Supplementary Information

for the paper entitled "A study of the thermodynamics and mechanisms of the atmospherically relevant reaction dimethyl sulphide (DMS) + atomic chlorine (Cl) in the absence and presence of water, using electronic structure methods".

by
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Contents
(with page no. indicated in Column 3)

	obtained in this work.	
	Summary of previous computation work on the DMS + Cl reaction (25,27-30)	22
	Cartesian coordinates for all stationary points for the DMS + Cl using the UM06-2X/aVDZ and UM06-2X/aVTZ methods, with total energies and nuclear repulsion energies	23
	Cartesian coordinates for all stationary points for the DMS + Cl +H_2O using the UM06-2X/aVDZ and UM06-2X/aVTZ methods, with total energies and nuclear repulsion energies	27
	More detail on comparison of Figure 1 with Figures 4 and 5 (for Channel A) and Figure 1 with Figures 6 and 7 (for Channel B)	33

Table S1: Enthalpy of the Cl + DMS →DMS•Cl reaction (values in kcal.mol^{-1}).

(this can also be written Cl● + DMS →DMS•Cl)

Ref.	ΔH^{ϕ}(298K)	Method	Comments
1. Stickel et al. (1992), ref [21]	-14 ±3	Adduct bond strength estimated from unpublished studies on $CH_3S(X)CH_3$ where X= Br and OH, where the bond strength was "found to be" 14.0 kcal.mol^{-1}	Probably not reliable as the estimated value comes from unpublished material and is not on $CH_3S(X)CH_3$, X=Cl
2. M. L. McKee (1993), ref [30]	–12.2	PMP2/6-31G(d)//3-21G(d)	The lower level basis set , 3-21G*, is too small
3. Wilson and Hirst (1997), ref [28]	-19.4	MP2(full)/6-311G(d,p)	Reasonably good
4. K.C.Thompson et al. (2002), ref [29]	-23.2	B3LYP/6-311++G(2df,p)//B3LYP/6-311++G(d,p)	Reasonably good
5. Resende and Almeida (1997), ref [27]	-12.7	UQCISD(T)/DZP//UMP2/DZP	DZP basis set is too small
6. S. Enami et al. (2004), ref [25]	-17.7	QCISD(T)/6-311++G(3df,3dp)//B3LYP/6-311++G(3df,3pd)	Reasonably good

Conclusion

ΔH^{ϕ}(298K) is much closer to -23.0 kcal.mol^{-1} than -14.0 kcal.mol^{-1}, as indicated by the calculations of this work (see Table S3).

Table S2: Computed geometrical parameters of Cl-S$(CH_3)_2$ from refs [21, 25, 27, 28-30].

Ref (method used)	S-Cl/Å	∠C-S-Cl/º	C-S/º	∠C-S-C/º
[21]	no	parameters	given	
[30] (HF 3-21G(d))	2.760	94.5	1.807	100.2
[28] (MP2/6-311G(d,p))	2.590	91.7	1.790	99.8
[29] B3LYP/6-311++G(d,p)	2.680	93.7	1.820	100.7
[27] UMP2/DZP	2.587	91.9	1.807	99.6
[25] B3LYP/6-311++G(3df,3p)	2.620	93.5	1.800	101.1
[25] MP2/6-311++G(2df,2p)	2.500	91.8	1.790	99.5

Table S3: Relative electronic energies (including ZPE), thermodynamic parameters computed at different levels and heat of reactions (298 K) computed in this work for the four channels of the DMS + Cl reaction. The values within brackets are those reported by Resende and De Almeida (ref [27]).

	Methods	ΔE/kcal/mol	ΔH/kcal/mol	ΔG/kcal/mol	ΔS/cal/K .mol	$\Delta H_{f,298\ K}$ /kcal/mol
DMS + Cl → Adduct 1	PUMP2/DZP[a]	-13.61 -12.62	-13.01	-5.96	-23.65	-14 ± 3[a] (ref [27])
	UQCISD(T)//UMP2/DZP[b]	-11.00 (-12.32)	-11.39 (-12.72)	-4.34 (-5.63)	-23.65 (-23.78)	
	PUMP2/aVDZ[a]	-21.79 -20.83	-21.24	-14.12	-23.88	
	UQCISD(T)//UMP2/aVDZ[b]	-18.04	-18.45	-11.32	-23.91	
	UB3LYP/aVTZ	-22.50	-22.78	-16.07	-22.51	
	PUMP2/cc-pVTZ//UB3LYP/aVTZ[c]	-18.81	-19.08	-12.38	-22.47	
	UM06-2X/6-31++G(d,p)	-21.28	-21.57	-14.84	-22.57	
	UM06-2X/cc-pVDZ	-21.59	-21.87	-15.14	-22.57	
	UQCISD(T)//UM06-2X/cc-pVDZ[b]	-12.01	-12.29	-5.56	-22.57	
	UM06-2X/aVDZ	-23.29	-23.59	-16.84	-22.64	
	UCCSD(T)/CBS//UM06-2X/aVDZ[d]	-20.78	-21.06	-	-	
DMS + Cl ⟶ CH_3SCH_2 + HCl	PUMP2/DZP	0.84 -3.76	-3.05	-5.92	9.63	-9.38 ± 1.49
	UQCISD(T)//UMP2/DZP	-3.74 (-3.19)	-3.04 (-2.50)	-5.90 (-5.33)	9.59 (9.49)	
	PUMP2/aVDZ	-2.76 -7.18	-6.46	-9.36	9.73	
	UQCISD(T)//UMP2/aVDZ	-6.73	-6.02	-8.91	9.69	
	UB3LYP/aVTZ	-10.82	-9.98	-13.28	11.07	
	PUMP2/cc-pVTZ//UB3LYP/aVTZ	-8.71	-7.87	-11.17	11.07	
	UM06-2X/6-31++G(d,p)	-5.11	-4.38	-7.29	9.76	
	UM06-2X/cc-pVDZ	-5.83	-5.15	-7.96	9.42	
	UQCISD(T)//UM06-2X/cc-pVDZ	-4.28	-3.60	-6.41	9.42	
	UM06-2X/aVDZ	-7.79	-7.05	-9.98	9.83	
	UCCSD(T)/CBS//UM06-2X/aVDZ[d]	-10.53	-9.79	-	-	

DMS + Cl → CH_3S + CH_3Cl	PUMP2/DZP	-6.35 -7.66	-7.74	-10.66	9.79	-10.2 ± 0.76
	UQCISD(T)//UMP2/DZP	-7.38 (-8.46)	-7.46 (-8.55)	-10.39 (-12.13)	9.83 (12.01)	
	PUMP2/aVDZ	-8.36 -9.59	-9.67	-12.62	9.89	
	UQCISD(T)//UMP2/ aVDZ	-9.33	-9.41	-12.36	9.89	
	UB3LYP/aVTZ	-13.26	-13.32	-16.28	9.93	
	PUMP2/cc-pVTZ//UB3LYP/aVTZ	-8.95	-9.02	-11.98	9.93	
	UM06-2X/6-31++G(d,p)	-10.02	-10.16	-13.04	9.66	
	UM06-2X/cc-pVDZ	-9.68	-9.81	-12.75	9.86	
	UQCISD(T)//UM06-2X/cc-pVDZ	-7.62	-7.74	-10.68	9.86	
	UM06-2X/aVDZ	-10.30	-10.44	-13.36	9.79	
DMS + Cl → CH_3SCl + CH_3	PUMP2/DZP	21.15 16.87	17.56	14.33	10.83	8.05 ± 1.66
	UQCISD(T)//UMP2/DZP	16.28 (12.45)	20.95 (13.12)	14.28 (9.23)	22.37 (13.05)	
	PUMP2/aVDZ	15.95 11.98	12.65	9.40	10.90	
	UQCISD(T)//UMP2/aVDZ	12.03	12.70	9.45	10.90	
	UB3LYP/aVTZ	4.81	5.47	2.23	10.87	
	PUMP2/cc-pVTZ//UB3LYP/aVTZ	8.48	9.14	5.90	10.87	
	UM06-2X/6-31++G(d,p)	11.08	11.81	8.42	11.37	
	UM06-2X/cc-pVDZ	9.93	10.74	7.15	12.04	
	UQCISD(T)//UM06-2X/cc-pVDZ	13.58	14.39	10.80	12.04	
	UM06-2X/aVDZ	8.37	9.12	5.64	11.67	

[a]Based on the PUMP2/DZP method, the thermal corrections for the thermodynamic parameters obtained using the UMP2/DZP method were added to the projected UMP2 energy. Same applies for PUMP2/aVDZ method. Note also that ZPE is not included in the projected energy for those highlighted in blue.

[b]Based on the UQCISD(T)//UMP2/DZP and UQCISD(T)//UMP2/aVDZ methods, ZPE obtained at the UMP2/DZP and UMP2/aVDZ methods were added to the UQCISD(T) energy, respectively. Same applies for the UQCISD(T)//UM06-2X/cc-pVDZ method.

[c]Based on the PUMP2/cc-pVTZ//UB3LYP/aVTZ method, the ZPE and thermal corrections obtained using the UB3LYP/aVTZ method were added to the projected UMP2 energies.

[d]The energetic parameters at the UCCSD(T)/aVnZ//UM06-2X/aVDZ (n = D, T and Q) methods were extrapolated to the complete basis set (CBS) limit using the two- and three- parameter formulae. As recommended by Feller's group, the best CBS estimate was taken as the average of these two limits and the spread as an estimate in the uncertainty of the extrapolation procedure. The thermal correction to the enthalpy obtained using the UM06-2X/aVDZ method were added to the UCCSD(T) single point energy.

Table S4: DMS + Cl: Relative electronic energies (ΔE, kcal.mol^{-1}), relative enthalpies (in bracket, $\Delta H^{\phi}_{f,298K}$, kcal.mol^{-1})[a] and relative free energies (in italic, $\Delta G^{\phi}_{f,298K}$, kcal.mol^{-1}) for the three possible channels.

	UM06-2X/aVTZ	UCCSD(T)/aVnZ//UM06-2X/aVTZ (n = T and Q)			DLPNO-UCCSD(T)/aVnZ//UM06-2X/aVTZ (n = T and Q)		
		n = T	n = Q	CBS	n = T	n = Q	CBS
Channel A							
RC1[b]	-10.6 (-10.9) *-4.5*	-6.9 (-7.2) *-0.7*	-7.6 (-8.0) *-1.5*	-8.2 (-8.5) *-2.1*	-6.1 (-6.4) *0.0*	-6.9 (-7.2) *-0.7*	-7.4 (-7.7) *-1.3*
TS1	-11.5 (-12.0) *-5.2*	-8.2 (-8.7) *-1.8*	-9.0 (-9.6) *-2.7*	-9.7 (-10.2) *-3.3*	-7.5 (-8.0) *-1.1*	-8.3 (-8.8) *-2.0*	-8.9 (-9.4) *-2.6*
MS1	-12.9 (-12.7) *-7.6*	-12.4 (-12.2) *-7.1*	-13.5 (-13.3) *-8.2*	-14.4 (-14.1) *-9.1*	-11.8 (-11.6) *-6.5*	-12.9 (-12.7) *-7.7*	-13.7 (-13.5) *-8.5*
CH_3SCH_2 + HCl	-9.1 (-8.2) *-11.5*	-8.5 (-7.7) *-10.9*	-10.0 (-9.2) *-12.4*	-11.1 (-10.2) *-13.5*	-8.1 (-7.3) *-10.5*	-9.7 (-8.8) *-12.1*	-10.8 (-10.0) *-13.2*
Channel B							
RC2	-0.5 (-0.4) *4.2*	-1.0 (-0.8) *3.9*	-0.8 (-0.7) *3.9*	-0.8 (-0.7) *4.0*	-0.7 (-0.6) *4.0*	-0.6 (-0.5) *4.1*	-0.6 (-0.5) *4.2*
TS2	15.5 (15.4) *20.8*	17.7 (17.6) *22.9*	17.9 (17.8) *23.1*	18.0 (17.9) *23.3*	18.0 (17.9) *23.3*	18.2 (18.1) *23.5*	18.3 (18.2) *23.6*
MS2	-11.7 (-11.4) *-7.8*	-10.2 (-9.9) *-6.4*	-10.4 (-10.0) *-6.5*	-10.5 (-10.1) *-6.6*	-9.9 (-9.6) *-6.0*	-10.1 (-9.7) *-6.2*	-10.2 (-9.8) *-6.3*
CH_3S + CH_3Cl	-11.1 (-11.2) *-14.2*	-9.5 (-9.7) *-12.6*	-9.9 (-10.0) *-12.9*	-10.1 (-10.2) *-13.2*	-9.3 (-9.5) *-12.4*	-9.7 (-9.8) *-12.8*	-10.0 (-10.1) *-13.1*
Channel C, C′							
Adduct 1	-22.7 (-23.1) *-16.2*	-19.0 (-19.3) *-12.5*	-20.1 (-20.4) *-13.6*	-20.9 (-21.2) *-14.4*	-18.4 (-18.7) *-11.9*	-19.5 (-19.8) *-13.1*	-20.3 (-20.7) *-13.8*
TS3	7.2 (7.1) *13.4*	10.0 (9.9) *16.2*	8.8 (8.8) *15.0*	8.0 (7.9) *14.2*	10.7 (10.6) *16.9*	9.6 (9.5) *15.8*	8.8 (8.7) *15.0*
MS3	4.3 (5.1) *8.9*	7.9 (8.7) *12.5*	6.5 (7.4) *11.1*	5.5 (6.3) *10.1*	8.4 (9.3) *13.0*	7.0 (7.9) *11.6*	6.0 (6.9) *10.6*
CH_3SCl + CH_3	5.6 (6.4)	8.1 (8.9)	6.5 (7.3)	5.4 (6.2)	8.3 (9.1)	6.7 (7.5)	5.6 (6.3)

	2.8	*5.3*	*3.7*	*2.6*	*5.5*	*3.9*	*2.8*

[a]The thermal correction to the enthalpy obtained using the UM06-2X/aVTZ method were added to the UCCSD(T) single point energy (ZPE is included in the electronic energies).
[b]The structure of RC1 was obtained from its respective IRC and the energetic parameters were obtained by single point calculations.

Table S5: DMS + Cl + H_2O:Relative electronic energies (ΔE, kcal.mol^{-1}), relative enthalpies (in bracket, $\Delta H^{\phi}_{f,298K}$, kcal.mol^{-1})[a] and relative free energies (in italic, $\Delta G^{\phi}_{f,298K}$, kcal.mol^{-1}) for the channel A.

	UM06-2X/aVTZ	UCCSD(T)/aVnZ//UM06-2X/aVTZ (n = T and Q)		UCCSD(T)/CBS//UM06-2X/aVTZ	DLPNO-UCCSD(T)/aVnZ//UM06-2X/aVTZ (n = T and Q)		DLPNO-UCCSD(T)/CBS//UM06-2X/aVTZ
		n = T	n = Q		n = T	n = Q	
Pathway (a)							
DMS•H_2O + Cl	-4.4 (-4.5) *2.5*	-4.2 (-4.3) *2.7*	-3.9 (-4.0) *3.0*	-3.8 (-3.9) *3.1*	-4.0 (-4.1) *2.9*	-3.8 (-3.9) *3.1*	-3.7 (-3.8) *3.2*
DMS•H_2O + Cl → DMS•H_2O•Cl-1	-26.0 (-26.2) *-11.8*	-21.9 (-22.1) *-7.7*	-22.8 (-23.0) *-8.7*	-23.5 (-23.7) *-9.3*	-21.0 (-21.3) *-6.9*	-22.0 (-22.3) *-7.9*	-22.8 (-23.0) *-8.6*
TS1•H_2O-A	-7.7 (-8.2) *6.3*	-4.0 (-4.5) *10.0*	[b] – 	[b] – 	-2.8 (-3.3) *11.2*	-2.7 (-3.2) *11.4*	-2.6 (-3.1) *11.4*
TS1•H_2O-B	-14.1 (-14.7) *0.0*	-10.8 (-11.4) *3.3*	-11.5 (-12.0) *2.7*	-12.0 (-12.5) *2.2*	-9.9 (-10.5) *4.2*	-10.6 (-11.2) *3.5*	-11.1 (-11.7) *3.0*
MS1•H_2O-1	-15.8 (-15.4) *-3.6*	-15.0 (-14.6) *-2.8*	-16.0 (-15.5) *-3.7*	-16.6 (-16.2) *-4.4*	-14.3 (-13.8) *-2.0*	-15.2 (-14.7) *-2.9*	-15.8 (-15.4) *-3.6*
Pathway (c)							
DMS•Cl + H_2O	-22.7 (-23.1) *-16.2*	-19.0 (-19.3) *-12.5*	-20.1 (-20.4) *-13.6*	-20.9 (-21.2) *-14.4*	-18.4 (-18.7) *-11.9*	-19.5 (-19.8) *-13.0*	-20.3 (-20.7) *-13.8*
DMS•Cl + H_2O → DMS•H_2O•Cl-2	-29.9 (-30.5) *-15.1*	-25.9 (-26.5) *-11.1*	-26.7 (-27.3) *-11.9*	-27.3 (-27.9) *-12.5*	-25.1 (-25.7) *-10.3*	-25.9 (-26.5) *-11.1*	-26.5 (-27.1) *-11.7*
TS1•H_2O-C	-4.7 (-6.4) *11.2*	0.7 (-1.0) *16.5*	-0.3 (-2.0) *15.6*	-1.1 (-2.7) *14.8*	2.0 (0.4) *17.9*	1.0 (-0.7) *16.9*	0.3 (-1.4) *16.1*
MS1•H_2O-2	-18.1 (-18.3) *-4.1*	-17.0 (-17.2) *-3.0*	-18.0 (-18.2) *-4.0*	-18.7 (-18.9) *-4.7*	-14.3 (-13.8) *-2.2*	-15.2 (-14.7) *-3.2*	-17.9 (-18.1) *-3.9*
CH_3SCH_2•H_2O + HCl	-12.4 (-11.9) *-7.1*	-11.6 (-11.1) *-6.3*	-12.7 (-12.2) *-7.4*	-13.5 (-13.0) *-8.2*	-11.0 (-10.5) *-5.7*	-12.1 (-11.6) *-6.8*	-12.9 (-12.4) *-7.6*
CH_3SCH_2 + HCl•H_2O	-13.0 (-12.7) *-9.7*	-12.5 (-12.2) *-9.2*	-13.9 (-13.7) *-10.7*	-15.0 (-14.7) *-11.7*	-12.0 (-11.7) *-8.7*	-13.5 (-13.3) *-10.3*	-14.6 (-14.4) *-11.4*
CH_3SCH_2	-9.1	-8.5	-10.0	-11.1	-8.4	-9.7	-10.8

+ HCl + H_2O	(-8.2) *-11.5*	(-7.7) *-10.9*	(-9.2) *-12.4*	(-10.2) *-13.5*	(-7.3) *-10.5*	(-8.8) *-12.1*	(-10.0) *-13.2*

[a]The thermal correction to the enthalpy obtained using the UM06-2X/aVTZ method was added to the UCCSD(T) single point energy (ZPE is included in the electronic energies).

[b] Reliable value could not be obtained; calculations were very lengthy involving several re-starts, thus extrapolation to the CBS limit could not be performed. However, a reliable DLPNO-UCCSD(T)/CBS//UM06-2X/aVTZ value was obtained.

Table S6: DMS + Cl + H_2O: Relative electronic energies (ΔE, kcal.mol^{-1}), relative enthalpies (in bracket, $\Delta H^{\phi}_{f,298K}$, kcal.mol^{-1})[a] and relative free energies (in italic, $\Delta G^{\phi}_{f,298K}$, kcal.mol^{-1}) for channel B.

	UM06-2X/aVTZ	UCCSD(T)/aVnZ //UM06-2X/aVTZ (n = T and Q)		UCCSD(T) /CBS//UM 06-2X/aVTZ	DLPNO-UCCSD(T)/aVnZ/ /UM06-2X/aVTZ (n = T and Q)		DLPNO-UCCSD(T)/ CBS//UM06 -2X/aVTZ
		n = T	n = Q		n = T	n = Q	
Pathway (a)							
DMS•H_2O + Cl	-4.4 (-4.5) *2.5*	-4.2 (-4.3) *2.7*	-3.9 (-4.0) *3.0*	-3.8 (-3.9) *3.1*	-4.0 (-4.1) *2.9*	-3.8 (-3.9) *3.1*	-3.7 (-3.8) *3.2*
DMS•H_2O + Cl → DMS•H_2O•Cl-3	-15.5 (-16.1) *-1.6*	-11.1 (-11.7) *2.8*	-11.6 (-12.2) *3.0*	-12.1 (-12.6) *1.9*	-9.9 (-10.4) *4.1*	-10.4 (-11.0) *3.5*	-10.8 (-11.4) *3.1*
TS2•H_2O-A	9.8 (9.3) *23.8*	12.2 (11.7) *26.2*	12.6 (12.1) *26.6*	12.9 (12.4) *26.9*	13.0 (12.5) *27.0*	13.4 (12.9) *27.4*	13.6 (13.2) *27.7*
MS2•H_2O-1	-18.4 (-18.3) *-5.4*	-15.2 (-15.1) *-2.2*	-15.0 (-14.9) *-2.0*	-14.8 (-14.8) *-1.9*	-14.2 (-14.1) *-1.2*	-14.1 (-14.0) *-1.1*	-14.0 (-14.0) *-1.1*
Pathway (c)							
DMS•Cl + H_2O	-22.7 (-23.1) *-16.2*	-19.0 (-19.3) *-12.5*	-20.1 (-20.4) *-13.6*	-20.9 (-21.2) *-14.4*	-18.4 (-18.7) *-11.9*	-19.5 (-19.8) *-13.0*	-20.3 (-20.7) *-13.8*
DMS•Cl + H_2O → DMS•Cl •H_2O-4	-29.5 (-30.0) *-14.9*	-25.4 (-25.9) *-10.7*	-26.2 (-26.8) *-11.6*	-26.9 (-27.4) *-12.2*	-24.5 (-25.1) *-9.9*	-25.4 (-25.9) *-10.8*	-26.0 (-26.7) *-11.4*
TS2•H_2O-B	32.1 (31.7) *46.2*	34.2 (33.8) *48.3*	34.4 (34.4) *48.5*	34.6 (34.2) *48.7*	35.3 (34.9) *49.4*	35.5 (35.1) *49.6*	35.7 (35.3) *49.8*
MS2•H_2O-2	-18.8 (-18.7) *-6.1*	-15.7 (-15.6) *-2.9*	-15.5 (-15.5) *-2.8*	-15.4 (-15.4) *-2.7*	-15.0 (-14.9) *-2.2*	-14.9 (-14.8) *-2.1*	-14.8 (-14.7) *-2.1*
DMS•Cl + H_2O → DMS•Cl •H_2O-2	-29.9 (-30.5) *-15.1*	-25.9 (-26.5) *-11.1*	-26.7 (-27.3) *-11.9*	-27.3 (-27.9) *-12.5*	-25.1 (-25.7) *-10.3*	-25.9 (-26.5) *-11.1*	-26.5 (-27.1) *-11.7*
TS2•H_2O-C	31.7 (31.2) *46.0*	33.5 (33.1) *47.9*	33.8 (33.4) *48.2*	34.1 (33.7) *48.5*	34.6 (34.2) *49.0*	35.0 (34.5) *49.3*	35.2 (34.7) *49.5*
MS2•H_2O-3	-17.6 (-17.3)	-15.3 (-14.9)	-15.1 (-14.7)	-14.9 (-14.6)	-14.6 (-14.2)	-14.5 (-14.1)	-14.4 (-14.0)

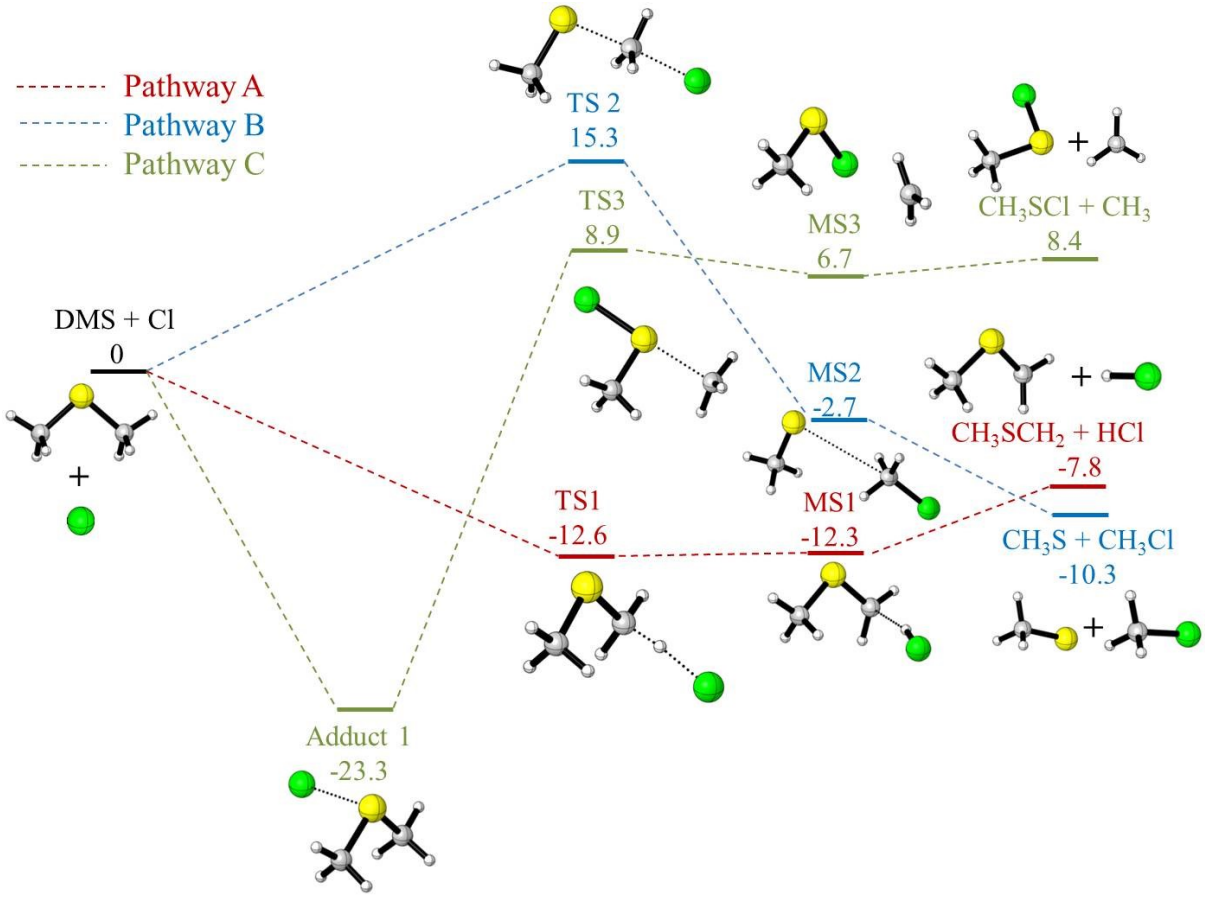
	-5.6	*-3.2*	*-3.0*	*-2.9*	*-2.5*	*-2.4*	*-2.3*
CH_3S + CH_3Cl• H_2O	-13.8 (-13.9) *-10.9*	-12.1 (-12.3) *-9.3*	-12.3 (-12.4) *-9.4*	-12.4 (-12.5) *-9.5*	-11.9 (-12.0) *-9.0*	-12.1 (-12.2) *-9.2*	-12.2 (-12.3) *-9.3*
CH_3S•H_2O + CH_3Cl	-15.0 (-15.2) *-10.9*	-13.1 (-13.3) *-9.0*	-13.3 (-13.5) *-9.2*	-13.4 (-13.6) *-9.3*	-12.7 (-13.0) *-8.7*	-13.0 (-13.2) *-8.9*	-13.1 (-13.4) *-9.0*
CH_3S + CH_3Cl + H_2O	-11.1 (-11.2) *-14.2*	-9.5 (-9.7) *-12.6*	-9.9 (-10.0) *-12.9*	-10.1 (-10.2) *-13.2*	-9.3 (-9.5) *-12.4*	-9.7 (-9.8) *-12.8*	-10.0 (-10.1) *-13.1*

[a]The thermal correction to the enthalpy obtained using the UM06-2X/aVTZ method was added to the UCCSD(T) single point energy (ZPE is included in the electronic energies).

Table S7: Summary of TST (Transition State Theory) and TST+W (Wigner correction) rate coefficients[71] for the DMS+Cl+H_2O reaction, obtained using DLPNO-UCCSD(T)/CBS//UM06-2X/aVTZ relative energies

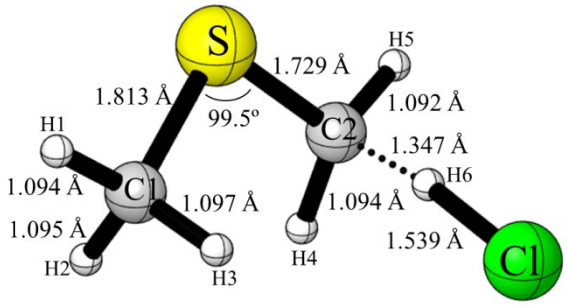
Reaction		**TST Rate coefficient (TST+W values in brackets) at 298K $cm^3.molecule^{-1}s^{-1}$**	**Reference Figure**
DMS+Cl			
	Channel A via TS1 ΔE set as 0 $kcal.mol^{-1}$	2.25×10^{-9} (3.02×10^{-9})	Fig.1
	Channel B via TS2 with ΔE =18.3 $kcal.mol^{-1}$	6.06×10^{-25} (9.84×10^{-25})	Fig.1
	Channel C via TS3 ΔE =8.8 $kcal.mol^{-1}$	1.32×10^{-18} (1.44×10^{-18})	Fig.1
DMS+Cl +H_2O			
via DMS•H_2O + Cl	Channel A via TS1.H_2O-A ΔE =1.1 $kcal.mol^{-1}$	1.20×10^{-13} (1.69×10^{-13})	Fig.4
via DMS•H_2O + Cl	Channel A via TS1.H_2O-B ΔE set as 0 $kcal.mol^{-1}$	1.05×10^{-9} (1.64×10^{-9})	Fig,4
via DMS•Cl + H_2O	Channel A via TS1.H_2O-C ΔE =20.6 $kcal.mol^{-1}$	1.33×10^{-29} (3.89×10^{-29})	Fig.5
via DMS•H_2O + Cl	Channel B via TS2.H_2O-A ΔE =17.3 $kcal.mol^{-1}$	3.07×10^{-25} (4.60×10^{-25})	Fig.6
via DMS•Cl + H_2O	Channel B via TS2.H_2O-B ΔE =56.0 $kcal.mol^{-1}$	2.90×10^{-54} (4.08×10^{-54})	Fig.7
via DMS•Cl + H_2O	Channel B via TS2.H_2O-C ΔE =56.0 $kcal.mol^{-1}$	4.26×10^{-54} (5.93×10^{-54})	Fig.7

Figure S1: Energy profiles for the reaction of DMS + Cl using the UM06-2X/aVDZ method. The relative electronic energies (ΔE) are reported in kcal.mol^{-1} *.

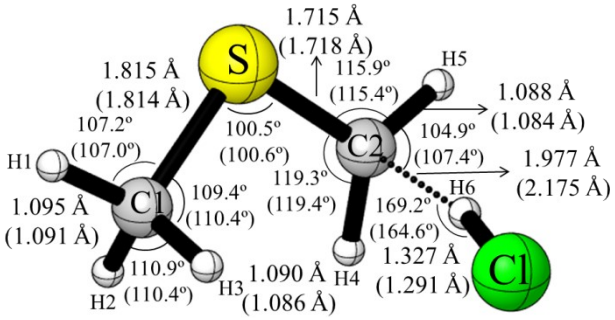


*RC1 and RC2 were only located at the UM06-2X/aVTZ level

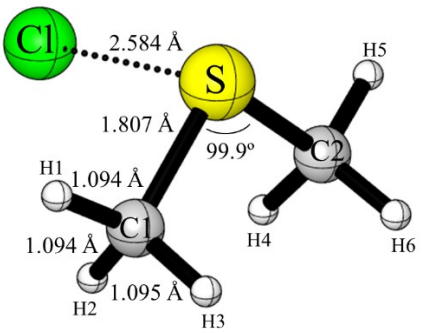
Figure S2: UM06-2X/aVDZ optimised geometries of the stationary points shown in Figure S1.



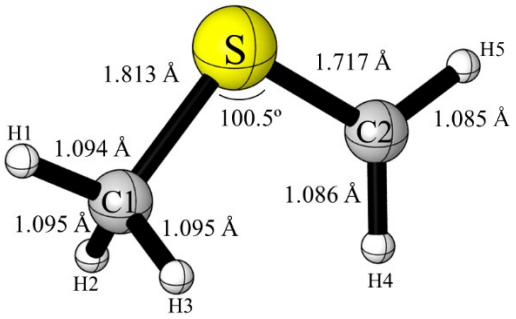
TS1



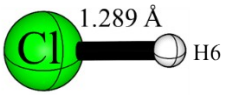
MS1
(UMP2/DZP[21])



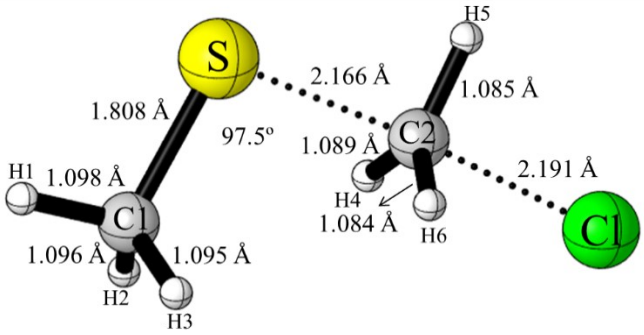
Adduct 1



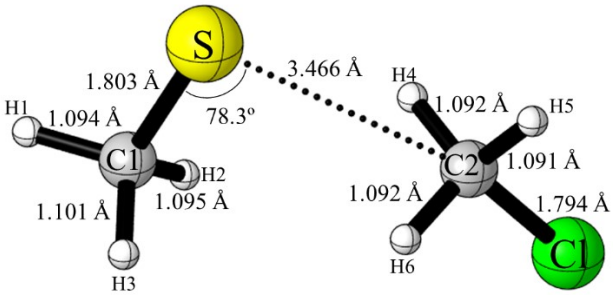
CH_3SCH_2



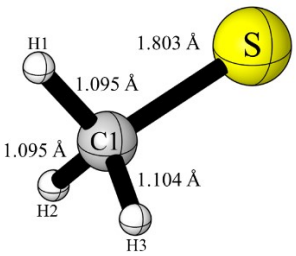
HCl



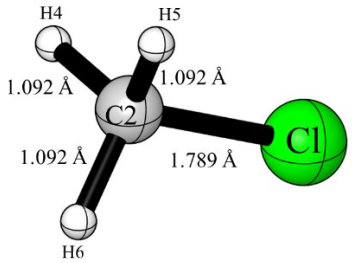
TS2



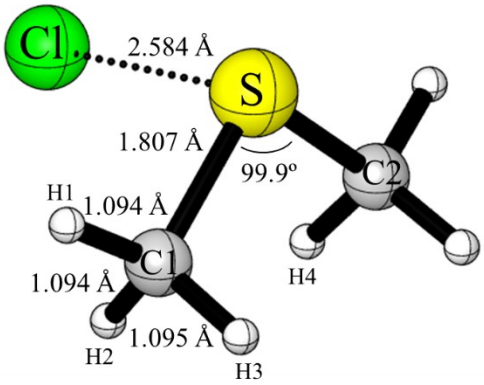
MS2



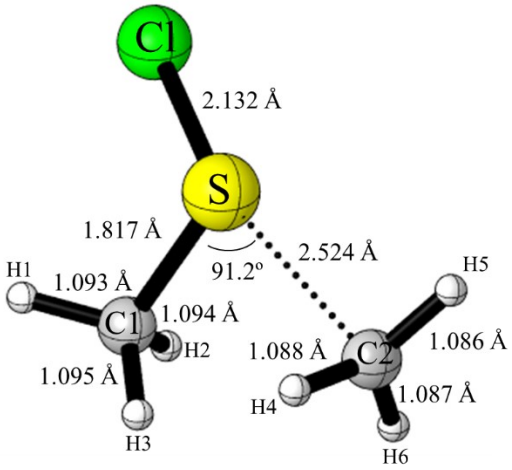
CH_3S



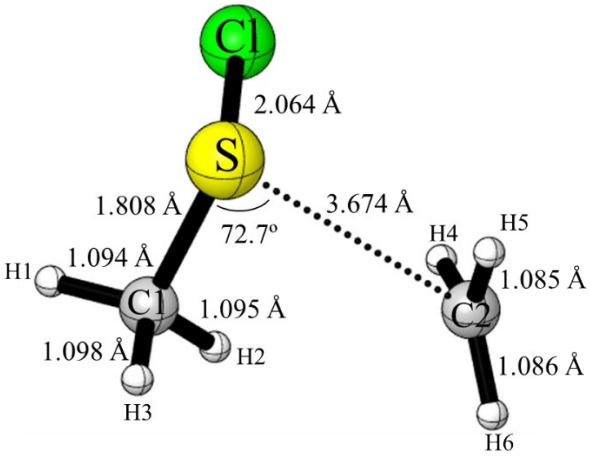
CH_3Cl



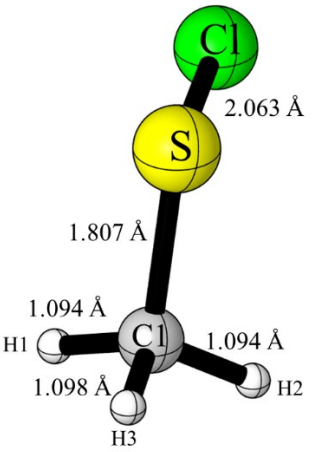
Adduct 1



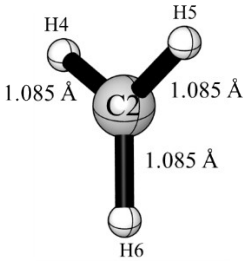
TS3



MS3

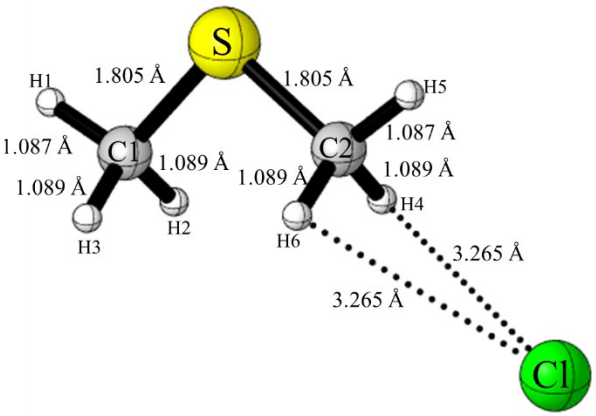


CH_3SCl

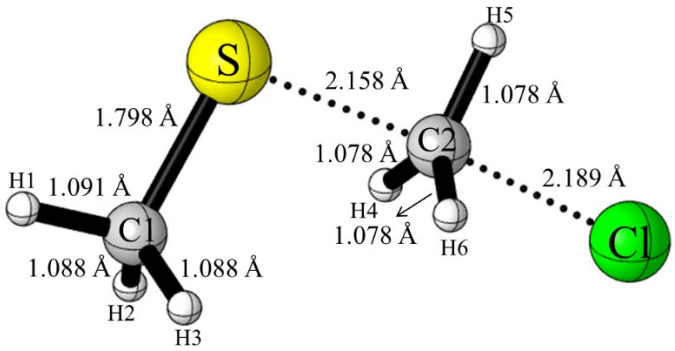


CH_3

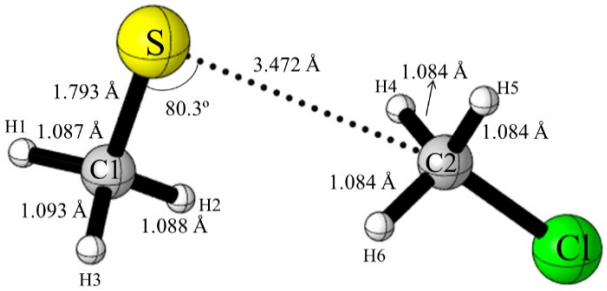
Figure S3: UM06-2X/aVTZ optimised geometries of the stationary points RC2, TS2, MS2, CH_3S, CH_3Cl, TS3, MS3, CH_3SCl and CH_3 shown in Figure 1.



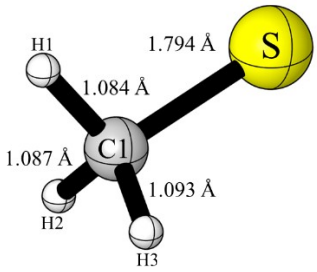
RC2



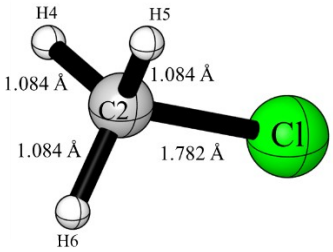
TS2



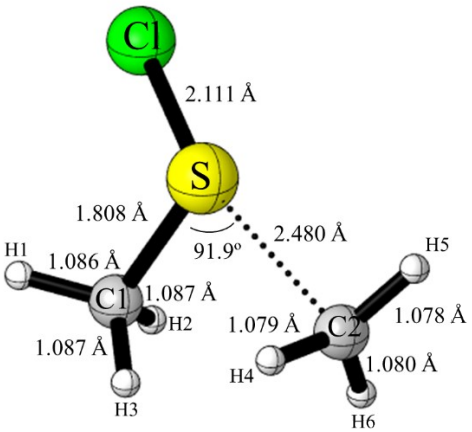
MS2



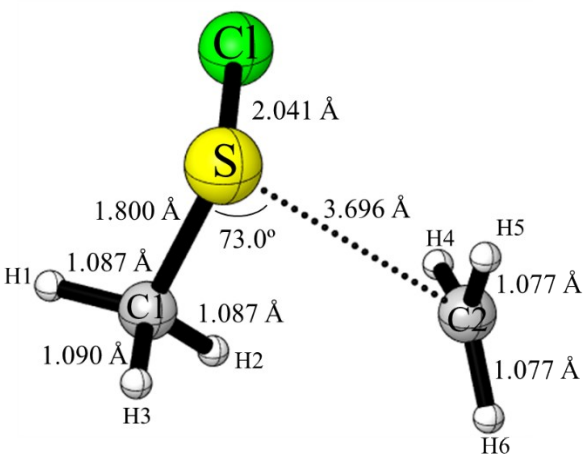
CH_3S



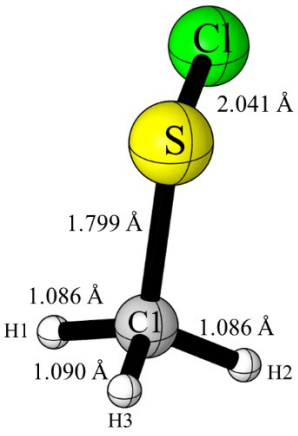
CH_3Cl



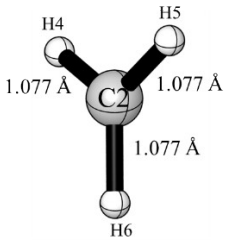
TS3



MS3



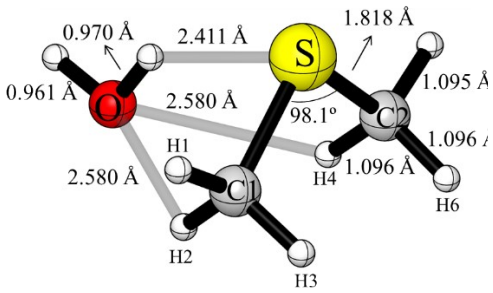
CH_3SCl



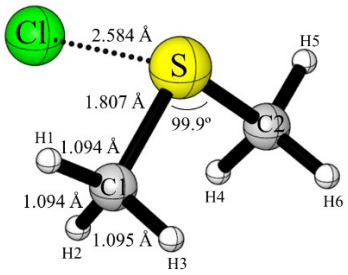
CH_3

Figure S4: UM06-2X/aVDZ and UM06-2X/aVTZ optimised geometries for DMS•H_2O, Cl•H_2O and DMS•Cl.

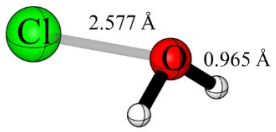
UM06-2X/aVDZ



DMS•H_2O

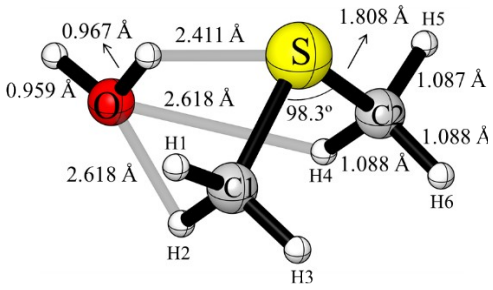


DMS•Cl

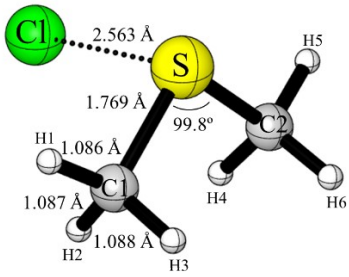


Cl•H_2O

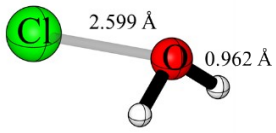
UM06-2X/aVTZ



DMS•H_2O



DMS•Cl



Cl•H_2O

A discussion of the geometrical parameters of the stationary points of the DMS + Cl reaction shown in Figure 2.

For channel A the TS involved in the hydrogen abstraction, TS1, consists of the simultaneous breaking of the C-H bond (TS1 bond length 1.310 Å) and forming of the H-Cl bond (TS1 bond length 1.565 Å). The S-C2 bond length of TS1 is shortened by 0.084 Å compared to the equivalent bond length in DMS and this is also accompanied by an increase in the C-S-C bond angle by 0.9º (see Figure 2). Consequently, TS1 leads to a weakly bound complex MS1 where the bond distance between C2 in CH_2 of CH_3SCH_2 and H6 of HCl is 2.063 Å. In MS1, the S-C2 bond length is further shortened to 1.702 Å which is comparable to the S-C2 bond length of CH_3SCH_2. The C-S-C bond angle of both MS1 (100.7º) and CH_3SCH_2 (100.6º) is comparable. The geometrical parameters obtained using the UM06-2X/aVDZ method are close to those obtained by the UM06-2X/aVTZ method and are in good agreement with those reported using the UMP2/DZP method.[27] The geometrical parameters of TS1 were compared with the parameters of the hydrogen abstraction TS obtained for the DMS + Cl_2 reaction[41] using the MP2/aVDZ method (refer to TS2 of ref [41]). The reported TS[41] was re-optimised in our work using the M06-2X/aVTZ method so that comparison could be made with the DMS-Cl TS. It was observed that for the DMS + Cl_2 reaction, the C-H and H-Cl bond distances are 1.321 Å and 1.637 Å, respectively (C-S-C bond angle = 101.3º; S-C2 = 1.697 Å), indicating that TS1 for the DMS + Cl reaction is more advanced on the reaction surface compared with the TS of the reaction with Cl_2.

For channel C′, the Cl atom of adduct 1 interacts with the S atom of DMS in a C_s symmetry structure with a computed S-Cl bond distance of 2.563 Å and C-S-Cl bond angle of 92.0º at the UM06-2X/aVTZ level (see Figure 2). Upon the formation of adduct 1, the C-S-C bond angle increases slightly from 98.6º (DMS) to 99.8º along with the shortening of the S-C bond length from 1.806 Å (DMS) to 1.769 Å in adduct 1. The UM06-2X/aVDZ and UM06-2X/aVTZ geometrical parameters are in excellent agreement with the computed values reported using the UMP2/DZP method[41] where the S-Cl bond distance is 2.587 Å and the C-S-Cl bond angle is 99.6º. However, the significant difference between these methods lies in their electronic energies relative to the reactants (UMP2/DZP = -11.9 kcal/mol; UM06-2X/aVDZ = -23.3 kcal/mol; UM06-2X/aVTZ = -22.7 kcal.mol^{-1}).

On comparing the computed UM06-2X geometrical parameters for adduct 1 with available theoretical values,[25,27-29] it is found that there are differences in the computed S-Cl bond distance (see Table S2 where comparison is made with results B3LYP/6-311++G(2df,2p)

(2.50 Å), B3LYP/6-311++G(3df,3pd) (2.62 Å) and MP2/6-311++G(2df,2p) (2.59 Å) calculations; UM06-2X/aVTZ value this work 2.563 Å))

It is also interesting to compare the computed structure of adduct 1, ((CH_3)$_2$SCl), with that of the covalent complex, (CH_3)$_2$$SCl_2$, obtained in the DMS + Cl_2 study.[41] The (CH_3)$_2$$SCl_2$ complex has been observed experimentally by photoelectron spectroscopy and studied theoretically using the MP2/aVDZ method.[41] The computed geometrical parameters of both complexes are similar; the C-S-C bond angle and the S-C bond length of (CH_3)$_2$$SCl_2$ is computed in ref [41] as 110.3º and 1.828 Å. These values compare with those computed in this work for adduct1 at the UM06-2X/aVDZ level of 99.9° and 1.807 Å, and at the UM06-2X/aVTZ level of 99.8º and 1.769 Å. In addition, the Cl-S-C bond angle of (CH_3)$_2$$SCl_2$ is computed as 91.9º while that of adduct 1 is 92.0º (UM06-2X/aVTZ).

The UM06-2X/aVDZ and UM06-2X/aVTZ optimised geometries of RC2, TS2, MS2, TS3, MS3, CH_3SCl, CH_3, CH_3S and CH_3Cl are displayed in Figures S2 and S3.

Comparison of the potential energy profiles obtained in ref.(27) with those obtained in this work.

In the work of Resende and De Almeida,[27] the potential profiles of these reactions were obtained at the UQCISD(T)/DZP//UMP2/DZP level (see Fig.(5) of ref.[27]). On comparing these profiles with those obtained in this work (Figure 1), a number of differences were noted in the stationary points obtained:-

(i) Figure 1 of this work obtained from UM06-2X/aVTZ calculations shows that channel A proceeds via a reaction complex (RC1) to a transition state (TS1), and then to a product complex (MS1) and on to the separate products (CH_3SCH_2 + HCl). These stationary points were found in the UMP2 calculations of ref [27], apart from RC1 and TS1 which were not located [27].

(ii) This figure also shows that channel B proceeds via a reaction complex (RC2) to a transition state (TS2), a product complex (MS2) and then on to the products (CH_3S +CH_3Cl). These features were also found in ref [27]. Channel C proceeds via an adduct (adduct 1 of C′) via a transition state (TS3) to a product complex (MS3) and on to the products (CH_3SCl + CH_3). All these features were located in ref [27].

Summary of previous computation work on the DMS + Cl reaction (25,27-30)

The DMS + Cl reaction has also been the subject of a number of theoretical studies.[25,27-30]. Resende and Almeida[27] used UQCISD(T)/DZP//UMP2/DZP calculations to locate maxima and minima on the potential energy surfaces of channels A – C′ and calculate the activation energies, reaction enthalpies ($\Delta H^{\phi}_{f,298}$) and free energies ($\Delta G^{\phi}_{f,298}$) for all four channels. The minimum energy geometry of the adduct ($CH_3S(Cl)CH_3$) was determined and the enthalpy of channel C′ ($\Delta H^{\phi}_{f,298}$) evaluated as -12.72 kcal.mol-1. Wilson and Hirst[28] used MP2(full)/6-311G(d,p) calculations to determine the geometry of the reagents and adduct, and evaluate the enthalpy of channel C′ ($\Delta H^{\phi}_{f,298}$) as -19.35 kcal.mol-1. Similar calculations have been made by Thompson et al.,[29] Enami et al.[25] and McKee[30] at the B3LYP/6-311++G)(2df,p)//B3LYP/6-311++G(d.p), QCISD(T)/6-311++G(3df,3dp)//B3LYP/6-311++G(3df,3pd), and PMP2/6-31G(d,p)//UHF/3-21G(d) levels, respectively and values of the reaction enthalpy for channel C′ ($\Delta H^{\phi}_{f,298}$) of -23.2, -17.7 and -12.1 kcal.mol-1 have been obtained. A summary of these values, and their expected reliability, is given in Table S1.

Cartesian coordinates for all stationary points for the DMS + Cl using the UM06-2X/aVDZ and UM06-2X/aVTZ methods.

UM06-2X/aVDZ				UM06-2X/aVTZ			
DMS							
Total energy = -477.9505539 Hartrees Nuclear repulsion energy = 110.5081635842 Hartrees				Total energy = -477.9971871 Hartrees Nuclear repulsion energy = 111.1417188779 Hartrees			
6	0.000000000	1.376298000	-0.517288000	6	0.000000000	1.368528000	-0.514712000
1	-0.898057000	1.347478000	-1.145004000	1	-0.890710000	1.338894000	-1.139167000
1	0.000000000	2.304043000	0.064006000	1	0.000000000	2.291181000	0.059645000
1	0.898057000	1.347478000	-1.145004000	1	0.890710000	1.338894000	-1.139167000
6	0.000000000	-1.376298000	-0.517288000	6	0.000000000	-1.368528000	-0.514712000
1	0.000000000	-2.304043000	0.064006000	1	0.000000000	-2.291181000	0.059645000
1	-0.898057000	-1.347478000	-1.145004000	1	-0.890710000	-1.338894000	-1.139167000
1	0.898057000	-1.347478000	-1.145004000	1	0.890710000	-1.338894000	-1.139167000
16	0.000000000	0.000000000	0.666216000	16	0.000000000	0.000000000	0.663371000
Adduct 1 (DMS•Cl)							
Total energy = -938.112414 Hartrees Nuclear repulsion energy = 216.1200072096 Hartrees				Total energy = -938.1757205 Hartrees Nuclear repulsion energy = 217.4425066686 Hartrees			
6	0.304095000	1.113614000	1.382749000	6	0.301245000	1.110030000	1.374735000
1	-0.169992000	0.741711000	2.295731000	1	-0.172714000	0.753177000	2.284822000
1	1.290425000	0.654143000	1.267448000	1	1.280466000	0.650002000	1.268912000
1	0.367319000	2.206885000	1.406417000	1	0.371160000	2.195808000	1.388547000
6	0.304095000	1.113614000	-1.382749000	6	0.301245000	1.110030000	-1.374735000
1	1.290425000	0.654143000	-1.267448000	1	1.280466000	0.650002000	-1.268912000
1	-0.169992000	0.741711000	-2.295731000	1	-0.172714000	0.753177000	-2.284822000
1	0.367319000	2.206885000	-1.406417000	1	0.371160000	2.195808000	-1.388547000
17	0.304095000	-1.769806000	0.000000000	17	0.301245000	-1.759422000	0.000000000
16	-0.737142000	0.594866000	0.000000000	16	-0.730871000	0.586989000	0.000000000
TS1							
Total energy = =-938.0879833 Hartrees Nuclear repulsion energy = 201.7328642301 Hartrees				Total energy = -938.1503603 Hartrees Nuclear repulsion energy = 202.3664870835 Hartrees			
6	-0.270262000	-1.139662000	0.544867000	6	-0.263969000	-1.127791000	0.539289000
1	-0.257609000	-0.882927000	1.608454000	1	-0.266862000	-0.884088000	1.598398000
1	-0.165420000	-2.201941000	0.316018000	1	-0.166331000	-2.184379000	0.316608000
1	0.898740000	-0.579556000	0.179086000	1	0.873988000	-0.586222000	0.182995000
6	-1.395264000	1.307908000	0.306962000	6	-1.401455000	1.300237000	0.302430000
1	-2.082310000	1.944442000	-0.257677000	1	-2.106525000	1.922698000	-0.240581000
1	-1.692682000	1.276101000	1.360341000	1	-1.668545000	1.266922000	1.356124000
1	-0.367219000	1.675496000	0.204517000	1	-0.388892000	1.681982000	0.177617000
16	-1.476261000	-0.353777000	-0.413709000	16	-1.474363000	-0.354670000	-0.409974000
17	2.192931000	0.201137000	-0.111904000	17	2.194443000	0.201361000	-0.110700000
TS2							
Total energy = -938.0484727 Hartrees Nuclear repulsion energy = 190.6583222755 Hartrees				Total energy = -938.1121088 Hartrees Nuclear repulsion energy = 191.1443694485 Hartrees			
6	2.213315000	1.071568000	0.006273000	6	2.221967000	1.060503000	-0.000095000
1	3.310647000	1.063645000	-0.021767000	1	3.312342000	1.043603000	-0.000231000
1	1.853073000	1.616547000	-0.873207000	1	1.883457000	1.578931000	-0.894334000
1	1.885667000	1.562476000	0.928725000	1	1.883723000	1.578890000	0.894269000
6	-0.434021000	-0.329358000	0.124904000	6	-0.430128000	-0.309438000	-0.000567000
1	-0.350729000	0.196925000	-0.824819000	1	-0.358533000	0.216230000	-0.938658000
1	-0.664260000	-1.390001000	0.133321000	1	-0.657809000	-1.362606000	-0.000761000
1	-0.363602000	0.200957000	1.067982000	1	-0.358321000	0.215920000	0.937708000
16	1.700040000	-0.660933000	-0.039576000	16	1.699555000	-0.659873000	-0.000052000
17	-2.561600000	0.168889000	-0.033181000	17	-2.567575000	0.163565000	0.000401000

TS3

Total energy = -938.0566962 Hartrees Nuclear repulsion energy = 211.2111176546 Hartrees				Total energy = -938.1233919 Hartrees Nuclear repulsion energy = 213.1398342603 Hartrees			
6	0.399975000	1.532546000	0.027350000	6	0.393986000	1.533181000	0.029550000
1	-0.281045000	2.049828000	-0.653833000	1	-0.284241000	2.046668000	-0.645479000
1	0.186926000	1.800905000	1.066447000	1	0.177521000	1.799380000	1.060731000
1	1.435142000	1.786402000	-0.224657000	1	1.421407000	1.792152000	-0.215939000
6	2.700575000	-0.601513000	0.146448000	6	2.655173000	-0.608750000	0.145857000
1	2.850961000	0.004608000	1.035816000	1	2.815301000	-0.065463000	1.064015000
1	2.700881000	-1.681013000	0.260873000	1	2.656754000	-1.685508000	0.195991000
1	2.975955000	-0.189661000	-0.821823000	1	2.960118000	-0.149159000	-0.782496000
17	-1.885888000	-0.304811000	0.092795000	17	-1.862715000	-0.309588000	0.091972000
16	0.224249000	-0.260968000	-0.205195000	16	0.226521000	-0.251354000	-0.205800000

MS1

Total energy = -938.0890949 Hartrees Nuclear repulsion energy = 197.2804636077 Hartrees				Total energy = -938.1536389 Hartrees Nuclear repulsion energy = 196.9792110223 Hartrees			
6	-0.600844000	-1.268519000	0.567920000	6	-0.650912000	-1.269677000	0.569526000
1	-0.488234000	-0.990763000	1.615832000	1	-0.549950000	-1.000665000	1.611926000
1	-0.562221000	-2.319074000	0.288103000	1	-0.604482000	-2.310280000	0.286636000
1	1.185225000	-0.554077000	0.113683000	1	1.225788000	-0.537743000	0.126478000
6	-1.306474000	1.345662000	0.371143000	6	-1.323561000	1.339411000	0.375138000
1	-1.865865000	2.088073000	-0.205545000	1	-1.862100000	2.084615000	-0.203390000
1	-1.720409000	1.275980000	1.382469000	1	-1.758690000	1.263078000	1.368835000
1	-0.246410000	1.618877000	0.401483000	1	-0.271724000	1.610012000	0.437397000
16	-1.495233000	-0.246654000	-0.479112000	16	-1.493163000	-0.236989000	-0.488968000
17	2.297974000	0.139094000	-0.092036000	17	2.326977000	0.133200000	-0.086610000

MS2

Total energy = -938.0933105 Hartrees Nuclear repulsion energy = 177.6801638416 Hartrees				Total energy = -938.1577727 Hartrees Nuclear repulsion energy = 177.8066283713 Hartrees			
6	2.087911000	1.177245000	-0.004398000	6	2.139648000	1.170365000	-0.001969000
1	2.915688000	1.705687000	-0.487479000	1	2.964802000	1.665777000	-0.507671000
1	1.129656000	1.442119000	-0.464270000	1	1.185822000	1.468713000	-0.431723000
1	2.062759000	1.483458000	1.052525000	1	2.156477000	1.477834000	1.046814000
6	-1.096289000	-0.433190000	0.023940000	6	-1.115768000	-0.433052000	0.034725000
1	-0.653495000	-0.253277000	-0.958184000	1	-0.658757000	-0.247633000	-0.931042000
1	-1.089966000	-1.499893000	0.255121000	1	-1.114481000	-1.494883000	0.252295000
1	-0.567332000	0.128260000	0.796801000	1	-0.591389000	0.110427000	0.812803000
16	2.365373000	-0.603853000	-0.009458000	16	2.351705000	-0.609884000	-0.012884000
17	-2.799589000	0.128881000	-0.009437000	17	-2.806649000	0.138472000	-0.013639000

MS3

Total energy = -938.058863 Hartrees Nuclear repulsion energy = 208.6554333659 Hartrees				Total energy = -938.1266003 Hartrees Nuclear repulsion energy = 209.9883899044 Hartrees			
6	-0.169575000	1.580836000	0.734965000	6	-0.298071000	1.572905000	0.715064000
1	-0.845528000	1.504399000	1.591400000	1	-0.942979000	1.448581000	1.580466000
1	0.852205000	1.287544000	0.997328000	1	0.740748000	1.367465000	0.962400000
1	-0.173393000	2.609543000	0.351075000	1	-0.391913000	2.588045000	0.328793000
6	2.778341000	-0.239369000	-0.161308000	6	2.786392000	-0.075315000	-0.166183000
1	2.672052000	-1.020203000	0.584507000	1	2.842617000	-0.745770000	0.674647000
1	2.189206000	-0.281675000	-1.071368000	1	2.195231000	-0.345348000	-1.024729000
1	3.545262000	0.520015000	-0.044656000	1	3.401431000	0.808933000	-0.190058000
17	-0.678146000	-1.283698000	0.257760000	17	-0.554849000	-1.306544000	0.263712000
16	-0.772745000	0.572152000	-0.639510000	16	-0.833914000	0.506487000	-0.631744000

RC1

Not located	Total energy = -938.1503895 Hartrees Nuclear repulsion energy = 202.1276913837 Hartrees

	6 -0.261849000 -1.129392000 0.537158000 1 -0.284411000 -0.898265000 1.599258000 1 -0.181749000 -2.188044000 0.314868000 1 0.835077000 -0.616901000 0.193636000 6 -1.397645000 1.301142000 0.305162000 1 -2.098807000 1.928787000 -0.236977000 1 -1.665476000 1.267037000 1.358697000 1 -0.382639000 1.677994000 0.182358000 16 -1.477523000 -0.350893000 -0.411462000 17 2.198549000 0.200775000 -0.110728000
RC2	
Not located	Total energy = -938.1392506 Hartrees Nuclear repulsion energy = 175.4514992408 Hartrees 6 -2.456344000 1.136087000 -0.000005000 1 -3.541797000 1.197077000 0.000067000 1 -2.071905000 1.629779000 0.890830000 1 -2.072025000 1.629689000 -0.890940000 6 -0.215489000 -0.432038000 -0.000107000 1 0.120081000 0.099956000 0.889108000 1 0.216731000 -1.429837000 -0.000201000 1 0.119952000 0.100044000 -0.889306000 16 -2.011187000 -0.613618000 0.000047000 17 3.261115000 0.139229000 0.000021000
CH_3SCH_2	
Total energy = -477.2930583 Hartrees Nuclear repulsion energy = -477.2930583 Hartrees 6 -1.370533000 0.432250000 -0.000052000 1 -2.240350000 -0.231425000 -0.000013000 1 -1.385488000 1.056240000 0.899607000 1 -1.385432000 1.056081000 -0.899820000 16 0.108964000 -0.615561000 0.000054000 6 1.339118000 0.581903000 -0.000170000 1 1.086045000 1.637804000 0.000841000 1 2.370293000 0.245361000 -0.000145000	Total energy = -477.3376793 Hartrees Nuclear repulsion energy = 104.4828631141 Hartrees 6 -1.365228000 0.427332000 0.000128000 1 -2.228066000 -0.232949000 -0.000078000 1 -1.382111000 1.048330000 0.892628000 1 -1.382144000 1.048818000 -0.892036000 16 0.110225000 -0.610654000 -0.000150000 6 1.330561000 0.578079000 0.000655000 1 1.081781000 1.626525000 -0.002596000 1 2.354930000 0.247278000 -0.000208000
CH_3SCl	
Total energy = -898.2430669 Hartrees Nuclear repulsion energy = 144.4760578812 Hartrees 6 1.579335000 0.717147000 -0.000016000 1 1.430196000 1.315248000 -0.903747000 1 1.430326000 1.315024000 0.903883000 1 2.593442000 0.295943000 -0.000140000 17 -1.334126000 0.253068000 0.000115000 16 0.484386000 -0.720703000 -0.000116000	Total energy = =-898.2968244 Hartrees Nuclear repulsion energy = 145.6429586951 Hartrees 6 1.574684000 0.706922000 -0.000028000 1 1.429097000 1.304160000 -0.895847000 1 1.429159000 1.303943000 0.895947000 1 2.580133000 0.285438000 -0.000110000 17 -1.321411000 0.254423000 0.000160000 16 0.473593000 -0.716266000 -0.000159000
CH_3S	
Total energy = =-438.0167 Hartrees Nuclear repulsion energy = 48.3214490152 Hartrees 6 1.109354000 0.000480000 -0.008806000 1 1.419947000 -0.021995000 1.046593000 1 1.506507000 -0.894725000 -0.498108000 1 1.509741000 0.912153000 -0.463323000 16 -0.693270000 0.000105000 -0.002020000	Total energy = -438.0482552 Hartrees Nuclear repulsion energy = 48.5806745306 Hartrees 6 1.104024000 0.000456000 -0.008275000 1 1.414520000 -0.022413000 1.039130000 1 1.498928000 -0.886682000 -0.496712000 1 1.501925000 0.904751000 -0.461022000 16 -0.689970000 0.000101000 -0.001984000
CH_3	
Total energy = -39.8108334 Hartrees Nuclear repulsion energy = 9.6241877794 Hartrees 6 0.000000000 0.000000000 0.000008000	Total energy = -39.8253668 Hartrees Nuclear repulsion energy = 9.6993683513 Hartrees 6 0.000000000 0.000000000 0.000008000

1	0.000000000	1.084949000	-0.000017000	1	0.000000000	1.076539000	-0.000016000
1	0.939593000	-0.542474000	-0.000017000	1	0.932310000	-0.538270000	-0.000016000
1	-0.939593000	-0.542474000	-0.000017000	1	-0.932310000	-0.538270000	-0.000016000
CH_3Cl							
Total energy = -500.0732053 Hartrees Nuclear repulsion energy = 51.1619288801 Hartrees				Total energy = -500.1068852 Hartrees Nuclear repulsion energy = 51.3952348439 Hartrees			
6	0.000000000	0.000000000	-1.130781000	6	0.000000000	0.000000000	-1.126022000
1	0.000000000	1.037712000	-1.470870000	1	0.000000000	1.028979000	-1.467441000
1	-0.898685000	-0.518856000	-1.470870000	1	-0.891122000	-0.514490000	-1.467441000
1	0.898685000	-0.518856000	-1.470870000	1	0.891122000	-0.514490000	-1.467441000
17	0.000000000	0.000000000	0.658665000	17	0.000000000	0.000000000	0.656380000
HCl							
Total energy = =-460.7865311 Hartrees Nuclear repulsion energy = 6.9770492095 Hartrees				Total energy = -460.8074726 Hartrees Nuclear repulsion energy = 7.0355215280 Hartrees			
17	0.000000000	0.000000000	0.071632000	17	0.000000000	0.000000000	0.071036000
1	0.000000000	0.000000000	-1.217740000	1	0.000000000	0.000000000	-1.207620000

Cartesian coordinates for all stationary points for the DMS + Cl + H_2O using the UM06-2X/aVTZ method.

DMS•H_2O			
Total energy =-554.4366248 Hartrees			
Nuclear repulsion energy = 175.0412177806 Hartrees			
16	0.644375000	0.786118000	0.000000000
6	-0.528486000	0.631366000	1.367783000
1	0.038586000	0.695968000	2.292916000
1	-1.252749000	1.442697000	1.334584000
1	-1.034140000	-0.331270000	1.319595000
6	-0.528486000	0.631366000	-1.367783000
1	-1.252749000	1.442697000	-1.334584000
1	0.038586000	0.695968000	-2.292916000
1	-1.034140000	-0.331270000	-1.319595000
1	0.547916000	-1.623296000	0.000000000
8	-0.063148000	-2.373284000	0.000000000
1	0.485704000	-3.159496000	0.000000000
DMS •H_2O•Cl-1			
Total energy = -1014.6131482 Hartrees			
Nuclear repulsion energy = 296.1481993766 Hartrees			
16	0.077015000	-0.000011000	-0.522956000
6	0.369003000	1.373063000	0.599237000
1	0.135267000	2.285508000	0.057954000
1	-0.301443000	1.270573000	1.448623000
1	1.414082000	1.360920000	0.901125000
6	0.369034000	-1.373182000	0.599160000
1	-0.301396000	-1.270767000	1.448568000
1	0.135298000	-2.285580000	0.057798000
1	1.414148000	-1.361073000	0.901044000
1	2.860718000	0.000014000	-0.981947000
8	3.284743000	-0.000139000	-0.118836000
1	4.229246000	0.001563000	-0.289880000
17	-2.442607000	0.000050000	-0.083276000
DMS•H_2O•Cl-2			
Total energy =-1014.6201494 Hartrees			
Nuclear repulsion energy = 304.5838387149 Hartrees			
6	-0.963329000	0.734740000	1.381693000
1	-0.959251000	0.121397000	2.278318000
1	0.008362000	1.200800000	1.234943000
1	-1.750229000	1.484153000	1.443713000
6	-0.963263000	0.734835000	-1.381656000
1	-1.750405000	1.483971000	-1.443944000
1	0.008215000	1.201241000	-1.234604000
1	-0.958675000	0.121476000	-2.278268000
17	1.045831000	-1.423895000	-0.000010000
16	-1.307535000	-0.362796000	-0.000025000
1	2.832924000	1.910348000	0.000637000
8	1.916874000	1.626697000	-0.000038000
1	1.935056000	0.656537000	-0.000140000
DMS•H_2O•Cl-3			
Total energy =-1014.6201494 Hartrees			
Nuclear repulsion energy = 290.9616313619 Hartrees			
6	-1.486329000	0.562009000	1.108543000
1	-1.922546000	1.549203000	0.997533000

1	-2.028153000	-0.025570000	1.846197000
1	-0.437642000	0.664857000	1.382609000
6	-0.553796000	-1.605460000	-0.198860000
1	-0.669475000	-2.060398000	0.781850000
1	-0.566169000	-2.313193000	-1.020646000
1	0.601964000	-1.156915000	-0.133379000
16	-1.569016000	-0.246635000	-0.496234000
17	2.129004000	-0.522623000	0.157342000
8	0.516128000	2.256812000	-0.347874000
1	0.893651000	2.848398000	-1.001525000
1	1.151282000	1.530580000	-0.262809000

DMS•H_2O•Cl-4

Total energy =-1014.6192737 Hartrees
Nuclear repulsion energy = 305.2521035578 Hartrees

6	0.331038000	-1.413086000	0.964569000
1	0.385932000	-0.712302000	1.794096000
1	-0.673124000	-1.817970000	0.878056000
1	1.064961000	-2.209310000	1.073358000
17	-0.546850000	1.620348000	0.234973000
16	0.653654000	-0.522802000	-0.561751000
6	2.263103000	0.177963000	-0.175859000
1	2.525129000	0.850938000	-0.987274000
1	2.191341000	0.736134000	0.753986000
1	2.997288000	-0.621644000	-0.099253000
8	-2.478382000	-0.897593000	-0.269833000
1	-3.213508000	-0.824854000	-0.881138000
1	-2.177820000	0.009401000	-0.111945000

DMS•H_2O•Cl-2

Total energy =-1014.6201494 Hartrees
Nuclear repulsion energy = 304.5750557510 Hartrees

6	-0.963322000	-0.734639000	1.381685000
1	-0.958445000	-0.121237000	2.278267000
1	-1.750567000	-1.483649000	1.444194000
1	0.008043000	-1.201182000	1.234388000
17	1.046165000	1.423791000	-0.000055000
8	1.916671000	-1.626956000	0.000031000
1	1.935101000	-0.656753000	0.000032000
1	2.832656000	-1.910814000	-0.000476000
16	-1.307619000	0.362959000	0.000035000
6	-0.963548000	-0.734717000	-1.381620000
1	-0.959400000	-0.121442000	-2.278293000
1	0.008092000	-1.200881000	-1.234788000
1	-1.750523000	-1.484055000	-1.443595000

TS1•H_2O-A

Total energy =-1014.5808168 Hartrees
Nuclear repulsion energy = 281.4141230649 Hartrees

16	-0.450828000	0.258283000	-0.945235000
6	-0.168966000	-1.230752000	-0.030737000
1	-0.231424000	-2.080036000	-0.704992000
1	0.866934000	-1.164235000	0.379619000
1	-0.879553000	-1.321560000	0.789129000
6	-0.495196000	1.415544000	0.431756000
1	0.452897000	1.336189000	0.963899000
1	-0.612172000	2.415372000	0.023661000
1	-1.331216000	1.169851000	1.083733000
1	-3.024586000	-0.231298000	-0.308433000
8	-3.262532000	-0.354204000	0.615852000

1	-4.208541000	-0.514261000	0.627165000
17	2.721537000	-0.118687000	0.290415000

TS1•H_2O-B

Total energy =-1014.5870086 Hartrees
Nuclear repulsion energy = 280.9115148779 Hartrees

16	-0.654209000	0.921997000	-0.733640000
6	0.031635000	-0.657744000	-0.786292000
1	0.121544000	-1.046556000	-1.794509000
1	1.281016000	-0.525157000	-0.364098000
1	-0.357317000	-1.357997000	-0.051776000
6	-0.722722000	1.156979000	1.054960000
1	0.291824000	1.088886000	1.444599000
1	-1.129248000	2.147376000	1.238530000
1	-1.363290000	0.395435000	1.492814000
1	-2.945908000	-0.661634000	-0.359028000
8	-2.907984000	-1.184273000	0.447303000
1	-3.745633000	-1.649438000	0.500254000
17	2.689691000	-0.392006000	0.261236000

TS1•H_2O-C

Total energy =-1014.5731679 Hartrees
Nuclear repulsion energy = 301.9492810067 Hartrees

6	-1.237574000	-1.198373000	0.956797000
1	-0.975734000	-2.226964000	0.729824000
1	-0.456357000	-0.765122000	1.575022000
1	-2.214940000	-1.134441000	1.430434000
6	-1.337682000	1.316731000	-0.086818000
1	-1.817365000	1.475433000	0.875128000
1	-0.010023000	1.641053000	0.173053000
1	-1.669613000	1.980939000	-0.877680000
17	1.799426000	-0.839860000	-0.188830000
16	-1.282004000	-0.311885000	-0.606636000
1	1.596597000	2.383273000	-0.177055000
8	1.173249000	1.799561000	0.463308000
1	1.534793000	0.806959000	0.261209000

TS2•H_2O-A

Total energy =-1014.5544117 Hartrees
Nuclear repulsion energy = 279.0952866164 Hartrees

6	-2.203529000	0.732251000	0.641184000
1	-3.217963000	1.069424000	0.434565000
1	-2.093909000	0.510854000	1.699842000
1	-1.506556000	1.515453000	0.344738000
6	0.189390000	-0.906809000	0.033265000
1	0.112142000	-0.913362000	1.106020000
1	0.319522000	-1.845208000	-0.478016000
1	0.210466000	0.029942000	-0.518070000
16	-1.914766000	-0.729575000	-0.365657000
17	2.371092000	-0.565733000	0.135988000
8	0.750745000	2.177831000	-0.271697000
1	1.039282000	2.888359000	-0.848101000
1	1.543571000	1.659900000	-0.075393000

TS2•H_2O-B

Total energy =-1014.5185919 Hartrees
Nuclear repulsion energy = 298.5121161761 Hartrees

6	-0.357564000	0.245903000	1.634175000
1	-0.725106000	1.230247000	1.864938000
1	-1.114598000	-0.521154000	1.557347000

1	0.551170000	-0.016921000	2.153640000
17	-0.361821000	1.444953000	-0.425827000
16	0.764158000	-0.983306000	-0.154708000
6	2.368822000	-0.173509000	-0.206195000
1	2.429650000	0.474797000	-1.076052000
1	2.542606000	0.409133000	0.696496000
1	3.122743000	-0.956952000	-0.278106000
8	-2.534541000	-1.003526000	-0.268432000
1	-2.572248000	-1.634665000	-0.989828000
1	-2.101000000	-0.221940000	-0.634467000

TS2•H_2O-C

Total energy =-1014.5194601 Hartrees
Nuclear repulsion energy = 298.4762291786 Hartrees

6	-0.290027000	-0.687752000	1.520735000
1	-1.170877000	-1.300955000	1.447235000
1	0.494762000	-1.113053000	2.125837000
1	-0.492888000	0.364322000	1.654679000
17	-0.507803000	-1.248458000	-0.784547000
8	-2.300084000	1.234655000	0.211937000
1	-1.993566000	0.505647000	-0.344898000
1	-3.101191000	1.564124000	-0.199732000
16	1.643439000	0.041447000	0.205033000
6	1.008610000	1.541342000	-0.554853000
1	0.852941000	1.376544000	-1.618092000
1	0.074482000	1.850972000	-0.089539000
1	1.763148000	2.314260000	-0.409509000

MS1•H_2O-1

Total energy =-1014.5904155 Hartrees
Nuclear repulsion energy = 274.1733118329 Hartrees

6	0.252622000	-1.048594000	0.597067000
1	0.475311000	-1.448410000	-0.382674000
1	0.174115000	-1.716674000	1.441208000
1	-1.747977000	-0.657630000	0.110316000
6	0.632908000	1.289471000	-0.712346000
1	0.921856000	2.331974000	-0.612681000
1	1.349380000	0.763875000	-1.338857000
1	-0.373307000	1.222269000	-1.119499000
16	0.651245000	0.573701000	0.947825000
17	-2.896145000	-0.233502000	-0.337464000
1	2.927991000	-0.530646000	0.125456000
8	3.205869000	-0.706366000	-0.779287000
1	4.127050000	-0.968761000	-0.725624000

MS1•H_2O-2

Total energy =-1014.5955419 Hartrees
Nuclear repulsion energy = 283.8617183630 Hartrees

6	-0.764154000	-1.053724000	1.123328000
1	-0.091026000	-1.900971000	1.031968000
1	-0.215002000	-0.202561000	1.520135000
1	-1.602922000	-1.306135000	1.767552000
6	-2.298398000	0.717612000	-0.232535000
1	-2.633811000	0.931508000	0.772073000
1	-0.369965000	1.803250000	0.006310000
1	-2.835321000	1.130420000	-1.072424000
17	2.435088000	-0.409675000	-0.218292000
16	-1.363315000	-0.673118000	-0.536962000
1	0.767132000	2.853203000	0.053338000
8	0.515646000	1.979149000	0.360795000

1	1.647612000	0.609128000	-0.007715000

MS2•H_2O-1

Total energy = -1014.6002765 Hartrees
Nuclear repulsion energy = 282.5068567880 Hartrees

6	-2.240493000	-0.130973000	0.838840000
1	-3.308930000	0.022601000	0.670127000
1	-2.120311000	-0.904756000	1.592778000
1	-1.805070000	0.811422000	1.164528000
6	1.286139000	-0.563427000	1.189152000
1	0.637508000	0.286594000	1.376882000
1	2.079185000	-0.621240000	1.925941000
1	0.720957000	-1.489423000	1.159610000
16	-1.551661000	-0.640935000	-0.739477000
17	2.035308000	-0.325124000	-0.415867000
8	-0.078267000	2.246254000	-0.029709000
1	-0.478998000	1.630654000	-0.656415000
1	0.854261000	2.242584000	-0.262366000

MS2•H_2O-2

Total energy =-1014.6009738 Hartrees
Nuclear repulsion energy = 285.2448930031 Hartrees

6	1.923092000	-0.254520000	1.001280000
1	2.998892000	-0.340992000	1.099053000
1	1.588190000	0.754191000	1.219353000
1	1.416060000	-0.979380000	1.628306000
17	1.498611000	-0.613183000	-0.701727000
16	-1.557630000	-0.423296000	0.795216000
6	-2.052106000	-0.393114000	-0.929832000
1	-1.641229000	0.470305000	-1.446895000
1	-1.761704000	-1.317354000	-1.422474000
1	-3.142047000	-0.326684000	-0.938518000
8	0.090927000	2.398845000	-0.122825000
1	-0.511847000	1.817739000	0.356959000
1	0.546030000	1.814058000	-0.735974000

MS2•H_2O-3

Total energy =-1014.5983024 Hartrees
Nuclear repulsion energy = 280.6655161220 Hartrees

6	-1.126411000	-1.016762000	1.079328000
1	-2.149534000	-1.175150000	1.399673000
1	-0.473631000	-1.811339000	1.419669000
1	-0.764253000	-0.048725000	1.406539000
17	-1.107931000	-1.032472000	-0.714074000
8	-1.867270000	1.941022000	0.259893000
1	-1.892523000	1.262884000	-0.424215000
1	-2.379495000	2.677715000	-0.079199000
16	2.151853000	-0.336375000	0.182348000
6	1.560078000	1.284824000	-0.310334000
1	1.503851000	1.369290000	-1.392439000
1	0.599242000	1.519758000	0.143270000
1	2.297692000	2.003044000	0.055283000

CH_3SCH_2•H_2O

Total energy =-553.7759646 Hartrees
Nuclear repulsion energy = 164.9440618870 Hartrees

16	1.053062000	-0.163655000	-0.466642000
6	0.295852000	-1.316058000	0.535563000
1	0.415847000	-2.352142000	0.261864000
1	0.023935000	-1.054356000	1.547660000

6	0.627208000	1.367542000	0.392013000
1	1.033773000	1.346933000	1.400375000
1	1.079565000	2.182935000	-0.165566000
1	-0.454028000	1.482363000	0.411662000
1	-1.778908000	-0.522368000	-0.059509000
8	-2.474580000	0.147432000	-0.071923000
1	-2.910895000	0.046746000	-0.920292000
$HCl•H_2O$			
Total energy = -537.2463179 Hartrees			
Nuclear repulsion energy = 46.2018511188 Hartrees			
17	-1.214515000	-0.000006000	0.007308000
1	0.078915000	0.000393000	-0.070829000
8	1.972394000	0.000031000	-0.084238000
1	2.393936000	-0.767431000	0.310107000
1	2.394755000	0.766898000	0.310388000
$CH_3Cl•H_2O$			
Total energy =-576.5434844 Hartrees			
Nuclear repulsion energy = 103.1088565394 Hartrees			
6	0.769266000	1.150709000	-0.002075000
1	1.275374000	1.525787000	-0.883827000
1	1.237927000	1.524893000	0.900490000
1	-0.287677000	1.391180000	-0.023882000
17	0.925331000	-0.633746000	0.000146000
8	-2.246385000	0.057921000	0.008322000
1	-1.538119000	-0.594834000	0.007328000
1	-3.062657000	-0.440973000	-0.056718000
$CH_3S•H_2O$			
Total energy =-514.4860212 Hartrees			
Nuclear repulsion energy = 99.0927863671 Hartrees			
6	0.648593000	1.134093000	-0.001137000
1	0.074478000	1.352281000	0.900316000
1	1.541726000	1.748659000	-0.046387000
1	-0.014443000	1.341725000	-0.841174000
16	1.034774000	-0.616988000	-0.000414000
8	-2.204959000	-0.021470000	-0.000784000
1	-1.437562000	-0.607270000	0.006813000
1	-2.972473000	-0.596374000	0.000148000

More detail on comparison of Figure 1 with Figures 4 and 5 (for Channel A) and Figure 1 with Figures 6 and 7 (for Channel B)

Inspection of Figure 1, Tables 1 and 2 shows that channels A, B and C′ are exothermic. Channel B is the most exothermic but it has a significant energy barrier (see TS2 in Figure 1 at 15.5 kcal.mol^{-1} at the UM06-2X/aVTZ level). It was important, therefore, to determine if introducing water gave rise to a reduced energy barrier for channel B, the most exothermic channel. Hence, in this work DMS + Cl + H_2O calculations only considered channels A, B and C′ as channel C (which produces of CH_3SCl + CH_3) is endothermic ($\Delta H^{\phi}_{f,298}$ = 8.05 ± 1.66 kcal.mol^{-1}; Table 1).

The energy profiles computed at the UM06-2X/aVTZ level of channel A via pathways (a) (DMS•H_2O +Cl) and (c) (DMS•Cl + H_2O) are shown in Figures 4 and 5, respectively. As can be seen, in each case, the reaction proceeds via a number of energy minima as well as a submerged TS (TS1 in each case). The computed relative energies, enthalpies($\Delta H^{\phi}_{f,298K}$) and free energies ($\Delta G^{\phi}_{f,298K}$) of these stationary points at the UM06-2X, UCCSD(T)/CBS//UM06-2X/aVTZ, and DLPNO-UCCSD(T)/CBS//UM06-2X/aVTZ levels are shown in Table 5. The lowest energy transition state in these figures is TS1.H_2O-B. It is interesting to note that TS1•H_2O-B (in Figure 4) has a very similar structure with similar geometrical parameters to TS1 (in Figure 1), indicating that the presence of the water molecule does not affect the transition state structure significantly (see the structures of TS1 and TS1•H_2O-B in Figures 2 and 8 respectively). Their relative energies are also comparable (-8.9 and -11.1 kcal.mol^{-1} at the DLPNO-UCCSD(T)/CBS//UM06-2X/aVTZ level) with TS1•H_2O-B lower than TS1 by 2.2 kcal.mol^{-1} and this can be explained by the additional stabilisation provided by the water molecule in TS1•H_2O-B via the S---H and O---H hydrogen bonds.

The corresponding information for channel B is shown in Figures 6 and 7, and Table 6. The hydrated TSs along with their selected geometrical parameters are illustrated in Figure 8. On inspection of these figures, it is immediately obvious that Figures 6 and 7 have significant energy barriers, with the pathway via DMS•H_2O + Cl (Figure 6) having a lower energy barrier than the pathway via DMS•Cl + H_2O (Figure 7). In Figure 6, the relative energy of TS2•H_2O-A is 9.8 kcal.mol^{-1} with the UM06-2X/aVTZ method and 13.6 kcal.mol^{-1} with the DLPNO-UCCSD(T)/CBS//UM06-2X/aVTZ method, and in Figure 7, the corresponding values for TS2•H_2O-C are 31.7 (UM06-2X/aVTZ) and 35.7 kcal.mol^{-1} (DLPNO-UCCSD(T)/CBS//UM06-2X/aVTZ). This relative energy of TS2•H_2O-A of 13.6 kcal.mol^{-1} compares with the relative energy of TS2 in channel B of the DMS + Cl reaction of 18.3

kcal.mol^{-1}, both at the DLPNO-UCCSD(T)/CBS//UM06-2X/aVTZ level. TS2 and TS2•H2O-A also have similar structures with similar geometrical parameters for the CH_3S---CH_3—Cl units (see Figure S2 and Figure 8).

The hydrated form of DMS•Cl (adduct 1 formed in channel C′ of the DMS + Cl reaction) can be formed via DMS•H_2O reacting with Cl, as shown in Figure 4, and from DMS•Cl reacting with H_2O, as shown in Figure 5. The hydrated form of adduct 1 formed from DMS•H_2O + Cl (DMS•H_2O•Cl-1 in Figure 4) has a relative energy of -26.0 kcal.mol^{-1} at the UM06-2X/aVTZ level (-22.8 kcal.mol^{-1} at the DLPNO-UCCSD(T)/CBS//UM06-2X/aVTZ level) (see Table 5). Formation of DMS•Cl•H_2O via DMS•Cl is shown in Figure 5 and is denoted as DMS•H_2O•Cl-2. This also occurs in Figure 7 (channel B, pathway (c)). It has relative energies of -29.9 and -26.5 kcal.mol^{-1} at the UM06-2X/aVTZ and DLPNO-UCCSD(T)/CBS//UM06-2X/aVTZ levels, respectively (see Table 6).

Inspection of Tables 5 and 6 indicates that the relative energies calculated from the UM06-2X/aVTZ method are lower than the higher level CBS values (by less than 5 kcal.mol^{-1}) except for MS1•H_2O-1 and MS1•H_2O-2 where the UM06-2X/aVTZ relative energies are slightly higher than the CBS values by ~1 kcal.mol^{-1}. Also, the differences between the extrapolated UCCSD(T)/CBS and DLPNO-UCCSD(T)/CBS values are less than 1.5 kcal.mol^{-1}. It is also worth pointing out that the T1 diagnostic value for each of the transition states is less than 0.02, the recommended upper limit to ensure low multireference character.