$_3$, PC	-679.75884	-678.87411	-679.80289	-678.91702
DMS-NO$_3$, RC	-758.34472	-757.30065	-758.39110	-757.34683
DMS-NO$_3$, TS	-758.31455	-757.27800	-758.36092	-757.32393
DMS-NO$_3$, PC	-758.37917	-757.34660	-758.43105	-757.39634
DMSO-NO$_3$, RC	-833.56442	-832.41747	-833.61346	-832.46614
DMSO-NO$_3$, TS	-833.54200	-832.40765	-833.58887	-832.45455
DMSO-NO$_3$, PC	-833.63844	-832.51084	-833.69218	-832.56296
SO$_2$-NO$_3$, RCa	-829.03505	Not found	-829.08834	Not found
SO$_2$-NO$_3$, RCb	-829.03608	-827.96135	-829.08980	-828.01175
SO$_2$-NO$_3$, TS1	-829.02192	-827.93336	-829.06358	-827.97491
SO$_2$-NO$_3$, RA	-829.03422	-827.95071	-829.07567	-827.99217
SO$_2$-NO$_3$, TS2	-829.03477	-827.95003	-829.07592	-827.99162
SO$_2$-NO$_3$, PC	-829.08169	Not found	-829.12993	Not found

a)B3LYP/aug-cc-pV(T+d)Z

Table S4. Cartesian co-ordinates (in Ångström) at the UB3LYP/aug-cc-pV(T+d)Z level, from the Gaussian 09 program output.

NO$_3$ (D$_{3h}$)
N	0.000012	0.000000	1.000007
O	1.066649	0.000000	1.615830
O	-1.066664	0.000000	1.615842
O	0.000003	0.000000	-0.231679

H$_2$S (C$_{2v}$)
S	0.000000	0.000000	0.000000
H	0.000000	0.000000	1.341599
H	1.340284	0.000000	-0.059381

SO$_2$ (C$_{2v}$)
S	-0.080167	-0.187831	0.702772
O	-0.810361	-0.115003	-0.534037

```
O    0.251861    1.029528    1.392685
```

DMS (C_{2v})
```
S   -0.048907   -6.799689    2.826121
C    0.713892   -6.232591    4.364597
C    1.340136   -6.495752    1.708734
H   -0.001459   -6.343795    5.183775
H    1.599848   -6.830596    4.593414
H    0.991083   -5.178127    4.286131
H    1.599912   -5.433970    1.704123
H    2.208677   -7.086439    2.011405
H    1.057169   -6.788653    0.694198
```

DMSO (C_s)
```
S   -1.099503   -5.472811    1.704493
C   -0.484399   -6.513710    0.345145
C   -0.708916   -3.870162    0.937283
O   -2.584496   -5.599364    1.706419
H   -0.689378   -7.544657    0.624323
H   -1.019769   -6.261003   -0.568959
H    0.588744   -6.367921    0.227435
H    0.368770   -3.777865    0.807592
H   -1.066666   -3.102327    1.619378
H   -1.229278   -3.794159   -0.016401
```

NO_2 (C_{2v})
```
N    0.000000    0.000000    1.106907
O    1.098455    0.000000    1.567639
O   -1.098455    0.000000    1.567639
```

H_2SO (C_s)
```
S   -0.325228   -1.989100    0.002680
H    0.731542   -1.862178    0.882917
H    0.608134   -2.022643   -1.014870
O   -1.048853   -0.693086   -0.059849
```

SO_3 (D_{3h})
```
S    0.000000    0.000000    0.000000
O    0.000000    1.426808    0.000000
O   -1.235652   -0.713404    0.000000
O    1.235652   -0.713404    0.000000
```

$DMSO_2$ (C_{2v})
```
S   -0.034841   -0.060348    0.950740
O   -0.690553   -1.196071    1.556167
O    0.031914    0.055272   -0.487503
C    1.636353    0.013967    1.587034
C   -0.806079    1.424108    1.587032
H    2.131848    0.902945    1.205119
H    1.612659    0.003688    2.673768
H    2.132290   -0.880188    1.214862
H   -0.283946    2.297707    1.205116
H   -1.828408    1.406525    1.214858
H   -0.803135    1.398450    2.673765
```

H_2S-NO_3, RC (reactant complex, C_1)
```
S   -0.147402   -2.121095    0.135337
H    0.919892   -1.440255    0.590661
H    0.270247   -2.043456   -1.138490
N    0.137963    1.181850    0.063288
```

```
O   -0.194696    2.340397    -0.105655
O    1.224966    0.788036     0.449732
O   -0.813531    0.313022    -0.217516
```

H$_2$S-NO$_3$, TS (transition state, C$_1$)
```
S   -0.559026   -1.746894     0.011039
H    0.402530   -1.729350     0.955502
H    0.326873   -1.776176    -1.004293
N    0.060188    1.464834     0.012956
O   -0.592884    2.457146    -0.046918
O    1.244545    1.297128     0.070318
O   -0.882225    0.033313     0.001398
```

H$_2$S-NO$_3$, PC (product complex, C$_1$)
```
S   -0.247273   -1.982015     0.112429
H    0.987830   -1.574316     0.570319
H    0.356481   -2.273606    -1.093250
N    0.349708    1.646095     0.360789
O   -0.109194    2.452849    -0.379602
O    1.388133    1.054900     0.405603
O   -1.094810   -0.769984    -0.067084
```

SO$_2$-NO$_3$, RCa (reactant complex a, C$_s$)
```
S    0.500109    2.128627     0.025831
O    1.344481    2.096921     1.189741
O    1.047476    1.733755    -1.244614
O   -1.164914   -0.875816     0.206893
N   -0.885776   -2.042490     0.011339
O    0.260567   -2.485816     0.186326
O   -1.727588   -2.868324    -0.375516
```

SO$_2$-NO$_3$, RCb (reactant complex b, C$_1$)
```
S   -2.073447    0.328588     0.000038
O   -3.350755   -0.330249    -0.000137
O   -0.877426   -0.472173     0.000317
O    1.901508    1.243246    -0.001636
N    2.158126    0.042680    -0.000075
O    2.292646   -0.569055    -1.062146
O    2.292561   -0.566290     1.063593
```

SO$_2$-NO$_3$, TS1 (transition state 1, C$_s$)
```
S    0.314026    1.608006     0.000000
O    1.012682    1.598458     1.253747
O    1.012682    1.598458    -1.253747
O   -1.090262   -0.029552     0.000000
N   -0.529595   -1.266371     0.000000
O    0.665044   -1.383618     0.000000
O   -1.384577   -2.125380     0.000000
```

SO$_2$-NO$_3$, RA (reaction intermediate adduct, C$_s$)
```
S   -1.467189   -0.218453     0.000000
O   -1.633394    0.476288    -1.295801
O   -1.633394    0.476288     1.295801
O    0.071872   -0.984893     0.000000
N    1.291700   -0.089501     0.000000
O    1.085359    1.090933     0.000000
O    2.285046   -0.750663     0.000000
```

SO$_2$-NO$_3$, TS2 (transition state 2, C$_s$)
```
S   -1.459592   -0.229070     0.000000
```

```
O   -1.730058   0.434618   1.259007
O   -1.730058   0.434618   -1.259007
O   -0.065654   -0.947922   0.000000
N   1.421020    -0.030775   0.000000
O   2.307011    -0.791293   0.000000
O   1.257331    1.129823   0.000000
```

SO$_2$-NO$_3$, PC (product complex, C$_1$)
```
S   -1.343520   -0.155374   -0.066911
O   -1.165696   -0.178053   -1.482569
O   -1.824100   1.024220    0.574021
O   -1.081170   -1.329473   0.700713
N   2.258181    -0.011667   0.003619
O   1.348689    0.708470    0.298650
O   3.438219    0.087395    0.053654
```

DMS-NO$_3$, RC (reactant complex, C$_s$)
```
S   -1.391699   -0.254401   0.000000
C   -0.744706   0.689119    -1.389881
C   -0.744706   0.689119    1.389881
H   -1.051149   0.175614    -2.297597
H   -1.162752   1.694798    -1.375489
H   0.340661    0.721230    -1.317336
H   0.340661    0.721230    1.317336
H   -1.051149   0.175614    2.297597
H   -1.162752   1.694798    1.375489
N   1.696877    -1.559909   0.000000
O   1.958554    -0.355546   0.000000
O   0.445698    -1.939400   0.000000
O   2.525980    -2.451569   0.000000
```

DMS-NO$_3$, TS (transition state, C$_s$)
```
S   0.018501    1.322760    0.000000
C   -0.825564   0.544410    -1.387641
C   -0.825564   0.544410    1.387641
O   1.535398    0.262032    0.000000
N   1.911262    -1.363377   0.000000
O   0.973360    -2.119913   0.000000
O   3.081046    -1.594631   0.000000
H   -0.352890   0.914558    2.293853
H   -0.703176   -0.533986   1.313310
H   -1.878015   0.821523    1.378240
H   -0.703176   -0.533986   -1.313310
H   -0.352890   0.914558    -2.293853
H   -1.878015   0.821523    -1.378240
```

DMS-NO$_3$, PC (product complex, C$_1$)
```
C   1.650411    1.164300    -0.927901
S   1.577080    -0.509467   -0.222132
O   0.214367    -1.045265   -0.517706
N   -2.311893   0.235330    -0.221854
O   -3.009386   -0.715363   -0.083126
C   1.578859    -0.01040    1.526034
O   -1.974349   1.128957    0.496099
H   1.486297    -0.922851   2.110563
H   0.729764    0.644194    1.714272
H   2.519582    0.485952    1.761165
H   0.797415    1.741739    -0.575995
H   1.605586    1.048791    -2.008432
H   2.590648    1.636302    -0.645416
```

DMSO-NO$_3$, RC (reactant complex, C$_s$)

S	-0.201730	1.160158	0.000000
C	-0.863811	0.257999	-1.406999
C	-0.863811	0.257999	1.406999
O	-0.752067	2.535417	0.000000
O	2.051832	0.052707	0.000000
N	2.128958	-1.249560	0.000000
O	1.083641	-1.898189	0.000000
O	3.246896	-1.729186	0.000000
H	-0.502909	0.790285	2.298667
H	-0.451886	-0.758897	1.326467
H	-1.951064	0.274094	1.348660
H	-0.451886	-0.758897	-1.326467
H	-0.502909	0.790285	-2.298667
H	-1.951064	0.274094	-1.348660

DMSO-NO$_3$, TS (transition state, C$_s$)

S	0.165561	-1.182415	0.000000
C	-0.921841	-0.965518	1.412496
C	-0.921841	-0.965518	-1.412496
O	0.575454	-2.609444	0.000000
O	0.869938	0.486194	0.000000
N	0.278567	1.984720	0.000000
O	-0.921841	2.075309	0.000000
O	1.118667	2.825349	0.000000
H	-0.291167	-1.014072	-2.296716
H	-1.414267	-0.000456	-1.342579
H	-1.631864	-1.789199	-1.411497
H	-1.414267	-0.000456	1.342579
H	-0.291167	-1.014072	2.296716
H	-1.631864	-1.789199	1.411497

DMSO-NO$_3$, PC (product complex, C$_1$)

C	-0.579668	-1.122008	0.983909
S	0.132799	0.487820	0.667148
O	1.439693	0.525296	1.286899
N	2.077564	-0.177844	4.139299
O	2.928759	0.617407	4.366109
C	-0.930556	1.612876	1.563279
O	-0.001146	0.768984	-0.742790
O	0.909517	-0.241912	4.382683
H	-0.515616	2.605234	1.398745
H	-0.907458	1.365840	2.621713
H	-1.938493	1.556893	1.160025
H	-0.553116	-1.325242	2.051511
H	0.047116	-1.832404	0.448640
H	-1.594070	-1.150697	0.594202

S3. AIM parameters.

Table S5. AIM parameters computed for the CH⋯ON bond critical points in the two transition states where such points were found, at the B3LYP/aug-cc-pV(T+d)Z level. All values in atomic units. ρ is the electronic density and $\nabla_2(\rho)$ its Laplacian at the bond critical point.

Species	ρ	$\nabla_2(\rho)$	Energy density	Total path length
DMS + NO$_3$, TS	0.00646	0.0229	0.00111	5.07
DMSO + NO$_3$, TS	0.00857	0.0313	0.00149	4.83