Supplementary Information

Atmospheric reaction of methanethiol with hydroxyl radicals and chlorine atoms: implications for atmospheric sulfur cycle and HONO formation

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S1. Calculation details on the standard gas-phase concentration

The standard gas-phase concentration (c^0) is calculated as follows, based on the ideal gas law:

$$PV = nRT \quad \Rightarrow \quad \frac{n}{V} = \frac{P^0}{RT} \tag{S1}$$

$$N = nN_A \Rightarrow \frac{N}{V} = \frac{n}{V}N_A \tag{S2}$$

$$c^0 = \frac{N}{V} \Rightarrow c^0 = \frac{P^0 N_A}{RT} \tag{S3}$$

where P^0 is the standard atmospheric pressure (P^0 = 0.101325 J cm^{-3}), R is the universal gas constant (R = 8.314 J mol^{-1} K^{-1}), T is the absolute temperature (T = 298 K), N_A *is* the Avogadro's number (N_A = 6.02214076×10^{23} mol^{-1}), n is the number of moles of gas, V is the volume of gas, and N is the number of molecules of gas.

$$c^0 = \frac{0.101325\ \text{J cm}^{-3} \times 6.02214076\times10^{23}\ \text{mol}^{-1}}{8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 298\ \text{K}} = 2.46\times10^{19}\ \text{molecule cm}^{-3}$$

S2. Wigner tunneling coefficient

The Wigner tunneling coefficient (κ) is calculated as follows:

$$\kappa = 1+\frac{1}{24}\left(\frac{h\nu^{\pm}}{k_B T}\right)^2 \tag{S4}$$

where h is the Planck constant, $\nu^{\pm}$ is the imaginary frequency of the transition state, k_B is the Boltzmann constant, and T is the absolute temperature.

CH_3SH + $^{\bullet}OH/Cl^{\bullet}$ reaction pathways

$CH_3SH + {}^{\bullet}OH \rightarrow CH_3SH\ldots OH\ (RC1) \rightarrow TS1 \rightarrow CH_3S^{\bullet} + H_2O\ (PC1)$ (RS1)

$CH_3SH + {}^{\bullet}OH \rightarrow CH_3SH\ldots OH\ (RC2) \rightarrow TS2 \rightarrow {}^{\bullet}CH_2SH + H_2O\ (PC2)$ (RS2)

$CH_3SH\ldots H_2O \rightarrow CH_3SH\ldots H_2O + {}^{\bullet}OH \rightarrow CH_3SH\ldots H_2O\ldots OH\ (RCW1) \rightarrow TSW1 \rightarrow CH_3S^{\bullet} + 2H_2O\ (PCW1)$ (RS3)

$CH_3SH\ldots H_2O \rightarrow CH_3SH\ldots H_2O + {}^{\bullet}OH \rightarrow CH_3SH\ldots H_2O\ldots OH\ (RCW2) \rightarrow TSW2 \rightarrow {}^{\bullet}CH_2SH + 2H_2O\ (PCW2)$ (RS4)

$CH_3SH + Cl^{\bullet} \rightarrow CH_3SH\ldots Cl\ (RC3) \rightarrow TS3 \rightarrow CH_3S^{\bullet} + HCl\ (PC3)$ (RS5)

$CH_3SH + Cl^{\bullet} \rightarrow CH_3SH\ldots Cl\ (RC4) \rightarrow TS4 \rightarrow {}^{\bullet}CH_2SH + HCl\ (PC4)$ (RS6)

$CH_3SH\ldots H_2O \rightarrow CH_3SH\ldots H_2O + Cl^{\bullet} \rightarrow CH_3SH\ldots H_2O\ldots Cl\ (RCW3) \rightarrow TSW3 \rightarrow CH_3S^{\bullet} + HCl + H_2O\ (PCW3)$ (RS7)

$CH_3SH\ldots H_2O \rightarrow CH_3SH\ldots H_2O + Cl^{\bullet} \rightarrow CH_3SH\ldots H_2O\ldots Cl\ (RCW4) \rightarrow TSW4 \rightarrow {}^{\bullet}CH_2SH + HCl + H_2O\ (PCW4)$ (RS8)

Table S1. Electronic energies with zero-point energy correction (ΔE+ZPE), enthalpies (ΔH) and Gibbs free energies (ΔG) of relevant intermediate species involved in the $CH_3SH + {}^{\bullet}OH$ reaction in the absence and presence of water, calculated relative to the energies of the separate reactants with the DLPNO-CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pV(T+d)Z method. ΔG are calculated at 1 atm and 298 K. Energy units are kcal mol^{-1}.

Species	*ΔE*	*ΔE+ZPE*	*ΔH*	*ΔG*
In the absence of water				
$CH_3SH + {}^{\bullet}OH$	0.00	0	0	0
RC1	-5.45	-2.37	0.27	8.35
TS1	-1.15	-1.00	-1.41	6.05
PC1	-37.32	-34.28	-31.18	-25.24
RC2	-5.45	-2.37	0.27	8.35
TS2	2.99	2.79	1.91	10.02
PC2	-24.39	-22.67	-20.64	-14.40
In the presence of water				
$CH_3SH + {}^{\bullet}OH + H_2O$	0	0	0	0
$CH_3SH\ldots H_2O + {}^{\bullet}OH$	-4.49	-2.41	-0.22	6.58

RCW1	-4.15	-1.73	-4.35	5.90
TSW1	-1.86	-1.50	-1.74	4.50
PCW1	-40.04	-36.14	-33.20	-24.02
RCW2	-7.05	-5.36	-5.28	5.45
TSW2	0.11	-0.42	-2.35	7.90
PCW2	-29.05	-27.36	-26.58	-16.93

Table S2. Electronic energies with zero-point energy correction (ΔE+ZPE), enthalpies (ΔH) and Gibbs free energies (ΔG) of relevant intermediate species involved in the $CH_3SH + Cl^{\bullet}$ reaction in the absence and presence of water, calculated relative to the energies of the separate reactants with the DLPNO-CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pV(T+d)Z method. *ΔG* are calculated at 1 atm and 298 K. Energy units are kcal mol^{-1}.

Species	*ΔE*	*ΔE+ZPE*	*ΔH*	*ΔG*
$CH_3SH + Cl^{\bullet}$	0	0	0	0
RC3	-13.91	-12.40	-11.08	-0.17
TS3	-3.82	-5.23	-6.85	3.49
PC3	-18.98	-20.03	-20.95	-15.99
RC4	-13.91	-12.40	-11.08	0.03
TS4	0.32	-2.77	-6.29	5.13
PC4	-6.10	-8.97	-11.15	-7.49
$CH_3SH + Cl^{\bullet} + H_2O$	0	0	0	0
$CH_3SH\cdots H_2O + Cl^{\bullet}$	-4.49	-2.41	-0.22	6.58
RCW3	-18.32	-17.17	-16.68	-4.18
TSW3	-5.06	-6.85	-9.27	2.78

PCW3	-19.38	-20.25	-21.16	-15.01
RCW4	-1.34	-0.51	0.11	9.87
TSW4	-0.16	-3.56	-7.66	3.89
PCW4	-6.24	-9.46	-12.52	-6.25

Table S3. Rate coefficients (cm^3 $molecule^{-1}$ s^{-1}), k_{R2}, k_{R3}, k_{R4}, and k_{R5}, of pathways R2, R3, R4, and R5, respectively, over the temperature range of 260-360 K.

T (K)	k_{R2}	k_{R3}	k_{R4}	k_{R5}
260	2.56×10^{-11}	1.23×10^{-14}	1.55×10^{-9}	1.62×10^{-12}
270	2.27×10^{-11}	1.41×10^{-14}	1.01×10^{-9}	1.36×10^{-12}
280	2.03×10^{-11}	1.61×10^{-14}	6.80×10^{-10}	1.16×10^{-12}
290	1.84×10^{-11}	1.82×10^{-14}	4.70×10^{-10}	9.96×10^{-13}
298	1.70×10^{-11}	2.00×10^{-14}	3.55×10^{-10}	8.88×10^{-13}
300	1.67×10^{-11}	2.04×10^{-14}	3.33×10^{-10}	8.67×10^{-13}
310	1.54×10^{-11}	2.27×10^{-14}	2.41×10^{-10}	7.63×10^{-13}
320	1.42×10^{-11}	2.52×10^{-14}	1.79×10^{-10}	6.76×10^{-13}
330	1.32×10^{-11}	2.78×10^{-14}	1.35×10^{-10}	6.04×10^{-13}
340	1.23×10^{-11}	3.04×10^{-14}	1.04×10^{-10}	5.43×10^{-13}
350	1.16×10^{-11}	3.33×10^{-14}	8.08×10^{-11}	4.93×10^{-13}
360	1.09×10^{-11}	3.62×10^{-14}	6.39×10^{-11}	4.51×10^{-13}

Table S4. Computed branching ratios (%) for pathways R2, R3, R4, and R5, of the CH_3SH + $^{\bullet}OH$ reaction over the temperature range of 260-360 K.

T (K)	R2	R3	R4	R5
260	100	0	99.9	0.1
270	99.9	0.1	99.9	0.1
280	99.9	0.1	99.8	0.2
290	99.9	0.1	99.8	0.2
298	99.9	0.1	99.8	0.2
300	99.9	0.1	99.7	0.3
310	99.9	0.1	99.7	0.3
320	99.8	0.2	99.6	0.4
330	99.8	0.2	99.6	0.4
340	99.8	0.2	99.5	0.5
350	99.7	0.3	99.4	0.6
360	99.7	0.3	99.3	0.7

Table S5. Effective rate coefficients (cm^3 $molecule^{-1}$ s^{-1}) for the monohydrated CH_3SH + $^{\bullet}OH$ reaction and the corresponding ratios relative to the bare reaction over 260-360 K.

T (K)	$k_{eff,R4}$	$k_{eff,R5}$	$k_{eff,R4}$ / k_{R2}	$k_{eff,R5}$ / k_{R3}
260	2.56×10^{-11}	1.23×10^{-14}	1.00	1.00
270	2.27×10^{-11}	1.41×10^{-14}	1.00	1.00
280	2.03×10^{-11}	1.61×10^{-14}	1.00	1.00
290	1.84×10^{-11}	1.82×10^{-14}	1.00	1.00
298	1.70×10^{-11}	2.00×10^{-14}	1.00	1.00
300	1.67×10^{-11}	2.04×10^{-14}	1.00	1.00
310	1.54×10^{-11}	2.27×10^{-14}	1.00	1.00
320	1.42×10^{-11}	2.52×10^{-14}	1.00	1.00
330	1.32×10^{-11}	2.78×10^{-14}	1.00	1.00
340	1.23×10^{-11}	3.04×10^{-14}	1.00	1.00
350	1.16×10^{-11}	3.33×10^{-14}	1.00	1.00
360	1.09×10^{-11}	3.62×10^{-14}	1.00	1.00

Table S6. Rate coefficients (cm^3 $molecule^{-1}$ s^{-1}) for the CH_3SH + $Cl^{\bullet}$ reaction, in the absence and presence of water, over the temperature range of 260-360 K.

T (K)	k_{R6}	k_{R7}	k_{R8}	k_{R9}
260	1.63×10^{-9}	5.51×10^{-11}	9.93×10^{-9}	6.48×10^{-10}
270	1.28×10^{-9}	5.16×10^{-11}	6.53×10^{-9}	5.45×10^{-10}
280	1.02×10^{-09}	4.85×10^{-11}	4.43×10^{-9}	4.63×10^{-10}
290	8.28×10^{-10}	4.59×10^{-11}	3.10×10^{-9}	4.00×10^{-10}
298	7.05×10^{-10}	4.41×10^{-11}	2.35×10^{-9}	3.58×10^{-10}

300	6.83×10^{-10}	4.37×10^{-11}	2.22×10^{-9}	3.50×10^{-10}
310	$5.70 \times 1\ 0^{-10}$	4.17×10^{-11}	1.62×10^{-9}	3.08×10^{-10}
320	4.83×10^{-10}	4.00×10^{-11}	1.21×10^{-9}	2.73×10^{-10}
330	4.13×10^{-10}	3.85×10^{-11}	9.23×10^{-10}	2.45×10^{-10}
340	3.58×10^{-10}	3.71×10^{-11}	7.15×10^{-10}	2.21×10^{-10}
350	3.10×10^{-10}	3.59×10^{-11}	5.63×10^{-10}	2.01×10^{-10}
360	2.73×10^{-10}	3.49×10^{-11}	4.48×10^{-10}	1.84×10^{-10}

Table S7. Computed branching ratios (%) for $CH_3SH + Cl^{\bullet}$ reaction in the absence and presence of water over the temperature range of 260-360 K.

T (K)	R6	R7	R8	R9
260	96.7	3.3	93.9	6.1
270	96.1	3.9	92.3	7.7
280	95.5	4.5	90.5	9.5
290	94.7	5.3	88.6	11.4
298	94.1	5.9	86.8	13.2
300	94.0	6.0	86.4	13.6
310	93.2	6.8	84.0	16.0
320	92.4	7.6	81.6	18.4
330	91.5	8.5	79.0	21.0
340	90.6	9.4	76.4	23.6
350	89.6	10.4	73.7	26.3
360	88.7	11.3	70.9	29.1

Table S8. Effective rate coefficients (cm^3 $molecule^{-1}$ s^{-1}) for the monohydrated CH_3SH + $Cl^{\bullet}$ reaction and the corresponding ratios relative to the bare reaction over 260-360 K.

T (K)	$k_{eff,R8}$	$k_{eff,R9}$	$k_{eff,R8}/k_{R6}$	$k_{eff,R9}/k_{R7}$
260	1.63×10^{-9}	5.51×10^{-11}	1.00	1.00
270	1.28×10^{-9}	5.16×10^{-11}	1.00	1.00
280	1.02×10^{-9}	4.85×10^{-11}	1.00	1.00
290	8.28×10^{-10}	4.59×10^{-11}	1.00	1.00
298	7.05×10^{-10}	4.41×10^{-11}	1.00	1.00
300	6.83×10^{-10}	4.37×10^{-11}	1.00	1.00
310	$5.70 \times 1\ 0^{-10}$	4.17×10^{-11}	1.00	1.00
320	4.83×10^{-10}	4.00×10^{-11}	1.00	1.00
330	4.13×10^{-10}	3.85×10^{-11}	1.00	1.00
340	3.58×10^{-10}	3.71×10^{-11}	1.00	1.00
350	3.10×10^{-10}	3.59×10^{-11}	1.00	1.00
360	2.73×10^{-10}	3.49×10^{-11}	1.00	1.00

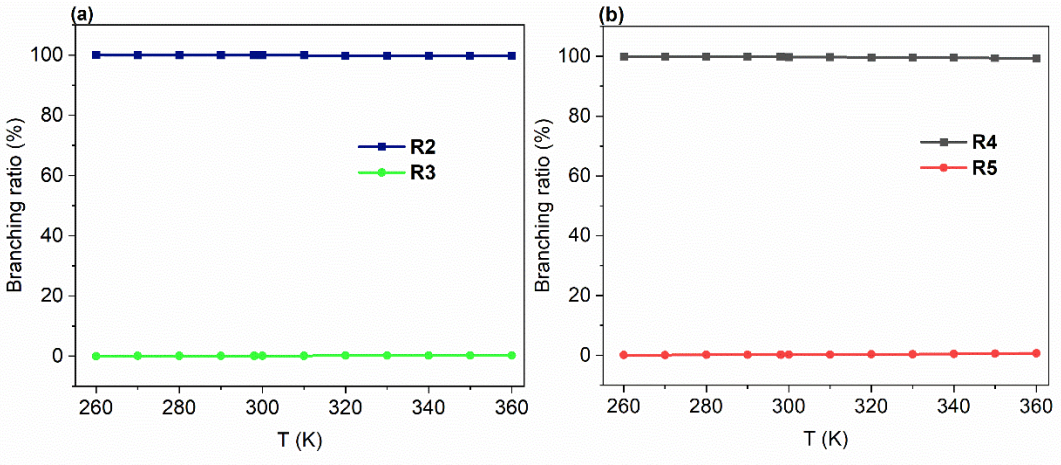

Fig. S1 Computed branching ratios for CH_3SH + $^{\bullet}OH$ reaction (a) in the absence of water and (b) in the presence of water over the temperature range of 260-360 K.

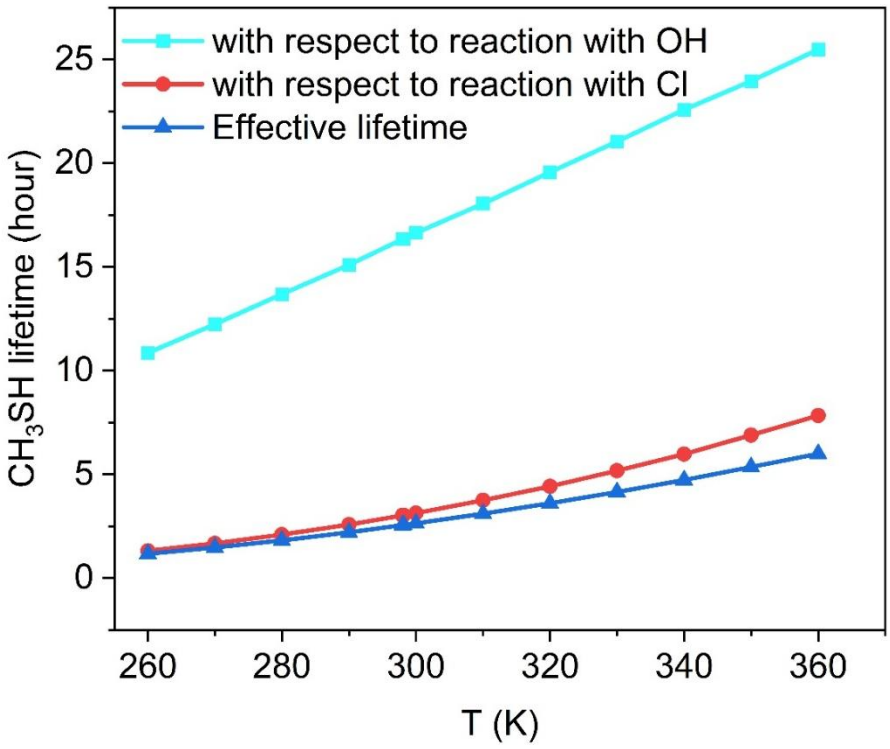

Fig. S2 Lifetime of CH_3SH with respect to its reactions with $^{\bullet}OH$ and $Cl^{\bullet}$.

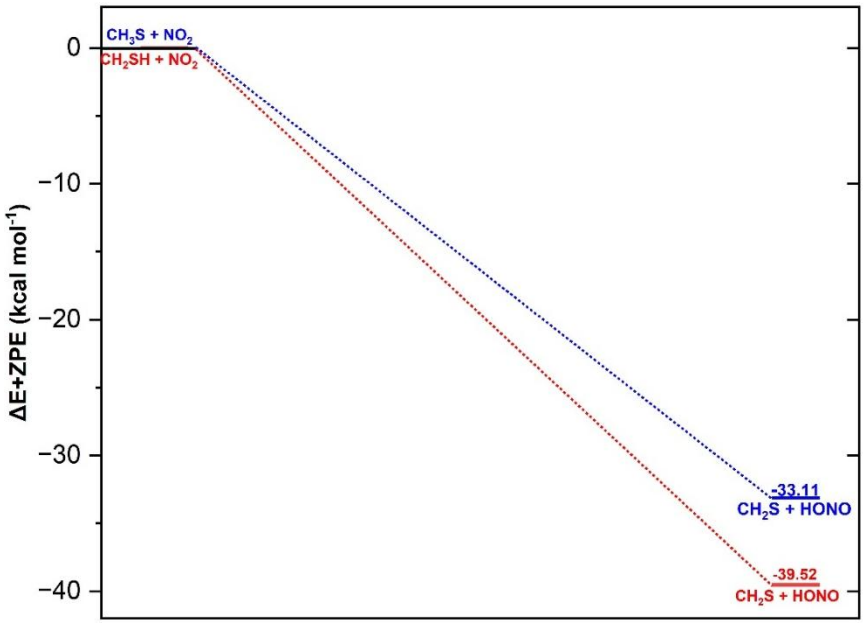

Fig. S3 ZPE-corrected electronic energy profiles of the relevant species involved in $CH_3S^{\bullet} + NO_2$ and $^{\bullet}CH_2SH + NO_2$ reactions, calculated with the DLPNO-CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pV(T+d)Z method with respect to the initial reactants.

Cartesian coordinates of reactants, pre-reactive complexes, transition states, and product complexes involved in the CH_3SH + $^{\bullet}OH/Cl^{\bullet}$ reactions, calculated with the method M06-2X/aug-cc-pV(T+d)Z.

RC1

S	0.26606500	-0.72743100	-0.07866900
C	1.12530700	0.85116200	0.00133000
H	2.11845200	0.72429900	0.42201400
H	0.52298100	1.54470500	0.57845600
H	1.20015500	1.20692900	-1.02240300
H	0.13671800	-0.92772800	1.23440800
O	-1.59713100	0.50783100	0.05550700
H	-2.21013000	-0.07893400	-0.40579900

TS1

S	0.57508600	-0.73745800	-0.00087800
C	1.17947500	0.96565400	0.00088200
H	1.64679900	1.18323700	0.95872300
H	0.34682300	1.64284800	-0.16473100
H	1.91891000	1.08290900	-0.78715300
H	-0.78778000	-0.38616800	0.01351900
O	-2.07081600	0.34171000	-0.00516900
H	-2.83645300	-0.25110300	0.02974400

PC1

S	1.03593700	-0.61509800	-0.00004800
C	0.64783400	1.13088700	0.00077700

H	0.02249500	1.34347100	0.86882700
H	0.03214000	1.34536200	-0.87378100
H	1.54030300	1.74853100	0.00571100
H	-1.44187000	-0.61377900	-0.00160900
O	-2.20475500	-0.02211000	-0.00224500
H	-2.97702400	-0.59045200	0.01491300

RC2

S	-0.26605200	-0.72743000	-0.07866400
C	-1.12532700	0.85114000	0.00132700
H	-0.52301500	1.54469200	0.57844900
H	-2.11846600	0.72425200	0.42202200
H	-1.20020200	1.20690000	-1.02240700
H	-0.13660300	-0.92764700	1.23441400
O	1.59712300	0.50784300	0.05550700
H	2.21008700	-0.07890400	-0.40587000

TS2

S	-1.21718300	-0.32947800	-0.07555600
C	-0.00312100	0.97799500	0.01745600
H	1.05958300	0.54195200	0.08585700
H	-0.13875100	1.61828900	0.88416500
H	-0.05200900	1.55387800	-0.90208600
H	-1.10195900	-0.74514800	1.18974900
O	2.24600200	-0.31241100	0.02430200
H	1.75876800	-1.06600300	-0.34793800

PC2

S	-1.09826600	-0.50761600	-0.03162400
C	-0.61063600	1.13341700	0.02194200

H	1.67944700	0.33782900	-0.60049300
H	0.12753000	1.45847500	0.73712600
H	-1.28596300	1.84635200	-0.42174400
H	-0.01431300	-1.02207100	0.56238600
O	2.21182700	-0.11875900	0.05919200
H	3.03474900	-0.34915100	-0.37647400

RCW1

S	0.36335500	-0.51663400	-0.23990600
C	0.06057100	1.25160300	-0.08405000
H	0.77797500	1.65854300	0.62062200
H	-0.96813800	1.42510500	0.21822700
H	0.23935300	1.67507500	-1.06860100
H	0.19254500	-0.84388500	1.04322200
O	-2.89055500	-0.09608000	0.18721800
H	-3.74342400	-0.52989300	0.11811900
H	-2.26660600	-0.66317700	-0.27730500
H	2.91937100	-0.78209300	-0.15639000
O	2.47453200	-0.05181400	0.29339600

TSW1

S	-0.33676000	0.28352600	0.80109300
C	0.12558400	1.19252700	-0.70174600
H	-0.77404300	1.48668700	-1.24821700
H	0.78785100	0.58703000	-1.32534500
H	0.66267300	2.08662200	-0.36857800
H	-0.94947600	-0.79117300	0.16202800
O	2.66156600	-0.65068300	-0.25409300
H	3.31096500	-1.29266600	0.04721900

H	1.94023300	-0.69775500	0.38728300
H	-2.95999900	-0.49775700	0.07680400
O	-2.33450900	-0.92088600	-0.53818300

PCW1

S	1.26932000	-0.28508700	-0.63550700
C	1.28791900	0.39215400	1.02065900
H	1.04031700	-0.36852400	1.75776000
H	0.49986500	1.14970800	1.03061000
H	2.24199500	0.86091500	1.24453100
H	-0.79083300	-1.34319200	-0.08837700
O	-1.44977900	1.47745000	-0.19871500
H	-2.09213100	1.91087700	-0.76253300
H	-1.79190300	0.58592900	-0.03408400
H	-2.16623700	-2.04466900	-0.02432400
O	-1.67243500	-1.29527200	0.31378700

RCW2

S	-1.62757200	0.24179000	-0.23793000
C	-0.64589800	-1.17913400	0.31869800
H	-1.29113700	-1.97510600	0.67693500
H	0.06463000	-0.88780800	1.08804500
H	-0.09490500	-1.52879000	-0.55148700
H	-2.16495700	0.55208100	0.94570700
O	1.34516200	1.52407300	0.22028500
H	1.66066300	2.31868900	-0.21515600
H	0.40261300	1.44998200	0.00438300
H	2.11224800	-0.14377600	-0.07510500
O	2.30826200	-1.09646200	-0.21761400

TSW2

S	-1.40297800	-0.59307800	-0.13612800
C	-0.90380000	1.00621900	0.48378400
H	-1.54954200	1.80939100	0.14118500
H	0.17675400	1.28768200	0.11023300
H	-0.87378800	0.96028300	1.56827100
H	-1.32337800	-0.29504000	-1.43721800
O	1.86307600	-1.26469800	0.08961700
H	2.18529700	-1.71191200	0.87481900
H	0.91334000	-1.44075600	0.04592500
H	1.79598000	0.63469100	-0.17586000
O	1.45514800	1.54064700	-0.32111800

PCW2

S	-1.48609800	0.17273100	-0.47903600
C	-1.02531500	-0.44727200	1.04883700
H	-0.33816300	0.11676300	1.66002300
H	2.28487900	1.94874700	0.33904300
H	-1.68133200	-1.17880700	1.49240500
H	-0.49109300	1.06643700	-0.58522900
O	1.72835400	-1.35704600	-0.22211300
H	1.59239200	-1.64260000	-1.12887600
H	0.85639200	-1.41858600	0.19420800
H	1.81696300	0.51376000	-0.00504300
O	1.50782300	1.42132400	0.14774000

RC3

S	0.80595200	-0.70863900	-0.08785600
C	1.47848500	0.95939400	0.02096200

H	2.49487800	0.92867400	0.40340700
H	0.83073900	1.56577100	0.64547600
H	1.47418600	1.35110000	-0.99235500
H	0.70906000	-0.94935900	1.22329500
Cl	-1.60441300	0.15798100	0.00000600

TS3

S	0.97993500	-0.72615900	-0.02305000
C	1.52595000	0.98783800	0.00845100
H	1.38049800	1.42288700	0.99200000
H	0.97135500	1.54920300	-0.73924100
H	2.58146000	0.98977200	-0.25570800
H	-0.32406400	-0.48819800	0.60284500
Cl	-1.73199500	0.13046200	-0.01657700

PC3

S	1.46495800	-0.67248300	-0.00117600
C	1.40531100	1.11531400	-0.00394300
H	0.99464100	1.42949600	0.95819100
H	0.70762800	1.45376000	-0.77012600
H	2.38642200	1.55644400	-0.14851300
H	-0.86081800	-0.47701600	0.01092900
Cl	-2.06465100	0.00618600	-0.00047100

RC4

S	-2.23574400	-0.15131900	-0.10320300
C	-0.55184700	0.47469500	0.07217000
H	0.12491900	-0.34529900	0.33653500
H	-0.48376200	1.26046700	0.81806300
H	-0.26387000	0.87482500	-0.89620300

H	-2.40571000	-0.51906300	1.17005100
Cl	2.47714200	-0.09988200	-0.01236600

TS4

S	-1.80452100	-0.32382200	-0.09043800
C	-0.59089500	0.91254000	0.04728400
H	0.55494700	0.37538500	-0.00717400
H	-0.55572800	1.43916700	0.99443400
H	-0.59736600	1.56633100	-0.81827000
H	-1.73301000	-0.77434500	1.16708000
Cl	2.04405100	-0.17062500	-0.01016300

PC4

S	-1.82342400	-0.43366900	-0.08747500
C	-1.01600000	1.06848200	0.04352500
H	1.01697700	0.33171300	-0.09415400
H	-0.85382300	1.52242000	1.00773700
H	-1.02605200	1.68649200	-0.84029900
H	-1.65505900	-0.83841800	1.17600100
Cl	2.22286600	-0.12790600	-0.00652000

RCW3

S	1.09748900	-0.24929000	-0.67368000
C	1.53817100	0.35765200	0.96439200
H	0.67888100	0.86195000	1.39380000
H	2.38787700	1.03065800	0.88492900
H	1.80044300	-0.51304000	1.55820100
H	0.42783200	0.84402900	-1.06856200
O	-1.13108300	1.98498600	-0.07966000
H	-1.51626200	1.10975700	0.07842400

H	-1.86772100	2.58840200	-0.19224700
Cl	-1.15595500	-1.17405400	0.17501600

TSW3

S	1.35374100	-0.56606700	-0.48939200
C	1.52754200	0.68284600	0.78584900
H	1.16607900	1.63962300	0.42181000
H	2.57482800	0.71780600	1.07348100
H	0.93146900	0.36947100	1.64220800
H	-0.10030700	-0.45733800	-0.65115200
O	-1.03325400	2.12375100	-0.25236200
H	-1.48487400	1.30123100	-0.02488500
H	-1.66456300	2.63288200	-0.76435100
Cl	-1.41068900	-1.07256900	0.20217500

PCW3

S	1.36221100	-0.49661600	-0.69797600
C	1.57522500	-0.41774500	1.07608700
H	1.33652200	0.61154300	1.35255300
H	2.60345000	-0.63301500	1.35336400
H	0.88248800	-1.08481300	1.58489000
H	-0.76775500	-0.65969600	-0.39744400
O	-0.02816000	2.11094800	0.03234800
H	-0.88417400	1.66915300	0.07320100
H	-0.16070700	2.88767700	-0.51510500
Cl	-2.00184000	-0.54271200	0.05887300

RCW4

S	-1.32780600	-1.29802000	-0.08136000
C	-0.07269200	0.00211100	0.02230200

H	-0.48924100	0.92740700	0.40961400
H	0.75669400	-0.33564000	0.64733200
H	0.27970000	0.16607900	-0.99309200
H	-1.60183800	-1.36814800	1.22546100
O	-2.82976500	1.63973900	0.02894400
H	-3.73103300	1.92664400	-0.12864600
H	-2.80875400	0.69947500	-0.18637900
Cl	3.05374400	0.33070200	-0.00222800

TSW4

S	1.85284100	-0.23041000	-0.35046100
C	0.72384800	-0.56038600	0.91744700
H	0.85209300	-1.50352500	1.43663800
H	-0.43724000	-0.68511800	0.39908100
H	0.59509300	0.30275600	1.56324800
H	2.06871800	-1.49991100	-0.71453600
O	-0.32633800	2.21546200	0.11329800
H	-0.76709900	2.80650600	-0.49995800
H	-0.79378300	1.37592800	0.02919000
Cl	-1.93503600	-0.67479200	-0.17749200

PCW4

S	1.78557900	-0.29517400	-0.45349900
C	1.02443600	-0.57244100	1.05312000
H	1.21183700	-1.48686000	1.59231100
H	-0.89650200	-0.72671600	0.35018400
H	0.71115300	0.31797700	1.57566200
H	2.20253500	-1.54751000	-0.66995600
O	-0.17288000	2.13638400	0.16240200

H	0.01560500	2.76781400	-0.53482300
H	-0.95155400	1.65116200	-0.13215700
Cl	-2.09564200	-0.58291200	-0.14959900

Cartesian coordinates of reactants, pre-reactive complexes, transition states, and product complexes involved in the $CH_3S^{\bullet}$ + O_2/NO_2 and $^{\bullet}CH_2SH$ + O_2/NO_2 reactions, calculated with the method M06-2X/aug-cc-pV(T+d)Z.

RC5

S	-0.39444300	-0.65071500	-0.00010400
C	-1.75390600	0.51684700	0.00024700
H	-2.65894800	-0.10409400	0.00078100
H	-1.74302300	1.13211500	-0.90442900
H	-1.74223300	1.13250500	0.90464900
O	0.84593100	0.57537900	-0.00056900
O	2.02641000	0.06835000	0.00046600

TS5

S	0.10289900	-0.42380600	-0.46520400
C	1.54023300	0.32836300	0.29895000
H	2.16309600	0.75772700	-0.49417500
H	2.09963900	-0.42998100	0.85632300
H	1.15709100	1.11125300	0.96004700
O	-0.93772100	-0.49651600	0.71051100
O	-1.10072900	0.91798000	-0.16959100

PC5

S	0.20220800	0.00000200	-0.27223900
C	-1.56935200	-0.00001300	0.09682400

H	-1.99086200	0.90962000	-0.33776100
H	-1.64667700	0.00004700	1.18960100
H	-1.99082300	-0.90969500	-0.33769100
O	0.73808300	-1.28092400	0.20379600
O	0.73806100	1.28093400	0.20379500

RC6

S	-1.30350600	-0.60400100	-0.00304700
C	-0.96844100	1.15344800	0.00489300
H	-0.41060600	1.45624700	-0.87845100
H	-0.44962200	1.45825200	0.91088200
H	-1.94004200	1.65232500	-0.01839400
O	2.05848400	0.44031800	-0.00883900
O	1.62489300	-0.66825500	0.00950900

TS6

S	-0.93045800	-0.59301700	-0.00000600
C	-0.93476600	1.05430800	0.00001500
H	0.50091300	1.06814200	-0.00012500
H	-1.13444500	1.59086000	0.92209700
H	-1.13457600	1.59089500	-0.92201800
O	1.56547000	0.53295500	-0.00000800
O	1.21753300	-0.66888900	0.00001400

PC6

S	-1.15980500	-0.62150500	-0.00234900
C	-1.46578100	0.94906200	0.00313600
H	0.93355800	0.95555800	-0.00232400
H	-1.59150300	1.50915700	0.92731100

H	-1.57256300	1.51907400	-0.91742500
O	1.87003700	0.66781200	-0.00361800
O	1.82772200	-0.63457200	0.00502000

RC7

S	0.99489400	-0.29698400	-0.01443600
C	2.58020300	0.34619600	-0.00619400
H	3.38817600	-0.35092600	-0.14505200
H	2.77052700	1.37852900	0.22669300
H	0.32818300	0.84704900	0.16625600
O	-2.18496200	-0.51241400	0.06360600
O	-2.55084000	0.61240300	-0.06107500

TS7

S	0.65706800	-0.44700000	-0.24502100
C	1.82514400	0.53532400	0.23548700
H	2.72585000	0.10718600	0.65170000
H	1.70173400	1.60940600	0.25711700
H	-0.33634300	0.41548600	-0.84092100
O	-1.78397800	0.50330600	-0.31490100
O	-1.41042100	-0.27730900	0.61984100

PC7

S	-1.36732700	-0.51463000	-0.00028200
C	-1.10150000	1.06138900	0.00051500
H	-1.92020200	1.77517500	0.00114300
H	-0.09457600	1.47776100	0.00055900
H	0.77817800	-0.82713400	-0.00116000
O	1.76596300	-0.70869300	0.00092600

O	1.94939000	0.63868500	-0.00081500

$CH_3S^{\bullet} + NO_2$ Reactants

S	0.17014169	-0.03211846	-0.02785060
C	1.70621499	0.90939840	-0.03384760
H	1.98675519	1.07018001	1.01449240
H	1.57761675	1.88755617	-0.50160460
H	2.51474586	0.35613010	-0.51637560
N	7.23699774	0.66106758	-0.01361410
O	6.04492546	0.52337311	-0.01163628
O	8.16173457	-0.10369492	-0.01328072

$CH_3S^{\bullet} + NO_2$ Products

S	1.77891500	-0.68622300	-0.00264100
C	2.11259000	0.87807100	0.00668700
H	-0.49813800	0.04745300	-0.00824800
H	3.13591400	1.24265700	0.01364100
H	1.33042600	1.63410000	0.00629500
N	-2.37840300	0.36841500	0.00098500
O	-1.09985100	0.82866600	-0.00818500
O	-2.45734500	-0.80266300	0.00612800

$^{\bullet}CH_2SH + NO_2$ Reactants

S	2.31743200	1.32085902	0.38509446
C	0.59117115	0.91260660	0.06987301
H	0.46167181	0.43147017	-0.90165383
H	-0.05112669	1.79204892	0.15170182
N	7.72400804	-0.18422314	-0.11387250
O	8.83982349	0.25731051	-0.11189468

O	6.63284576	0.31514121	-0.11353912
H	3.24428164	1.41527310	0.11502832

$^{\bullet}CH_2SH + NO_2$ Products

S	1.94047100	-0.44521600	0.00003800
C	1.68870900	1.13500700	0.00040300
H	2.51741100	1.83737800	0.00032600
H	0.68724700	1.55661100	0.00063800
H	-0.32335900	-1.01135200	0.00012200
N	-1.62647900	0.31438700	-0.00039600
O	-1.30188100	-1.01316600	0.00016100
O	-2.78258700	0.47942400	-0.00032900