Supporting information

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Computational study on the reaction mechanism of CH$_3$CH$_2$S with OH radical

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Table S1 Spin contamination for the species that involved in C_2H_5S+OH reaction

Species	$\langle S^2\rangle$	Species	$(\langle S^2\rangle)$	Species	$(\langle S^2\rangle)$
C_2H_5S	0.7500	OH	0.7500	$^1CH_3CH_2SOH$	0.0001
TS1	0.0001	CH_3	0.7501	SCH_2OH	0.7501
TS2	0.0001	CH_3OH	0.0000	$^1CH_2S$	0.0002
TS3	2.0004	TS4	2.0005	$^3CH_2S$	2.0007
TS5	2.0009	CH_2SOH	0.7505	TS6a	0.0000
TS6b	0.0000	$^1CH_3CHS$	0.0000	H_2O	0.0000
TS7a	0.0000	TS7b	0.0000	$^1CH_2CH_2S$	0.0000
$^3CH_3CH_2SOH$	2.0002	TS8a	2.0000	TS8b	2.0000
$^3CH_3CHS$	2.0000	TS9a	2.0001	TS9b	2.0001
TS9c	2.0001	$^3CH_2CH_2S$	2.0000	TS10	0.0007
HCSOH	0.0000	CH_4	0.0000	TS11	0.0006
CH_2SO	0.0000	TS11-1	0.0005	c-CH_3CHSO	0.0000
TS12	0.0000	CH_2CH_2	0.0000	HSOH	0.0000
TS13	0.0000	CH_3CHSO	0.0002	H_2	0.0000
TS13-1	0.0000	c-CH_3CHSO	0.0007	TS14	0.0008
SO	0.0004	TS15	0.0003	CH_3CH_2SHO	0.0000
CH_3CH_2SH	0.0000	TS16	0.0003	CH_3OH	0.0004

Table S2 Relative energies (ΔE in kcal·mol^{-1}), enthalpies (ΔH(298) in kcal·mol^{-1}), and free energies (ΔG(298) in kcal·mol^{-1}) for the C_2H_5S+OH reaction

| species	ΔE	ΔH	ΔG
C_2H_5S+OH	0.00	0.00	0.00
TS1	24.78	24.19	33.77
P1(CH_3+SCH_2OH)	-5.74	-5.74(-5.14)	-7.53
TS2	18.23	17.64	27.85
P2($CH_3OH+^1CH_2S$)	-53.90	-53.90(-52.16)	-54.78
TS3	31.95	31.35	40.43
TS4	33.34	32.75	41.39
P4($CH_3OH+^3CH_2S$)	10.08	10.08	7.79
TS5	30.02	29.42	36.75
P5(CH_3+CH_2SOH)	-10.91	-10.91(-11.08)	-12.98
$^1CH_3CH_2SOH$	-69.82	-70.41	-59.24
TS6a	-17.88	-18.47	-7.49
TS6b	-17.99	-18.59	-7.62
P6($^1CH_3CHS+H_2O$)	-73.84	-73.84(-72.51)	-73.82
TS7a	-2.04	-2.63	8.69
TS7b	-2.40	-3.00	8.35
P7($^1CH_2CH_2S+H_2O$)	-72.24	-72.24(71.02)	-71.37
$^3CH_3CH_2SOH$	-13.37	-13.97	-3.61
TS8a	-1.24	-1.91	6.46
TS8b	-0.72	-1.45	7.21
P8($^3CH_3CHS+H_2O$)	-24.06	-26.24(-27.37)	-26.91
TS9a	4.73	4.14	12.44
TS9b	1.82	1.22	9.20
TS9c	0.57	-0.02	8.80
P9($^3CH_2CH_2S+H_2O$)	-18.02	-18.02(-17.58)	-19.23
TS10	9.27	8.56	18.00
P10(HCSOH+CH_4)	-20.28	-20.06(-19.79)	-19.79
TS11	4.70	3.40	14.36
P11(CH_2SO+CH_4)	-58.15	-58.15(-57.46)	-57.13
TS11-1+CH_4	-6.04	-6.04	-4.79
c-CH_2SO+CH_4	-37.26	-37.61	-36.33
TS12	-13.28	-14.58	-3.47
P12(CH_2CH_2+HSOH)	-42.69	-42.94(-42.97)	-43.41
TS13	-0.18	-1.90	9.98
P13($CH_3CHSO+H_2$)	-46.88	-46.88(-47.42)	-43.69
TS13-1+H_2	-2.11	-2.11	0.71
c-$CH_3CHSO+H_2$	-31.47	-31.33	-28.26
TS14	11.40	9.84	21.50
P14($CH_2CH_2+SO+H_2$)	2.00	2.59(1.04)	-4.95
TS15	-11.80	-13.08	-2.33
P15(CH_3CH_2SHO)	-51.25	-52.62(-52.09)	-41.61
$CH_3CH_2SH + O$	64.10	64.10	66.31
TS16	20.85	20.25	30.60
P16(CH_3OH+CH_2S)	-53.89	-53.89(-49.94)	-54.77

The values without and with parentheses were the values respectively obtained from CBS-QB3 and CCSD(T)/aug-cc-pVTZ//B3LYP/CBSB7 level of theory.

Table S3 Rate constants ($cm^3 \cdot molecule^{-1} \cdot s^{-1}$) for Channel R6, Channel R12, Channel R13, Channel R15 and the total rate constant in the $C_2H_5S + OH$ reaction

| T(K)	k_{R6}	k_{R12}	k_{R13}	k_{R15}	k_{total}
200	1.82E-13	8.96E-14	2.65E-14	6.62E-14	3.64E-13
236	1.81E-13	8.90E-14	2.19E-14	6.19E-14	3.54E-13
250	1.80E-13	8.86E-14	2.05E-14	6.07E-14	3.50E-13
275	1.79E-13	8.83E-14	1.86E-14	5.92E-14	3.45E-13
298	1.81E-13	8.99E-14	1.73E-14	5.82E-14	3.46E-13
300	1.82E-13	9.01E-14	1.72E-14	5.82E-14	3.48E-13
309	1.84E-13	9.09E-14	1.68E-14	5.79E-14	3.50E-13
325	1.87E-13	9.26E-14	1.61E-14	5.77E-14	3.53E-13
350	1.93E-13	9.59E-14	1.52E-14	5.75E-14	3.62E-13
420	2.17E-13	1.08E-13	1.37E-14	5.85E-14	3.97E-13
500	2.55E-13	1.27E-13	1.31E-14	6.15E-14	4.57E-13
600	3.19E-13	1.57E-13	1.33E-14	6.75E-14	5.57E-13
800	5.00E-13	2.41E-13	1.55E-14	8.50E-14	8.42E-13
1000	7.62E-13	3.58E-13	1.96E-14	1.09E-13	1.25E-12
1200	1.11E-12	5.13E-13	2.53E-14	1.40E-13	1.79E-12
1250	1.22E-12	5.58E-13	2.70E-14	1.48E-13	1.95E-12
1500	1.83E-12	8.25E-13	3.72E-14	1.98E-13	2.89E-12
1750	2.62E-12	1.17E-12	5.03E-14	2.60E-13	4.10E-12
2000	3.60E-12	1.59E-12	6.66E-14	3.33E-13	5.59E-12
2250	4.79E-12	2.09E-12	8.62E-14	4.20E-13	7.39E-12
2500	6.20E-12	2.69E-12	1.10E-13	5.19E-13	9.52E-12
2750	7.83E-12	3.38E-12	1.37E-13	6.33E-13	1.20E-11
3000	9.71E-12	4.18E-12	1.68E-13	7.61E-13	1.48E-11

Table S4 The branching ratios of channel R6, R12, R13 and R15 in the $C_2H_5S + OH$ reaction
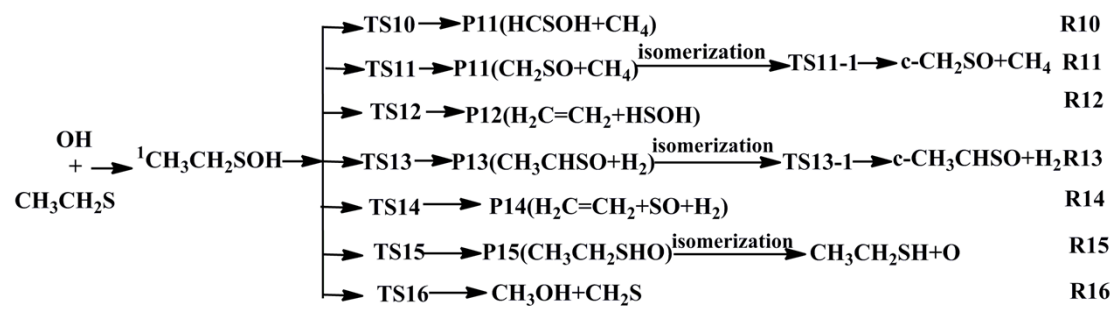
T(K)	k_{R6}/k_{total}	k_{R12}/k_{total}	k_{R13}/k_{total}	k_{R15}/k_{total}
200	0.50	0.25	0.07	0.18
236	0.51	0.25	0.06	0.17
250	0.51	0.25	0.06	0.17
275	0.52	0.26	0.05	0.17
298	0.52	0.26	0.05	0.17
300	0.52	0.26	0.05	0.17
309	0.53	0.26	0.05	0.17
325	0.53	0.26	0.05	0.16
350	0.53	0.27	0.04	0.16
420	0.55	0.27	0.03	0.15
500	0.56	0.28	0.03	0.13
600	0.57	0.28	0.02	0.12
800	0.59	0.29	0.02	0.10
1000	0.61	0.29	0.02	0.09
1200	0.62	0.29	0.01	0.08
1250	0.62	0.29	0.01	0.08
1500	0.63	0.29	0.01	0.07
1750	0.64	0.29	0.01	0.06
2000	0.64	0.28	0.01	0.06
2250	0.65	0.28	0.01	0.06
2500	0.65	0.28	0.01	0.05
2750	0.65	0.28	0.01	0.05
3000	0.66	0.28	0.01	0.05
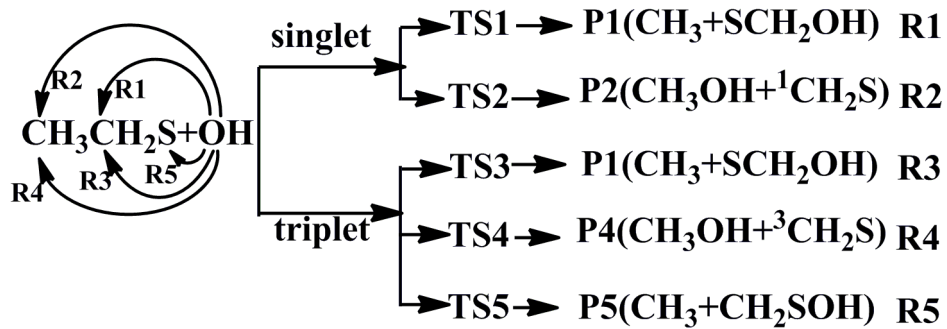
Scheme S1 Brief description of the processes for nucleophilic substitution reaction of C_2H_5S+OH on the singlet and triplet PES
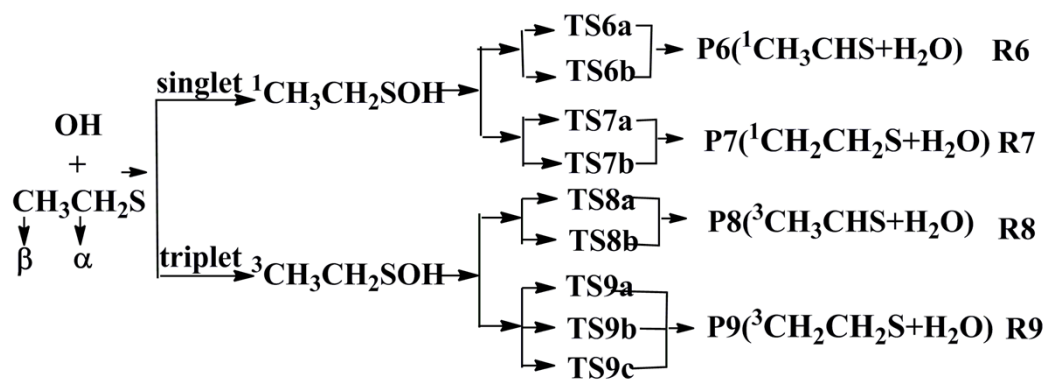
Scheme S2 Brief description of the processes for the formation of H_2O involves in the addition-elimination reaction of C_2H_5S+OH on the singlet and triplet PES

The scheme shows:

OH + CH_3CH_2S (β α) →

singlet $^1CH_3CH_2SOH$ →
- TS6a / TS6b → P6($^1CH_3CHS+H_2O$) R6
- TS7a / TS7b → P7($^1CH_2CH_2S+H_2O$) R7

triplet $^3CH_3CH_2SOH$ →
- TS8a / TS8b → P8($^3CH_3CHS+H_2O$) R8
- TS9a / TS9b / TS9c → P9($^3CH_2CH_2S+H_2O$) R9

$$\text{OH} + \xrightarrow{} \,^1\text{CH}_3\text{CH}_2\text{SOH} \xrightarrow{}$$

$$\text{CH}_3\text{CH}_2\text{S}$$

→TS10 →P11(HCSOH+CH$_4$) R10

→TS11 →P11(CH$_2$SO+CH$_4$) $\xrightarrow{\text{isomerization}}$ TS11-1 → c-CH$_2$SO+CH$_4$ R11

→ TS12 →P12(H$_2$C=CH$_2$+HSOH) R12

→TS13 →P13(CH$_3$CHSO+H$_2$) $\xrightarrow{\text{isomerization}}$ TS13-1 → c-CH$_3$CHSO+H$_2$ R13

→ TS14 → P14(H$_2$C=CH$_2$+SO+H$_2$) R14

→ TS15 →P15(CH$_3$CH$_2$SHO) $\xrightarrow{\text{isomerization}}$ CH$_3$CH$_2$SH+O R15

→ TS16 → CH$_3$OH+CH$_2$S R16

Scheme S3 Brief description of the processes for the formation of CH$_4$, H$_2$, O and CH$_3$OH involves in the addition-elimination reaction of C$_2$H$_5$S+OH on the singlet PES
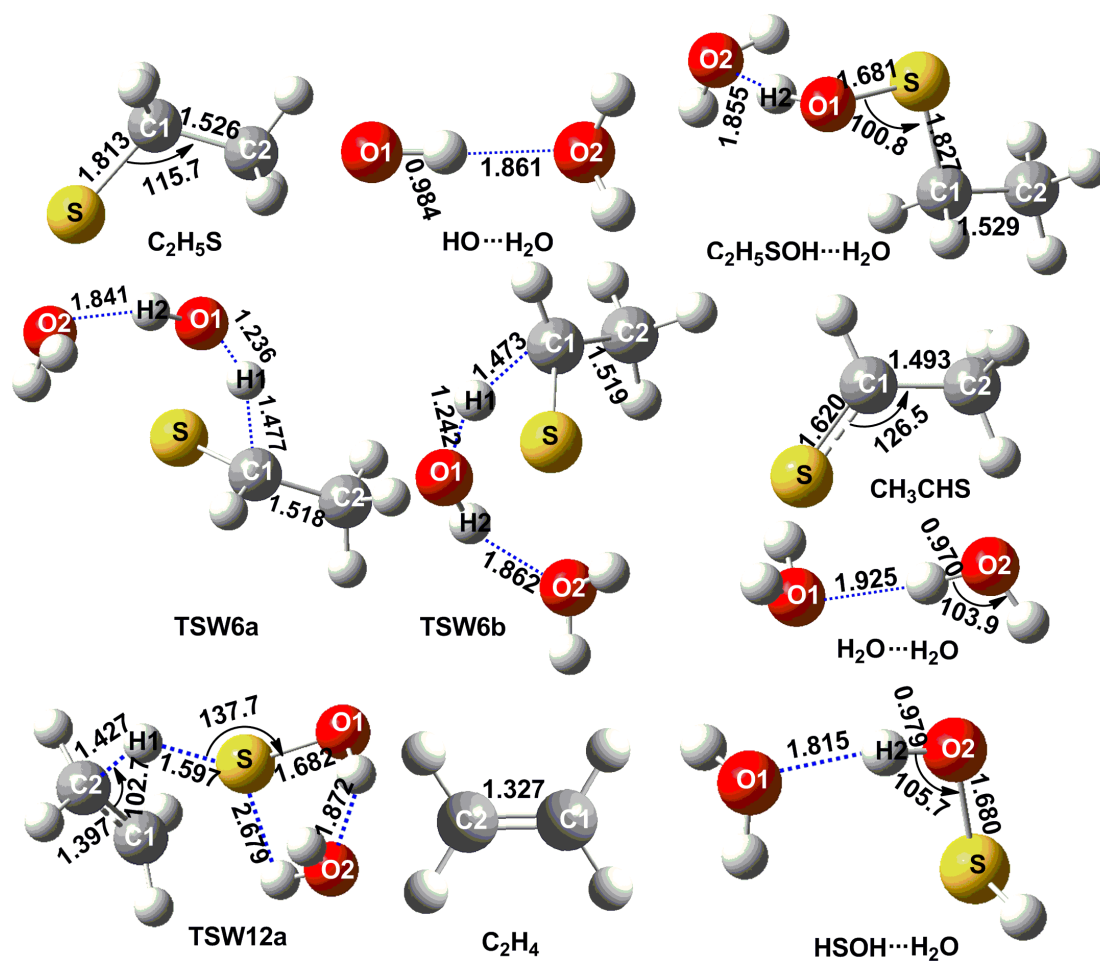
Figure S1 The geometrical structures of the optimized transition states products involving water-catalyzed the formation of H_2O and HSOH

Figure S2 Schematic energy diagram for water-catalyzed channels of H_2O and HSOH formation in the addition-elimination reaction of C_2H_5S+OH at the CBS-QB3 level of theory
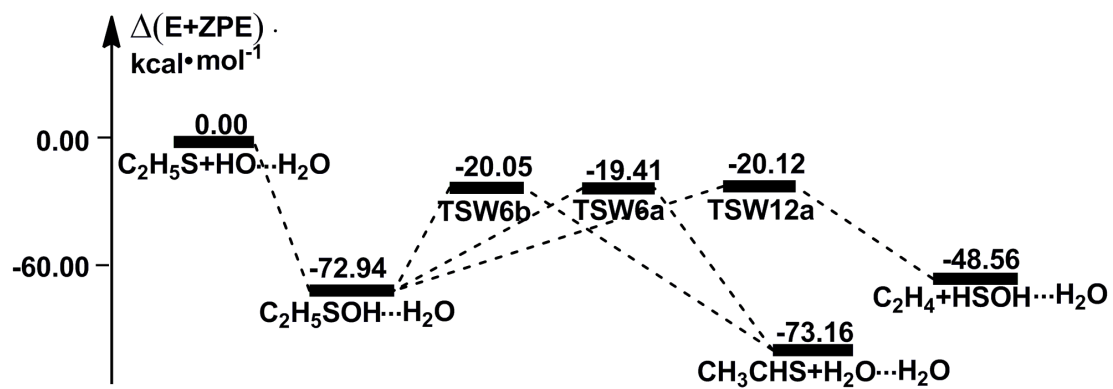
Table S5 Relative energies (ΔE in kcal·mol^{-1}), enthalpies (ΔH(298) in kcal·mol^{-1}), and free energies (ΔG(298) in kcal·mol^{-1}) for water-catalyzed channels of H$_2$O and HSOH formation in the addition-elimination reaction of C$_2$H$_5$S+OH at the CBS-QB3 level of theory

species	ΔE	ΔH	ΔG
C$_2$H$_5$S+HO···H$_2$O	0.00	0.00	0.00
C$_2$H$_5$SOH···OH$_2$	-72.94	-73.53	-61.84
TSW6a	-19.41	-20.01	-7.80
TSW6b	-20.05	-20.64	-7.50
CH$_3$CHS+H$_2$O···H$_2$O	-73.16	-73.16	-74.39
TSW12a	-20.12	-20.72	-7.72
C$_2$H$_4$+HSOH···H$_2$O	-48.56	-48.56	-47.76

The values without and with parentheses were the values respectively obtained from CBS-QB3 and CCSD(T)/aug-cc-pVTZ//B3LYP/CBSB7 level of theory.

The geometrical structures of the optimized transition states products involving water-catalyzed the formation of H$_2$O and HSOH were showed in Figure S1, meanwhile schematic energy diagram for water-catalyzed channels of H$_2$O and HSOH formation in the addition-elimination reaction of C$_2$H$_5$S+OH at the CBS-QB3 level of theory were displayed in Figure S2. Besides, relative energies (ΔE in kcal·mol^{-1}), enthalpies (ΔH(298) in kcal·mol^{-1}), and free energies (ΔG(298) in kcal·mol^{-1}) for water-catalyzed channels of H$_2$O and HSOH formation were involved in Table S5. As seen in Fig. S1 and Fig. S2, the hydrogen abstraction reaction of Channel RW6 and RW12, processes which were similar to the corresponding formations of $_{H2}$O and HSOH without a water molecule (Channel R6 in Fig. 3, Channel R12 in Fig. 5). From a geometric point of view, compared with TS6a, TS6b and TS12 in Fig.3 and Fig. 5, the water molecule in tthe corresponding transition states TSW6a, TSW6b and TSW12 did not change their features. The positive catalytic effect computed for TSW6a, TSW6b and TSW12 could be addressed at an additional stabilization originated by the one hydrogen bond (H(2)···O(4) and H(4)···O(2)) of water molecule, which would not have had a direct effect on the reaction side.

Table S6 Rate constants ($cm^3 \cdot molecule^{-1} \cdot s^{-1}$) for Channel RW6, Channel RW12, the total rate constant $k_{total}(w)$ and the effective rate constant $k_{total}'(w)$ in the $C_2H_5S + OH$ reaction with a water molecule

T(K)	k_{R6w}	k_{R12w}	$k_{total}(w)$	k_{total}	$K_{eq}[HO \cdots H_2O]$	$[H_2O]$	$k'_{total}(w)$	$k'_{total}(w)/k_{total}$
200	3.28E-16	3.13E-16	6.41E-16	3.64E-13				
236	3.01E-16	3.01E-16	6.02E-16	3.54E-13				
250	2.95E-16	2.98E-16	5.93E-16	3.50E-13				
275	2.86E-16	2.97E-16	5.84E-16	3.45E-13				
298	2.82E-16	2.99E-16	5.81E-16	3.46E-13	2.02E-19	2.15E+14	2.52E-20	7.29E-08
300	2.82E-16	2.99E-16	5.81E-16	3.48E-13				
309	2.81E-16	3.00E-16	5.81E-16	3.50E-13				
325	2.80E-16	3.04E-16	5.83E-16	3.53E-13				
350	2.80E-16	3.10E-16	5.90E-16	3.62E-13				
420	2.91E-16	3.37E-16	6.29E-16	3.97E-13				
500	3.17E-16	3.83E-16	7.01E-16	4.57E-13				
600	3.66E-16	4.61E-16	8.27E-16	5.57E-13				
800	5.13E-16	6.89E-16	1.20E-15	8.42E-13				
1000	7.30E-16	1.02E-15	1.75E-15	1.25E-12				
1200	1.03E-15	1.49E-15	2.51E-15	1.79E-12				
1250	1.11E-15	1.62E-15	2.74E-15	1.95E-12				
1500	1.64E-15	2.46E-15	4.11E-15	2.89E-12				
1750	2.34E-15	3.59E-15	5.93E-15	4.10E-12				
2000	3.24E-15	5.04E-15	8.28E-15	5.59E-12				
2250	4.35E-15	6.86E-15	1.12E-14	7.39E-12				
2500	5.71E-15	9.10E-15	1.48E-14	9.52E-12				
2750	7.34E-15	1.18E-14	1.91E-14	1.20E-11				
3000	9.26E-15	1.50E-14	2.43E-14	1.48E-11				

k_{R6w} and k_{R12w} was the rate constants ($cm^3 \cdot molecule^{-1} \cdot s^{-1}$) for Channel RW6, Channel RW12, respectively; $k_{total}(w) = k_{R6w} + k_{R12w}$; $K_{eq}[HO \cdots H_2O]$ was the equilibrium constant for the processes of $HO + H_2O \rightarrow HO \cdots H_2O$; $k'_{total}(w)$ was the effective rate constants of $k_{total}(w)$; water concentration taken from reference[1];

Beyond the water-catalyzed mechanisms of formations of H_2O and HSOH presented above, the effect of a single water molecule on the C_2H_5S+OH reaction under atmospheric conditions was also described. To meet this goal, Table S6 show the calculated rate constants for different conditions of Channel RW6 and RW12. It can be seen that The computed total rate constant for Channels RW6 (k_{RW6}) and RW12 (k_{RW12}) was 6.41×10^{-16}–2.43×10^{-14} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$, which was much smaller than the corresponding value for the total rate constant (k_{R3}), given that the ratio of k_{RW3a}/k_{R3} was 1.40×10^{-3}–1.76×10^{-3}. Besides, obtain a more complete understanding of the effects of water vapor on the C_2H_5S+OH reaction reaction, it is necessary to compare the effective rates of the naked and water-catalyzed reactions. The rate for the naked reaction was written as

$$v_{Rtotal} = k_{total}[C_2H_5S][OH] \tag{1}$$

while water-catalyzed C_2H_5S+OH reantion via the $HO\cdots H_2O$ + C_2H_5S reaction was written as

$$v\, k_{total}(w) = k_{total}(w)\, [HO\cdots H_2O]\, [C_2H_5S] = k'_{total}(w)\, [C_2H_5S][OH] \tag{2}$$

In these equations, $k'_{total}(w) = k_{total}(w)\, K_{eq}[HO\cdots H_2O]\, [H_2O]$. $K_{eq}[HO\cdots H_2O]$ was the equilibrium constants for the formation of the $HO\cdots H_2O$ complexes. The effective rate constants k'_{RW2a} and k'_{RW3b} depended parametrically on the water concentration and were directly compared to k_{R3}, the rate constant of the naked reaction. Table S6 shows the effective rate constant $k'_{total}(w)$ as well as the ratios of $k'_{total}(w)/k_{total}$ under 298 K. The results show that the effective rate constant of $k'_{total}(w)$ was 2.52×10^{-20} $cm^3\cdot molecule^{-1}\cdot s^{-1}$. The results indicate that water-catalyzed reactions were 8 orders of magnitude slower than the title reaction without water. In general, this finding indicates that a single water molecule has very little effect on the atmospheric C_2H_5S+OH reaction, and the catalytic effect of a single water molecule on the C_2H_5S+OH reaction is negligible under atmospheric conditions.

Reference

[1] Yung, Y. L.; Demore, W. B.; Eds, Photochemistry of Planetary Atmospheres, Oxford Univ, Oxford, 1999.