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Electronic Supplementary Information (ESI)

Reaction Mechanism, Energetics, and Kinetics of the Water-assisted Thioformaldehyde + ·OH Reaction and the Fate of its Product Radical Under Tropospheric Conditions

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This section contains: Tables S1-S19 which present the optimized geometries of all the stationary points, their vibrational frequencies and rotational constants, relative energies with respect to starting reactants, calculated total electronic energies including zero-point energy corrections, and imaginary frequencies of various TSs as discussed in the text at different levels of theory, temperature dependent unimolecular and bimolecular rate constants using the CVT/SCT method, equilibrium constants, tunneling contributions for each reaction path, T1 diagnostic values for all the stationary points in $H_2C(OH)S\bullet + {}^3O_2$ reaction, and the Figure S1 represents the optimized geometries of Thioformaldehyde + ·OH reaction catalyzed by the water dimer molecule.

Table S1: Calculated total electronic energies for reactants, their complexes, transition states (TS), and products at the M06-2X, and CCSD(T) levels. Zero-point energy (ZPE) corrections are given at the M06-2X level.

Species	M06-2X/6-311++G(3df,3pd)	ZPE (M06-2X)	CCSD(T)/aug-cc-pVTZ
H_2CS	-437.451265	0.025006	-436.9412869
•OH	-75.730361	0.008641	-75.6455807
H_2CS••OH (PRC1)	-513.190002	0.036265	-512.5943187
H_2CS••OH (TS1)	-513.181331	0.032292	-512.5851629
H_2CS••OH (PC1)	-513.227658	0.036078	-512.6307718
H_2O	-76.427028	0.021638	-76.3422947
HC•(=S)	-436.795168	0.011890	-436.2836499
H_2CS••OH (TS2)	-513.187341	0.036790	-512.591312
$H_2C(OH)S$•	-513.266523	0.042136	-512.6647303
H_2CS••H_2O (PRC2)	-513.886514	0.049439	-513.291262
H_2O••OH (PRC3)	-152.167302	0.033476	-151.9972549
H_2CS••OH••H_2O (RC1)	-589.630371	0.061087	-588.9501773
H_2CS••OH••H_2O (TS3)	-589.621928	0.057064	-588.9397511
H_2CS••OH••H_2O (TS3a)	-589.615739	0.056524	-588.9291149
H_2CS••OH••H_2O (PC2)	-589.668763	0.061348	-588.9864856
H_2CS••OH••H_2O (RC2)	-589.624544	0.060203	-588.943610
H_2CS••OH••H_2O (TS4)	-589.615348	0.056065	-588.933933
H_2CS••OH••H_2O (PC3)	-589.659501	0.059291	-588.977759
H_2CS••OH••H_2O (TS5)	-589.629268	0.062601	-588.947137
H_2CS••OH••H_2O (RC3)	-589.630616	0.061796	-588.9471347
H_2CS••OH••H_2O (TS5a)	-589.624875	0.061630	-588.9423864
H_2CS••OH••H_2O (PC4)	-589.706694	0.067146	-589.0192577
$H_2C(OH)S$•	-513.266523	0.042136	-512.6647303
H_2O••H_2O	-152.862657	0.046676	-152.6928965
OH••H_2O••H_2O (PRC4)	-228.611512	0.060035	-228.354823
H_2CS••H_2O••H_2O (PRC5)	-590.326773	0.074652	-589.647151
H_2CS••OH••H_2O••H_2O (RC4)	-666.073082	0.086974	-665.303885
H_2CS••OH••H_2O••H_2O (TS6)	-666.065842	0.083654	-665.297569

$H_2CS••OH••H_2O••H_2O$ (PC5)	-666.112142	0.087232	-665.342664
$H_2CS••OH••H_2O••H_2O$ (RC5)	-666.068543	0.085995	-665.302113
$H_2CS••OH••H_2O••H_2O$ (TS7)	-666.053137	0.083535	-665.279326
$H_2CS••OH••H_2O••H_2O$ (PC6)	-666.106260	0.086620	-665.336851
$H_2CS••OH••H_2O••H_2O$ (RC6)	-666.064550	0.085294	-665.299352
$H_2CS••OH••H_2O••H_2O$ (TS8)	-666.055382	0.081510	-665.289117
$H_2CS••OH••H_2O••H_2O$ (PC7)	-666.099760	0.084775	-665.299352

Table S2: Calculated total electronic energies for reactants, their complexes, and transition states (TS) at the MP2 and CCSD(T) levels. Zero-point energy (ZPE) corrections are given at the MP2 level.

Species	MP2/cc-pVTZ	ZPE (MP2)	CCSD(T)/aug-cc-pVTZ
H_2CS	-436.891583	0.024972	-436.9417152
•OH	-75.618907	0.008711	-75.6455525
$H_2CS••OH$ (PRC1)	-512.518378	0.036482	-512.5947951
$H_2CS••OH$ (TS1)	-512.500162	0.032673	-512.586257
$H_2CS••OH$ (PC1)	-512.551384	0.037210	-512.6270905
H_2O	-76.318658	0.021620	-76.3422970
HC•(=S)	-436.226701	0.012905	-436.2802297
$H_2CS••OH$ (TS2)	-512.499762	0.036836	-512.5894836
$H_2C(OH)S•$	-512.594094	0.042307	-512.6649054
$H_2CS••H_2O$ (PRC2)	-513.218497	0.049579	-513.2914224
$H_2O••OH$ (PRC3)	-151.948371	0.033667	-151.997252
$H_2CS••OH••H_2O$ (RC1)	-588.85221	0.061908	-588.9505625
$H_2CS••OH••H_2O$ (TS3)	-588.832517	0.059365	-588.9392949
$H_2CS••OH••H_2O$ (PC2)	-588.887715	0.063454	-588.9831123
$H_2CS••OH••H_2O$ (TS5)	-588.833216	0.063138	-588.9338135
$H_2CS••OH••H_2O$ (RC3)	-588.844097	0.06522	-588.942183
$H_2CS••OH••H_2O$ (TS5a)	-588.833216	0.063138	-588.9454092
$H_2CS••OH••H_2O$ (PC4)	-588.926654	0.067402	-589.0193837

Table S3: Calculated total electronic energies for the $H_2C(OH)S\bullet + {}^3O_2$ reactions and their complexes and transition states (TS) at the M06-2X and CCSD(T) levels. Zero-point energy (ZPE) corrections are given at the M06-2X level.

Species	M06-2X/6-311++G(2d,2p)	ZPE (M06-2X)	CCSD(T)/aug-cc-pVTZ
$H_2C(OH)S\bullet$	-513.258993	0.042194	-512.6648387
${}^3O_2$	-150.313852	0.004003	-150.1403944
TS6	-663.538228	0.042325	-662.7671225
PC4	-663.60814	0.049098	-662.8412152
HC(=S)OH	-512.697427	0.032164	-512.1019881
HO_2	-150.89693	0.014694	-150.7260659
TS7	-663.539405	0.043502	-662.7158848
PC5	-663.548171	0.048536	-662.7834012
CH_2SO_RING	-512.63713	0.031261	-512.0436741
TS8	-663.554217	0.045014	-662.7937784
PC6	-663.617494	0.049446	-662.8507643
RO_2	-663.594356	0.046858	-662.828054
TS9	-663.551433	0.044898	-662.7871173
PC7	-663.576682	0.047027	-662.8166605
SO_2H	-549.073759	0.017117	-548.4628074
CH_2O	-114.490817	0.027079	-114.3425534
TS10	-663.531733	0.048111	-662.7854385
PC8	-663.676242	0.051111	-662.9133113
SO_2	-548.598259	0.007238	-547.9894785
CH_2OH	-115.047343	0.037734	-114.8987756

Table S4. Relative energies ($\Delta E_0^{\ddagger}$, kcal mol^{-1}) obtained for all the stationary points in the H_2CS + ·OH reaction alone and assisted by a single water molecule at various levels of theory.[a]

Stationary point	M06-2X/ 6-311++G(3df,3pd)	MP2/cc-pVTZ	CCSD(T)/aug-cc-pVTZ// M06-2X/ 6-311++G(3df,3pd)[b]	CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ[c]
H_2CS + •OH	0.0	0.0	0.0	0.0
H_2CS••OH (D1)	-3.6	-3.2	-3.0	-3.2
TS1	-0.7	5.8	0.2	0.0
PC1	-27.4	-23.4	-26.0	-22.8
TS2	-1.6	8.7	-0.8	0.6
HC•S + H_2O	-25.5	-21.4	-24.6	-21.6
H_2C(OH)S•	-47.9	-47.1	-43.5	-43.3
H_2CS + •OH + H_2O	0.0	0.0	0.0	0.0
H_2CS••H_2O (D2)	-3.4	-3.3	-3.1	-3.1
H_2O••OH (D3)	-4.2	-4.7	-3.9	-3.6
RC1	-10.0	-10.3	-9.5	-9.0
TS3	-7.2	0.4	-5.5	-3.6
PC2	-33.9	-31.6	-32.2	-28.5
TS3a	-3.7	1.1	0.8	2.3
HC•(=S) + 2 H_2O	-25.5	-21.4	-24.6	-21.6
RC2	-6.9	-4.5	-6.0	-5.5
TS4	-3.7	2.4	-2.5	2.3
PC3	-29.4	-31.6	-28.0	-28.7
TS5	-8.3	2.4	-6.7	-5.0
RC3	-9.7	-3.2	-7.2	-1.7
TS5a	-6.2	4.0	-4.3	-2.7
PC4	-54.1	-53.6	-49.1	-48.8
HC(OH)S• + H_2O	-47.9	-47.1	-43.5	-43.3

[a]All barrier heights are relative to the separated reactants. [b]Corrected using M06-2X ZPE. [c]Corrected using MP2 ZPE.

Table S5. Relative energies ($\Delta E_0^{\ddagger}$, kcal mol^{-1}) obtained for all the stationary points from the $H_2C(OH)S\bullet + {}^3O_2$ reaction at the M06-2X and CCSD(T) levels of theory.[a]

Stationary point	M06-2X/ 6-311++G(2d,2p)	CCSD(T)/aug-cc-pVTZ// M06-2X/ 6-311++G(2d,2p)[b]
TS9	19.3	21.5
PC8	-20.3	-20.8
HC(=S)OH + HO_2	-13.1	-13.9
TS10	19.3	54.4
PC9	17.0	15.2
$CH_2SO\_RING + HO_2$	24.2	22.1
TS11	10.9	6.4
PC10	-26.0	-26.5
RO_2	-13.1	-13.9
TS12	12.6	10.6
PC11	-1.9	-6.6
$SO_2H + CH_2O$	3.9	-1.3
TS12	27.0	13.6
PC12	-61.8	-64.7
$SO_2 + CH_2OH$	-46.4	-52.9

[a]All barrier heights are relative to the separated reactants. [b]Corrected using M06-2X ZPE.

Table S6: Imaginary frequencies of all transition states obtained at the M06-2X/6-311++G(3df,3pd) and MP2/cc-pVTZ levels of theory.

Transition State	M06-2X/6-311++G(3df,3pd)	MP2/cc-pVTZ
H_2CS••OH (TS1)	720	1934
H_2CS••OH (TS2)	281	240
H_2CS••OH••H_2O (TS3)	1000	1954
H_2CS••OH••H_2O (TS3a)	1555	1541
H_2CS••OH••H_2O (TS4)	749	282
H_2CS••OH••H_2O (TS5)	304	282
H_2CS••OH••H_2O (TS5a)	247	241
H_2CS••OH••$2H_2O$ (TS6)	758	
H_2CS••OH••$2H_2O$ (TS7)	762	
H_2CS••OH••$2H_2O$ (TS8)	762	

Table S7: Imaginary frequencies of all transition states at the M06-2X/6-311++G(2d,2p) level of theory.

Transition State	M06-2X/6-311++G(2d,2p)
TS9	2404
TS10	2041
TS11	1197
TS12	1142
TS13	1535

Table S8: Calculated rotational constants (GHz) for monomers, their complexes, and transition states (TS) at the M06-2X and MP2 levels of theory.

Species	A	B	C
H_2CS[a]	291.99	18.85	17.71
•OH[a]	0.00	578.40	578.40
H_2CS••OH (PRC1) [a]	17.92	3.98	3.26
H_2CS••OH (TS1) [a]	32.82	3.46	3.13
H_2CS••OH (PC) [a]	35.96	2.47	2.31
H_2O [a]	919.02	408.08	282.60
HC•S [a]	991.27	20.71	20.28
H_2CS••OH (TS2) [a]	28.39	6.22	5.30
$H_2C(OH)S$• [a]	40.36	5.79	5.27
H_2CS••H_2O (PRC2) [a]	18.42	4.20	3.42
H_2O••OH (PRC3) [a]	375.04	6.86	6.76
H_2CS••OH••H_2O (RC1) [a]	5.43	2.38	1.66
H_2CS••OH••H_2O (TS3) [a]	5.319	2.77	1.83
H_2CS••OH••H_2O (PC2) [a]	6.04	1.95	1.55
H_2CS••OH••H_2O (RC2) [a]	6.98	1.73	1.39
H_2CS••OH••H_2O (TS4) [a]	7.06	1.78	1.43
H_2CS••OH••H_2O (PC3) [a]	7.12	1.79	1.43
H_2CS••OH••H_2O (RC3) [a]	5.21	3.03	2.29
H_2CS••OH••H_2O (TS5) [a]	5.63	3.32	2.49
H_2CS••OH••H_2O (PC4) [a]	5.99	3.57	2.35
H_2O••H_2O [a]	214.3	6.51	6.51
OH••H_2O••H_2O (PRC4) [a]	7.44	6.81	3.60
H_2CS••H_2O••H_2O (PRC5) [a]	5.42	2.17	1.56
H_2CS••OH••H_2O••H_2O (RC4) [a]	3.49	1.52	1.39
H_2CS••OH••H_2O••H_2O (TS6) [a]	3.18	1.63	1.50
H_2CS••OH••H_2O••H_2O (PC5) [a]	3.42	1.24	1.23
H_2CS••OH••H_2O••H_2O (RC5) [a]	2.45	1.84	1.12
H_2CS••OH••H_2O••H_2O (TS7) [a]	4.16	2.07	1.84
H_2CS••OH••H_2O••H_2O (PC6) [a]	2.91	1.65	1.54
H_2CS••OH••H_2O••H_2O (RC6) [a]	4.67	0.99	0.82
H_2CS••OH••H_2O••H_2O (TS8) [a]	3.41	1.20	0.89
H_2CS••OH••H_2O••H_2O (PC7) [a]	3.41	1.02	0.78
H_2CS [b]	291.99	18.85	17.71
•OH [b]	0.00	578.40	578.40
H_2CS••OH (PRC1) [b]	21.34	4.08	3.42
H_2CS••OH (TS1) [b]	38.5	3.57	3.28
H_2CS••OH (PC1) [b]	35.82	2.57	2.41
H_2O [b]	919.02	408.09	282.60
HC•S [b]	943.84	20.67	20.23

$H_2CS••OH$ (TS2) [b]	23.67	5.27	4.44
$H_2C(OH)S•$ [b]	40.36	5.79	5.27
$H_2CS••H2O$ (PRC2) [b]	18.31	3.84	3.18
$H_2O••OH$ (PRC3) [b]	359.52	6.91	6.82
$H_2CS••OH••H_2O$ (RC1) [b]	5.92	2.21	1.61
$H_2CS••OH••H_2O$ (TS3) [b]	7.26	3.60	2.44
$H_2CS••OH••H_2O$ (PC2) [b]	6.76	1.57	1.28
$H_2CS••OH••H_2O$ (RC2) [b]	5.88	2.21	1.61
$H_2CS••OH••H_2O$ (TS4) [b]	5.63	3.32	2.49
$H_2CS••OH••H_2O$ (PC3) [b]	6.88	1.64	1.33
$H_2CS••OH••H_2O$ (RC3) [b]	7.35	2.43	1.83
$H_2CS••OH••H_2O$ (TS5) [b]	5.63	3.32	2.49
H_2CS $••OH••H_2O$ (PC4) [b]	6.00	3.57	2.35

[a]Calculations carried out at M06-2X/6-311++G(3df,3pd) level. [b]Calculations carried out at MP2/ cc-pVTZ level.

Table S9: Calculated rotational constants (GHz) for monomers, their complexes, and transition states (TS) of the products at the M06-2X/6-311++G(2d,2p) theory level for the $H_2C(OH)S\bullet + {}^3O_2$ reaction.

Species	A	B	C
TS9	6.64	1.98	1.59
PC8	6.28	1.85	1.44
HC(=S)OH	57.79	6.76	6.05
HO_2	628.94	34.68	32.87
TS10	5.96	3.04	2.45
PC9	7.27	2.32	2.02
CH_2SO	28.02	11.67	8.73
TS11	5.85	3.33	2.54
PC10	5.40	2.77	1.99
TS12	5.96	3.31	2.40
PC11	5.38	4.19	2.56
SO_2H	56.51	6.61	6.04
CH_2O	282.25	39.25	34.45
TS13	8.92	2.95	2.79
PC12	8.59	3.31	2.83
SO_2	61.13	9.82	8.46
CH_2OH	190.50	29.66	26.72

Table S10: Calculated positive frequencies (cm^{-1}) for monomers, their complexes, and transition states (TSs) at the M06-2X and MP2 levels of theory.

Species	**Frequencies**
H_2CS[a]	1010 1045 1131 1505 3098 3187
OH[a]	3793
H_2CS••OH (PRC1)[a]	126 158 168 320 487 1021 1065 1124 1504 3103 3201 3642
H_2CS••OH (TS1)[a]	-720 16 80 226 634 989 1026 1152 1484 1645 3134 3789
H_2CS••OH (PC1)[a]	103 112 152 230 254 289 864 1238 1619 3154 3855 3967
H_2O	1620 3888 3989
HC•(=S)	818 1251 3151
H_2CS••OH (TS2)[a]	-281 141 259 420 655 998 1014 1064 1497 3112 3208 3781
$H_2C(OH)S$•	263 401 708 737 1108 1174 1290 1379 1455 2999 3100 3884
H_2CS••H_2O (PRC2)[a]	100 147 154 194 308 389 1025 1062 1123 1505 1627 3104 3203 3801 3961
H_2O••OH (PRC3)[a]	134 174 199 410 638 1618 3660 3881 3981
H_2CS••OH••H_2O (RC1)[a]	7 45 130 142 166 207 229 333 454 539 756 1020 1065 1118 1513 1626 3096 3197 3525 3704 3942
H_2CS••OH••H_2O (TS3) [a]	-1000 59 136 153 204 210 220 316 471 591 845 983 1037 1051 1179 1494 1626 3138 3617 3775 3943

$H_2CS••OH••H_2O$ (TS3a) [a]	-1555 104 216 286 381 442 520 591 612 642 695 949 1106 1262 1316 1457 1622 1653 3137 3896 3924
$H_2CS••OH••H_2O$ (PC2) [a]	60 73 114 135 167 182 198 210 325 375 519 668 872 1259 1621 1639 3115 3729 3767 3944 3959
$H_2CS••OH••H_2O$ (RC2) [a]	32 67 122 126 167 177 198 285 307 352 473 1033 1076 1118 1499 1621 3107 3213 3657 3830 3964
$H_2CS••OH••H_2O$ (TS4) [a]	-749 19 53 74 100 131 142 256 277 317 655 1004 1026 1146 1469 1578 1622 3142 3791 3838 3964
$H_2CS••OH••H_2O$ (PC3) [a]	16 33 50 70 101 128 182 203 207 219 243 450 856 1243 1617 1631 3158 3828 3865 3955 3970
$H_2CS••OH••H_2O$ (TS5) [a]	-304 99 148 169 210 218 325 416 546 605 831 1004 1017 1069 1497 1615 3128 3227 3633 3770 3951
$H_2CS••OH••H_2O$ (RC3) [a]	63 96 125 161 205 213 302 325 428 598 656 1012 1055 1109 1504 1618 3114 3210 3625 3755 3949
$H_2CS••OH••H_2O$ (TS5a) [a]	-247 86 121 163 168 217 254 302 457 503 635 1011 1028 1082 1492 1644 3117 3221 3774 3846 3930
$H_2CS••OH••H_2O$ (PC4) [a]	60 124 191 200 262 370 412 661 691 767 1139 1203 1311 1440 1463 1604 2992 3102 3725 3811 3949
$H_2O••H_2O$ [a]	168 199 210 226 244 295 355 491 522 632 878 1613

	1632	3502	3710	3767	3952	3955
$OH••H_2O••H_2O$ (PRC4) [a]	168	199	210	225	244	295
	355	491	521	632	878	1613
	1632	3502	3710	3767	3952	3955
$H_2CS••H_2O••H_2O$ (PRC5) [a]	38	56	145	150	172	198
	210	218	322	367	554	730
	1029	1085	1116	1519	1629	1645
	3093	3197	3679	3723	3939	3953
$H_2CS••OH••H_2O••H_2O$ (RC4) [a]	35	57	69	120	127	164
	207	219	240	256	279	381
	423	530	549	646	869	1007
	1071	1116	1505	1617	1649	3102
	3198	3541	3609	3786	3847	3952
$H_2CS••OH••H_2O••H_2O$ (TS6) [a]	-758	20	47	119	143	178
	197	205	237	304	308	350
	425	526	623	801	862	963
	1069	1139	1316	1597	1634	1665
	3146	3592	3655	3768	3874	3951
$H_2CS••OH••H_2O••H_2O$ (PC5) [a]	34	47	62	103	138	183
	187	200	220	223	247	325
	354	389	478	556	672	835
	876	1244	1622	1639	1655	3137
	3624	3679	3767	3896	3945	3949
$H_2CS••OH••H_2O••H_2O$ (RC5) [a]	32	54	60	108	155	165
	177	194	203	228	292	332
	371	408	516	651	694	1008
	1065	1106	1508	1625	1647	3123
	3223	3430	3706	3749	3952	3955
$H_2CS••OH••H_2O••H_2O$ (TS7) [a]	-762	39	85	127	158	286
	320	400	424	437	463	539
	671	709	814	847	982	1105
	1047	1272	1330	1460	1670	1689
	2341	2488	3159	3639	3947	3959
$H_2CS••OH••H_2O••H_2O$ (PC6) [a]	24	62	79	108	126	160
	167	178	209	229	238	309
	317	367	446	535	551	617
	838	1260	1607	1633	1671	3172
	3721	3761	3828	3912	3943	3946

$H_2CS••OH••H_2O••H_2O$ (RC6) [a]	23 37 43 81 120 150 167 191 198 200 216 262 343 377 458 521 713 1041 1098 1110 1513 1625 1642 3092 3202 3661 3698 3756 3941 3956
$H_2CS••OH••H_2O••H_2O$ (TS8) [a]	-762 25 42 63 79 129 137 153 169 210 217 245 329 362 501 657 710 1000 1054 1137 1465 1568 1625 1637 3103 3703 3765 3789 3940 3953
$H_2CS••OH••H_2O••H_2O$ (PC7) [a]	13 20 57 63 70 105 112 140 186 202 203 212 215 282 327 436 524 689 912 1231 1620 1629 1633 3095 3725 3820 3833 3945 3953 3957
H_2CS [b]	1015 1026 1101 1506 3109 3204
OH [b]	3819
$H_2CS••OH$ (PRC1) [b]	113 141 218 359 493 1024 1040 1100 1504 3120 3224 3677
$H_2CS••OH$ (TS1) [b]	-1934 94 174 235 701 797 1042 1331 1439 1555 3162 3810
$H_2CS••OH$ (PC1) [b]	32 52 127 157 335 520 741 1670 1863 3154 3749 3932
H_2O [b]	1651 3859 3780
HC•(=S) [b]	796 1706 3162
$H_2CS••OH$ (TS2) [b]	-240 61 184 421 569 1025 1032 1180 1524 3143 3241 3788
$H_2C(OH)S•$ [b]	254 400 712 765 1081 1178 1303 1390 1471 3029 3142 3844
$H_2CS••H_2O$ (PRC2) [b]	123 126 158 228 278 468 1029 1047 1100 1500 1661 3117 3225 3769 3932

H_2O••OH (PRC3)[b]	159 161 197 460 648 1648 3690 3849 3966
H_2CS••OH••H_2O (RC1)[b]	47 66 131 154 205 232 241 346 517 577 791 1034 1059 1097 1520 1660 3115 3224 3558 3680 3918
H_2CS••OH••H_2O (TS3) [b]	-1954 72 126 167 202 217 253 292 489 661 721 924 1114 1413 1501 1648 1823 3174 3593 3751 3916
H_2CS••OH••H_2O (TS3b) [b]	-1541 103 221 295 411 447 570 598 641 662 721 966 1158 1304 1454 1496 1675 1693 3155 3823 3871
H_2CS••OH••H_2O (PC2) [b]	60 83 129 153 195 204 215 269 383 461 618 693 869 1663 1678 1912 3095 3638 3688 3914 3931
H_2CS••OH••H_2O (TS5) [b]	-282 56 143 172 221 225 321 471 551 659 846 1026 1040 1195 1523 1651 3152 3251 3586 3716 3919
H_2CS••OH••H_2O (TS5b) [b]	-242 65 128 149 177 228 272 347 454 517 583 1036 1051 1217 1521 1671 3135 3241 3780 3812 3913
H_2CS••OH••H_2O (PC4)[b]	86 108 182 202 277 377 415 676 724 795 1115 1214 1318 1461 1487 1634 3016 3140 3649 3782 3927

[a]Calculations carried out at M06-2X/6-311++G(3df,3pd) level. [b]Calculations carried out at MP2/cc-pVTZ level.

Table S11: Optimized geometries of reactants, reactant complexes, transition states and products involved in the H_2CS + •OH and H_2CS + •OH + H_2O reactions obtained at the MO6-2X /6-311++g(3df,3pd) and MP2/cc-pVTZ levels of theory.

H_2CS[a]

C	-0.01100400	0.00000000	-0.00635700
H	0.02740300	0.00000000	1.07927300
H	0.94836800	0.00000000	-0.51590300
S	-1.39466200	0.00000000	-0.80521300

•OH[a]

O	0.00000000	0.00000000	-0.00543100
H	0.00000000	0.00000000	0.96543100

H_2CS••OH (PRC1)[a]

C	-0.00184600	0.00018400	-0.00897400
H	0.00645600	-0.00210400	1.07671000
H	0.96362600	0.00272900	-0.50765100
S	-1.37223700	0.00049200	-0.83613300
O	1.05609400	0.00683300	-3.07622900
H	0.13403100	0.00540500	-2.74912600

H_2CS••OH (TS1)[a]

C	0.00074000	0.00211700	-0.00028600
H	0.00278500	0.01729600	1.13502900
H	0.99817600	-0.01340300	-0.43419100
S	-1.34008900	0.00657700	-0.84308100
O	-0.28080300	0.16512500	2.62653500
H	-1.23658600	0.29617800	2.51784800

H_2CS••OH (PC1)[a]

C	0.63731200	-0.07919800	-0.23444300
H	1.63106700	-0.06839400	-0.67660000
S	-0.78700000	-0.00889600	-0.84603800
O	1.79197100	0.12359400	-3.07782700
H	1.96734000	0.21059200	-4.01624300
H	0.83411100	0.13189100	-2.99103300

H•C(=S)[a]

C	0.80016800	-0.05169000	-0.46024200
H	1.81632000	-0.00479100	-0.84346600
S	-0.58723300	-0.03366000	-1.14839500

H_2O[a]

O	-1.66816200	0.91440600	0.00000000
H	-0.71031900	0.95152800	0.00000000
H	-1.95290400	1.82970000	0.00000000

H_2CS••OH (TS2)[a]

C	0.00819700	-0.08893800	0.01022900
H	0.03102700	-0.26155100	1.08042200
H	0.97053000	-0.06568900	-0.48853500
S	-1.38674100	-0.01756800	-0.81012400
O	0.05180100	2.10376000	0.36078400
H	-0.10984300	2.41697700	-0.54425700

$H_2C(OH)S$•[a]

C	0.68573200	-0.09809000	0.41611400
H	0.67960400	-0.61081000	1.37747700
H	1.54478100	-0.47879700	-0.15129700
S	-0.74493100	-0.61412200	-0.51651500
O	0.78882500	1.27030100	0.67565800
H	0.55131900	1.75711100	-0.11779100

H_2CS••H_2O (PRC2)[a]

C	0.29728800	0.05855000	-0.19007300
H	0.19457700	-0.09097900	0.88109300
H	1.30453000	0.18211000	-0.57634800
S	-0.97747800	0.09547400	-1.15760400
O	-1.88636600	-0.48515400	1.94367600
H	-2.09440700	-0.33750200	1.01284800
H	-2.71606400	-0.38744300	2.41267000

H_2O••OH (PRC3)[a]

O	-0.00011000	0.00694100	0.01678300
H	0.01659200	-0.00324000	0.99421100
O	0.16386700	-0.00805400	2.88160100
H	0.62611700	-0.73305800	3.30702300
H	0.46611700	0.78979400	3.32033200

$H_2CS••OH••H_2O$ (RC1)[a]

C	-0.41066800	0.07695900	1.49003900
H	-0.62283600	0.08450000	2.55499500
H	0.63611000	0.02234000	1.20073400
S	-1.59904500	0.14240000	0.41667000
O	2.65067700	0.00407200	0.05252600
H	2.07991600	-0.05248400	-0.74663200
O	0.71534200	-0.10485800	-1.93134300
H	0.64584400	0.51376500	-2.66070700
H	-0.10224200	-0.00982400	-1.41805700

$H_2CS••OH••H_2O$ (TS3) [a]

C	-0.00094700	0.00340700	0.00363900
H	-0.00230000	0.02153000	1.09143000
H	1.07566500	-0.00294800	-0.43880700
S	-1.31558800	-0.01845700	-0.88219800
O	2.35753800	-0.06523900	-1.01006600
H	2.04781800	-0.14159800	-1.93562700
O	0.86060600	-0.18444400	-3.42102400
H	0.86978500	0.57628600	-4.00544100
H	0.02055900	-0.13608900	-2.94517100

$H_2CS••OH••H_2O$ (TS3a) [a]

C	-0.08884900	-0.43638000	2.35851500
H	-0.24892000	-0.49264700	3.43377900
H	1.01682100	-0.25359800	1.80172400
S	-1.31902000	-0.64322300	1.38132300
O	0.11156100	-0.77806000	-0.56331100
H	-0.18956200	-0.04655000	-1.11004100
O	1.93722600	-0.07751200	0.81024400
H	2.67853300	-0.68440600	0.85407700
H	1.06317600	-0.44701700	-0.00665100

$H_2CS••OH••H_2O$ (PC2)[a]

C	-0.93593800	-0.18593900	0.68345900
H	0.05712400	-0.29265100	1.12222600
H	2.96741400	0.32194500	0.77278500
S	-2.39162100	-0.34967400	1.18129800
O	2.17382500	-0.16273300	0.54339700
H	1.91828500	0.14307600	-0.33969500

O	0.76907300	0.60729700	-1.78429100
H	0.70950000	0.04124900	-2.55636300
H	-0.03870100	0.44288500	-1.27795000

$H_2CS••OH••H_2O$ (RC2)[a]

C	0.36834900	0.00083600	0.35653400
H	0.17885500	-0.29379300	1.38423900
H	1.40146400	0.09078000	0.03325000
S	-0.84084400	0.29508500	-0.65540300
O	-1.93365600	-0.57627700	2.31406700
H	-2.17802000	-0.31097400	1.42056200
H	-2.75863300	-0.67321100	2.79178300
O	1.92403500	0.78719300	-2.40879200
H	0.96142000	0.74362100	-2.24401400

$H_2CS••OH••H_2O$ (TS4)[a]

C	-0.00251000	-0.13827800	-0.00079200
H	0.00163100	-0.06799700	1.08536000
H	1.03222700	-0.21467500	-0.47408500
S	-1.32098400	-0.13383400	-0.88365100
O	-1.94252700	0.09609800	2.35644100
H	-2.33860100	0.05451700	1.47960100
H	-2.67555200	0.12709300	2.97290600
O	2.25986000	-0.11717100	-1.32957000
H	1.79052800	0.10370200	-2.15003900

$H_2CS••OH••H_2O$ (PC3)[a]

C	-0.14159600	0.08542900	0.18558600
H	-0.23401900	0.09680100	1.26935500
H	1.92998300	0.14793500	-0.79486300
S	-1.18215500	0.03448500	-0.96204200
O	-2.36198300	0.03968800	2.26890900
H	-2.75396000	0.01956500	1.39174600
H	-3.09932800	0.03067800	2.88175600
O	2.72477800	0.17139800	-1.33819900
H	2.40057800	0.15856900	-2.24028100

$H_2CS••OH••H_2O$ (TS5)[a]

O	-0.42939500	-0.05797500	-0.16553300
H	-0.14867500	-0.24717400	0.75305200

O	0.71023300	0.17941300	2.44002600
H	0.54052600	-0.16068200	3.32017700
H	0.39349200	1.09328500	2.43417200
C	0.75045700	1.79637100	-0.25213900
H	0.73491700	1.82183600	-1.33492800
H	1.59347300	1.29015100	0.20472400
S	-0.34204000	2.61201200	0.62826300

$H_2CS••OH••H_2O$ (RC3)[a]

O	-0.55956300	-1.70609900	-0.87160000
H	-0.20245700	-1.76771100	0.03844900
O	0.63221400	-1.18003100	1.66401100
H	0.47447600	-1.50487900	2.55214700
H	0.27444800	-0.28111000	1.63422700
C	0.75048700	0.59949000	-0.95113700
H	0.81483800	0.73687200	-2.02548400
H	1.49504100	-0.05177100	-0.50375000
S	-0.38785300	1.31873900	-0.07943900

$H_2CS••OH••H_2O$ (TS5a)[a]

C	0.00676100	0.06080400	0.00745500
H	0.21623700	-0.12791400	1.05420000
H	0.85690700	0.24731900	-0.64061300
S	-1.51366700	0.18212000	-0.54625900
O	0.74601700	-0.51114600	-3.01369100
H	0.58386000	-1.28731100	-2.46734900
H	-0.08896300	-0.03635900	-2.98706300
O	0.13070000	-2.10986100	-0.55431800
H	-0.72680000	-2.44309400	-0.24169100

$H_2CS••OH••H_2O$ (PC4)[a]

O	-0.01844300	-1.27343500	-0.84546000
H	0.25629500	-1.50205300	0.05509600
O	0.56727000	-1.23037900	1.90922300
H	0.19110000	-1.79439500	2.58784900
H	0.03211700	-0.42722900	1.89667400
C	0.37160600	0.02482700	-1.12179800
H	0.00653500	0.28208300	-2.11533900
H	1.46238100	0.15445000	-1.12895600
S	-0.20068000	1.30206800	0.01415600

H_2O••H_2O[a]

O	2.42913800	-0.77232100	0.64012000
H	2.01453400	-0.89128900	-0.22362600
H	2.84953700	-1.60982800	0.83820400
O	1.06931600	-0.81238300	-1.91249700
H	1.42195000	-0.08106200	-2.42435200
H	0.15688400	-0.57834000	-1.72832800

OH••H_2O••H_2O (PRC4)

O	1.90865500	-0.52587500	0.65253800
H	1.94363800	-0.73849800	-0.29396700
H	2.20459300	-1.30709300	1.12187800
O	1.06590900	-0.73772100	-1.97465800
H	1.29228900	-0.25056800	-2.76820400
H	0.27918100	-0.31022100	-1.60627300
O	-0.65312800	0.32152800	0.07192600
H	0.17989500	0.06884200	0.53466400

H_2CS••H_2O••H_2O (PRC5)

C	-0.03315600	-0.30153500	-0.14199800
H	-0.12102300	-0.12068100	0.92700100
H	0.96815400	-0.28931200	-0.56265700
S	-1.30592000	-0.58323300	-1.07612600
O	-3.24544900	-0.22014800	1.60215900
H	-3.82153500	0.53718600	1.48159300
H	-2.84526400	-0.38110400	0.73338700
O	-0.83788100	0.16238800	2.98176800
H	-0.76493500	-0.37368000	3.77222000
H	-1.74462900	0.03553500	2.65995300

H_2CS••OH••H_2O••H_2O (RC4)

C	-0.05863600	0.36647600	1.50280500
H	0.46929200	0.39056600	2.45119600
H	0.49416700	0.72602600	0.63818100
S	-1.56759800	-0.16076000	1.39893700
O	1.45177700	-1.65700900	0.14265500

H	1.86822100	-0.91467500	-0.34975700
O	-0.58581800	-0.64900400	-1.73232900
H	-1.24398500	-0.33869400	-1.09701000
H	-0.17295300	-1.39636900	-1.28015500
O	1.77645800	0.65774100	-1.35750500
H	0.92037600	0.38159100	-1.73483000
H	2.31456900	0.98758500	-2.07819800

$H_2CS••OH••H_2O••H_2O$ (TS6)

C	-0.45147000	0.42647400	1.37656300
H	0.14440200	0.82787400	2.19203100
H	0.06763200	-0.42024800	0.80601000
S	-1.90172900	0.93478500	0.99578400
O	0.96471800	-1.31510800	0.01265500
H	1.40110600	-0.58563900	-0.47591000
O	-1.05124900	-0.58082700	-1.92001300
H	-1.75778900	-0.26752100	-1.34539900
H	-0.54338100	-1.18723800	-1.36190700
O	1.15681900	1.03894300	-1.45751600
H	0.33879700	0.67413700	-1.83855600
H	1.64793100	1.43093800	-2.18077300

$H_2CS••OH••H_2O••H_2O$ (PC5)

C	-0.18761200	0.41738700	1.35715700
H	0.46386000	1.05394500	0.75988400
H	1.17269900	-1.66154100	0.83716100
S	-1.64165300	0.53462900	1.88198700
O	1.46331400	-1.81127500	-0.06761500
H	1.91501000	-0.98969800	-0.31070100
O	-0.46568400	-0.65657100	-1.72801200
H	-1.33664300	-0.53713800	-1.34569500
H	-0.00512400	-1.29953300	-1.16106200
O	1.74517200	0.84586900	-1.10166400
H	0.93266100	0.53488700	-1.53840500
H	2.28453600	1.25774000	-1.77810200

$H_2CS••OH••H_2O••H_2O$ (RC5)

C	-0.15748700	-0.16214500	1.42302000

H	0.45438300	0.19865000	2.24133200
H	0.07093800	0.25176400	0.44598000
S	-1.32555600	-1.23974300	1.65195600
O	-1.60748000	-1.36401000	-1.56745100
H	-1.71535700	-1.37589900	-0.58537400
O	2.45010600	-0.81993500	0.70744400
H	2.10385300	-0.77588600	-0.19594400
H	2.78496100	-1.71141600	0.81304500
O	1.07037200	-0.45572900	-1.72108100
H	1.36235700	-0.18201500	-2.59141000
H	0.16971000	-0.80024300	-1.82253200

$H_2CS••OH••H_2O••H_2O$ (TS7)

C	-0.54139000	-0.03904900	1.04953000
H	-0.47767200	-1.03341400	1.48378300
H	0.34381500	0.65887700	1.04989800
S	-1.91552800	0.42707800	0.39490600
O	-1.06178600	2.27210200	-0.73542000
H	-0.48132800	2.63868700	-0.03930700
O	1.27114400	1.98583900	0.58362100
H	2.13376300	2.22542100	0.91915800
H	1.27382000	1.47192200	-0.56495300
O	0.88358800	0.97798700	-1.54065200
H	1.39469400	1.25740400	-2.30019700
H	-0.33711200	1.73031400	-1.26973200

$H_2CS••OH••H_2O••H_2O$ (TS7)

C	-0.07668100	-1.34740300	0.95292000
H	0.30138300	-2.19054900	0.38295200
H	1.23243900	0.37081900	1.28936300
S	-1.47430500	-0.71405100	1.13897400
O	-0.61817300	1.63822700	-0.95809800
H	0.00645300	1.91697100	-0.28218000
O	1.73307800	1.08394400	0.86489500
H	2.40179700	1.35969400	1.49454900
H	1.82715200	0.10235700	-0.80334800
O	1.40008200	-0.47587900	-1.45172400
H	1.91250300	-0.39937400	-2.25856100

H	-0.18775200	0.86823800	-1.34758400

$H_2CS••OH••H_2O••H_2O$ (PC6)

C	0.03184000	0.07109700	-0.13202900
H	-0.03159200	0.08580500	0.95741400
H	1.08802700	0.19399600	-0.54913200
S	-1.20794500	-0.11199800	-1.11011800
O	2.33363400	0.19060800	-1.37243200
H	1.89481000	-0.04169000	-2.20660000
O	-3.27630600	-0.31328300	1.55591000
H	-3.90477600	0.41146900	1.55849600
H	-2.85909200	-0.29169500	0.68331300
O	-0.85318900	0.03368800	2.92220100
H	-0.69539100	-0.58504800	3.63630800
H	-1.76492900	-0.12096200	2.63004500

$H_2CS••OH••H_2O••H_2O$ (RC6)

C	0.01668400	-0.30281400	-0.13550600
H	-0.05781700	-0.12838700	0.93550800
H	1.00522700	-0.30212400	-0.58664700
S	-1.28300000	-0.56308300	-1.04367400
O	1.27840400	-0.70613400	-3.13439400
H	0.33925800	-0.74649700	-2.86688000
O	-3.29586000	-0.21950400	1.62230600
H	-3.88353000	0.53044100	1.51126100
H	-2.89443200	-0.36606600	0.75377400
O	-0.84448400	0.14508800	2.92875800
H	-0.74816700	-0.35428900	3.74048500
H	-1.76625900	0.02615400	2.65103500

$H_2CS••OH••H_2O••H_2O$ (TS8)

C	0.03184000	0.07109700	-0.13202900
H	-0.03159200	0.08580500	0.95741400
H	1.08802700	0.19399600	-0.54913200
S	-1.20794500	-0.11199800	-1.11011800
O	2.33363400	0.19060800	-1.37243200
H	1.89481000	-0.04169000	-2.20660000

O	-3.27630600	-0.31328300	1.55591000
H	-3.90477600	0.41146900	1.55849600
H	-2.85909200	-0.29169500	0.68331300
O	-0.85318900	0.03368800	2.92220100
H	-0.69539100	-0.58504800	3.63630800
H	-1.76492900	-0.12096200	2.63004500

$H_2CS••OH••H_2O••H_2O$ (PC7)

C	0.60162900	0.10011400	-0.14225700
H	0.56644800	0.12754300	0.94949500
H	2.64800200	0.23878000	-1.21279100
S	-0.44227200	-0.05718300	-1.27970500
O	3.37960400	0.23047000	-1.83862900
H	2.96273100	0.10768600	-2.69320500
O	-2.61378400	-0.28428600	1.41700200
H	-3.26755600	0.41796300	1.42754800
H	-2.24232300	-0.27773300	0.52715100
O	-0.22495600	0.08487300	2.86173800
H	-0.07170100	-0.51978600	3.58893600
H	-1.12472200	-0.09045300	2.54732500

H_2CS[b]

C	0.00404900	0.00000000	0.00253700
H	0.00204400	0.00000000	1.08888300
H	0.98000800	0.00000000	-0.47459700
S	-1.36386200	0.00000000	-0.85309800

•OH[b]

O	0.00000000	0.00000000	0.00167700
H	0.00000000	0.00000000	0.96918500

$H_2CS••HO$ (D1)[b]

C	-0.00091900	-0.00039000	0.00748400
H	-0.00186100	-0.00522300	1.09284800
H	0.96476100	0.00082800	-0.48867400
S	-1.38017800	0.00479400	-0.83431600
O	1.04965200	0.00643600	-3.13264100
H	0.15466800	0.00709400	-2.74610400

$H_2CS••OH$ (TS1)[b]

C	0.00115200	-0.00135100	0.00885500
H	0.00609800	-0.01794300	1.19152100
H	1.00313300	0.00100600	-0.41224300
S	-1.36830700	0.08983500	-0.83217300
O	0.09614500	0.58272400	2.37974500
H	-0.64652100	1.19107000	2.25500600

$H_2CS••OH$ (PC1)[b]

C	-0.02600300	0.00919500	0.01164400
H	-0.04198400	-0.17421900	2.22892300
H	0.99635200	0.16020000	-0.33320500
S	-1.33439500	-0.05085500	-0.72857700
O	0.03767200	-0.12345600	3.19017400
H	-0.66588400	0.48005200	3.43642800

H•C(=S)[b]

C	0.01375900	0.00000000	-0.00976400
H	0.00324600	0.00000000	1.07798100
S	1.11823500	0.00000000	-1.03475200

H_2O[b]

O	-1.67208400	0.90885600	0.00000000
H	-0.71459000	0.95870700	0.00000000
H	-1.94471000	1.82807000	0.00000000

$H_2CS••OH$ (TS2)[b]

C	-0.00684000	-0.02414600	-0.00736200
H	-0.05881700	0.07619200	1.07106800
H	0.99262300	-0.08149800	-0.42292300
S	-1.31464700	-0.19254300	-0.90821100
O	0.13677200	2.21316300	-0.10495300
H	-0.46774500	2.46422200	-0.82038600

$H_2CS••H_2O$ (D2)[b]

C	0.27657300	0.08229900	-0.15874500
H	0.15292600	-0.14876400	0.89480200
H	1.28224800	0.27593500	-0.51868900
S	-0.99559000	0.13147400	-1.15440500

O	-1.99430400	-0.72663300	1.93161200
H	-2.11447300	-0.56612000	0.98717800
H	-2.48530000	-0.01313400	2.34450900

H_2O••OH (D3)[b]

O	-0.00509900	0.00628600	0.01657900
H	0.02439200	-0.00228600	0.99059600
O	0.15523800	-0.00893100	2.88135400
H	0.62836600	-0.72634100	3.30911000
H	0.46968600	0.78365500	3.32231200

H_2CS••OH••H_2O (RC1)[b]

C	-0.41423700	0.08503500	1.50185400
H	-0.64344700	0.10189200	2.56283400
H	0.63378200	0.03720800	1.22049300
S	-1.60064700	0.12873700	0.40319000
O	2.66694400	-0.01094200	0.02814800
H	2.08393300	-0.05820100	-0.75978100
O	0.71910600	-0.12384500	-1.95754800
H	0.63325900	0.56485300	-2.62081200
H	-0.08559400	-0.04786800	-1.42015100

H_2CS••OH••H_2O (TS3)[b]

C	-0.00952300	-0.02046100	0.02497300
H	-0.04466600	-0.06831700	1.10973700
H	1.12366200	-0.00670600	-0.38618600
S	-1.30687400	-0.10829300	-0.93566000
O	2.13098300	-0.75165100	-0.62492400
H	1.81368200	-1.10392600	-1.48146600
O	0.90227400	-1.36279800	-3.10958600
H	1.24703200	-0.77191500	-3.78419900
H	0.08195500	-0.94140300	-2.81941900

H_2CS••OH••H_2O (TS3a)[b]

C	-0.07767500	-0.42085200	2.33611100
H	-0.26077100	-0.52689100	3.40444700
H	1.04724800	-0.20967800	1.76792500
S	-1.29014500	-0.63462400	1.34413500
O	0.11120400	-0.81051200	-0.54677700
H	-0.21604200	-0.04687600	-1.03884300

O	1.93541500	-0.05229100	0.80540600
H	2.62653300	-0.71877700	0.86575200
H	1.08520000	-0.43889200	0.02150200

$H_2CS••OH••H_2O$ (PC2)[b]

C	-0.92634700	-0.14385000	0.62913100
H	0.09104800	-0.24712600	1.02508200
H	2.84445700	0.37659900	0.81909800
S	-2.29136700	-0.39088500	1.22477200
O	2.14961600	-0.22402400	0.54379800
H	1.90994000	0.07317900	-0.34930100
O	0.79435900	0.60755000	-1.77606700
H	0.66487600	0.02770100	-2.53033200
H	-0.00762000	0.48631100	-1.24131600

$H_2CS••OH••H_2O$ (TS5)[b]

O	-0.31196100	-0.10723600	-0.12719000
H	-0.07885100	-0.24621800	0.81436500
O	0.69131600	0.11917700	2.49955700
H	0.32309800	-0.15262500	3.34358800
H	0.46931000	1.05933600	2.42399100
C	0.73290000	1.83851900	-0.29494200
H	0.59414600	1.84266700	-1.36970700
H	1.63182600	1.34399200	0.05327800
S	-0.24879600	2.62962500	0.68487400

$H_2CS••OH••H_2O$ (TS5a)[b]

C	0.01669100	-0.02983400	-0.01551500
H	0.05820600	-0.03384400	1.06894500
H	0.96892200	-0.00786300	-0.53443400
S	-1.37030700	-0.13965600	-0.79837500
O	-0.08923800	2.23765400	0.14501300
H	-0.52894900	2.50819300	-0.67683000
O	-1.58213500	1.03471400	2.49715200
H	-1.24454700	1.71720000	1.90699900
H	-2.19227400	0.55570500	1.92860100

$H_2CS••OH••H_2O$ (PC4)[b]

O	-0.03702200	-1.27799700	-0.83661600
H	0.21687800	-1.47187600	0.08159600

O	0.59255300	-1.23148300	1.89211200
H	0.19902500	-1.81296300	2.54757200
H	0.05522700	-0.42990500	1.91657200
C	0.37327700	0.02000800	-1.11952800
H	0.03840700	0.26320500	-2.12563300
H	1.46226800	0.15338100	-1.08828800
S	-0.23243100	1.32356500	-0.01634200

[a]Calculations carried out at M06-2X/6-311++G(3df,3pd) level. [b]Calculations carried out at MP2/cc-pVTZ level.

Table S12. Calculated equilibrium constants (cm^3 $molecule^{-1}$) for the formation of the dimer and reactant complexes.

T (K)	$H_2CS••OH$ (K_{eq1})	$H_2CS••H_2O$ (K_{eq2})	$OH••H_2O$ (K_{eq3})	$H_2CS••H_2O + OH$ (K_{eq1})	$OH••H_2O + H_2CS$ (K_{eq2})
200	1.89×10^{-21}	5.44×10^{-22}	4.44×10^{-22}	1.77×10^{-21}	1.08×10^{-21}
210	1.29×10^{-21}	3.73×10^{-22}	2.70×10^{-22}	1.03×10^{-21}	7.13×10^{-22}
220	9.12×10^{-22}	2.65×10^{-22}	1.72×10^{-22}	6.34×10^{-22}	4.89×10^{-22}
230	6.66×10^{-22}	1.95×10^{-22}	1.14×10^{-22}	4.06×10^{-22}	3.47×10^{-22}
240	5.01×10^{-22}	1.48×10^{-22}	7.84×10^{-23}	2.70×10^{-22}	2.55×10^{-22}
250	3.87×10^{-22}	1.15×10^{-22}	5.57×10^{-23}	1.86×10^{-22}	1.92×10^{-22}
260	3.05×10^{-22}	9.13×10^{-23}	4.07×10^{-23}	1.32×10^{-22}	1.48×10^{-22}
270	2.46×10^{-22}	7.41×10^{-23}	3.05×10^{-23}	9.64×10^{-23}	1.17×10^{-22}
280	2.01×10^{-22}	6.12×10^{-23}	2.34×10^{-23}	7.20×10^{-23}	9.42×10^{-23}
290	1.68×10^{-22}	5.14×10^{-23}	1.83×10^{-23}	5.49×10^{-23}	7.72×10^{-23}
298	1.46×10^{-22}	4.50×10^{-23}	1.51×10^{-23}	4.47×10^{-23}	6.64×10^{-23}
300	1.42×10^{-22}	4.37×10^{-23}	1.45×10^{-23}	4.27×10^{-23}	6.42×10^{-23}
400	4.50×10^{-23}	1.51×10^{-23}	2.98×10^{-24}	7.30×10^{-24}	1.85×10^{-23}

Table S13. Unimolecular rate constants (k_2 in s^{-1}) and bimolecular rate constants (cm^3 $molecule^{-1}$ s^{-1}) for the $H_2CS + H_2O + •OH$ abstraction reaction via the $H_2CS••H_2O + OH$ (k_{5a}), and $OH••H_2O + H_2CS$ (k_{5b}) pathways, computed at the CCSD(T)/aug-cc-pVTZ//M06-2X/6-311++G(3df,3pd) level of theory.

T (K)	k_2 (s^{-1})	k_{5a} (cm^3 $molecule^{-1}$ s^{-1})	k_{5b} (cm^3 $molecule^{-1}$ s^{-1})	$k_{total} = k_{5a} + k_{5b}$ (cm^3 $molecule^{-1}$ s^{-1})	k_{total}^{eff} (cm^3 $molecule^{-1}$ s^{-1})[a]
200	2.12 x 10^8	3.42 x 10^{-9}	2.09 x 10^{-9}	5.51 x 10^{-9}	3.04 x 10^{-16}
210	3.41 x 10^8	2.48 x 10^{-9}	1.64 x 10^{-9}	4.12 x 10^{-9}	9.32 x 10^{-16}
220	5.27 x 10^8	1.87 x 10^{-9}	1.38 x 10^{-9}	3.25 x 10^{-9}	8.42 x 10^{-16}
230	7.83 x 10^8	1.44 x 10^{-9}	1.18 x 10^{-9}	2.62 x 10^{-9}	2.41 x 10^{-15}
240	1.13 x 10^9	1.14 x 10^{-9}	1.03 x 10^{-9}	2.17 x 10^{-9}	2.07 x 10^{-15}
250	1.57 x 10^9	9.13 x 10^{-10}	9.06 x 10^{-10}	1.82 x 10^{-9}	3.43 x 10^{-15}
260	2.15 x 10^9	7.53 x 10^{-10}	8.15 x 10^{-10}	1.57 x 10^{-9}	6.12 x 10^{-15}
270	2.86 x 10^9	6.28 x 10^{-10}	7.36 x 10^{-10}	1.36 x 10^{-9}	1.03 x 10^{-14}
280	3.73 x 10^9	5.31 x 10^{-10}	6.72 x 10^{-10}	1.20 x 10^{-9}	1.30 x 10^{-14}
290	4.78 x 10^9	4.55 x 10^{-10}	6.19 x 10^{-10}	1.07 x 10^{-9}	1.80 x 10^{-14}
298	5.78 x 10^9	4.05 x 10^{-10}	5.83 x 10^{-10}	9.88 x 10^{-10}	2.07 x 10^{-14}
300	6.03 x 10^9	3.95 x 10^{-10}	5.76 x 10^{-10}	9.71 x 10^{-10}	2.11 x 10^{-14}
400	3.22 x 10^{10}	1.49 x 10^{-10}	3.68 x 10^{-10}	5.17 x 10^{-10}	1.92 x 10^{-13}

[a]The total effective bimolecular rate constants (cm^3 $molecule^{-1}$ s^{-1}) were calculated using the formula $k_{total}^{eff} = \left(\left\{ \kappa_{eq}^2 \times k_{5a} \right\} + \left\{ \kappa_{eq}^3 \times k_{5b} \right\}\right) \times [H_2O]$, where κ_{eq}^2 *and* κ_{eq}^3 are the equilibrium constants for the dimer formation, k_{5a} *and* k_{5b} are the bimolecular rate constants for reactions 5a and 5b, and water concentration calculated based on using a typical temperature-dependent water concentration, which corresponds to 10%–100% relative humidity.

Table S14. Unimolecular rate constants (k_3 in s^{-1}) and bimolecular rate constants (cm^3 $molecule^{-1}$ s^{-1}) for the $H_2CS + H_2O + •OH$ addition reaction via the $H_2CS••H_2O + OH$ (k_{6a}), and $OH••H_2O + H_2CS$ (k_{6b}) reaction paths, computed at the CCSD(T)/aug-cc-pVTZ//M06-2X/6-311++G(3df,3pd) level of theory.

T (K)	k_3 (s^{-1})	k_{6a} (cm^3 $molecule^{-1}$ s^{-1})	k_{6b} (cm^3 $molecule^{-1}$ s^{-1})	$k_{add}^{total} = k_{6a} + k_{6b}$ (cm^3 $molecule^{-1}$ s^{-1})	k_{total}^{eff} (cm^3 $molecule^{-1}$ s^{-1})[a]
200	5.46×10^{11}	9.66×10^{-10}	5.91×10^{-10}	1.56×10^{-9}	8.59×10^{-17}
210	5.45×10^{11}	5.63×10^{-10}	3.88×10^{-10}	9.51×10^{-10}	2.15×10^{-16}
220	5.45×10^{11}	3.45×10^{-10}	2.66×10^{-10}	6.12×10^{-10}	1.58×10^{-16}
230	5.44×10^{11}	2.21×10^{-10}	1.89×10^{-10}	4.10×10^{-10}	3.75×10^{-16}
240	5.44×10^{11}	1.47×10^{-10}	1.39×10^{-10}	2.86×10^{-10}	2.70×10^{-16}
250	5.43×10^{11}	1.01×10^{-10}	1.04×10^{-10}	2.05×10^{-10}	3.85×10^{-16}
260	5.42×10^{11}	7.17×10^{-11}	8.04×10^{-11}	1.52×10^{-10}	5.89×10^{-16}
270	5.42×10^{11}	5.22×10^{-11}	6.35×10^{-11}	1.16×10^{-10}	8.71×10^{-16}
280	5.41×10^{11}	3.89×10^{-11}	5.10×10^{-11}	8.99×10^{-11}	9.65×10^{-16}
290	5.40×10^{11}	2.96×10^{-11}	4.17×10^{-11}	7.13×10^{-11}	1.19×10^{-15}
298	5.40×10^{11}	2.41×10^{-11}	3.58×10^{-11}	5.99×10^{-11}	1.24×10^{-15}
300	5.40×10^{11}	2.31×10^{-11}	3.47×10^{-11}	5.77×10^{-11}	1.25×10^{-15}
400	5.39×10^{11}	3.94×10^{-12}	9.98×10^{-12}	1.39×10^{-11}	5.11×10^{-15}

[a]The total effective bimolecular rate constants (cm^3 $molecule^{-1}$ s^{-1}) were calculated using the formula $k_{total}^{eff} = \left(\left\{ \kappa_{eq}^2 \times k_{6a} \right\} + \left\{ \kappa_{eq}^3 \times k_{6b} \right\}\right) \times [H_2O]$, where κ_{eq}^2 *and* κ_{eq}^3 are the equilibrium constants for the dimer formation, k_{6a} *and* k_{6b} are the bimolecular rate constants for reactions 6a and 6b, and the water concentration calculated based on using a typical temperature-dependent water concentration, which corresponds to 10%–100% relative humidity.

Table S15. CVT/SCT calculated tunneling factors (κ) for the gas phase reaction of H_2CS + •OH with and without water catalyst computed at the CCSD(T)/aug-cc-pVTZ//M06-2X/6-311++G(3df,3pd) level.

T (K)	H_2CS + OH (R1)	H_2CS + OH (R2)	H_2CS + H_2O + OH (R5)	H_2CS + H_2O + OH (R6)
200	2.2	1.9	1.4	3.7
210	2.1	1.8	1.4	3.4
220	1.9	1.7	1.3	3.2
230	1.8	1.6	1.3	2.9
240	1.7	1.6	1.2	2.7
250	1.6	1.5	1.2	2.6
260	1.6	1.5	1.2	2.4
270	1.5	1.4	1.2	2.3
280	1.4	1.4	1.1	2.2
290	1.4	1.3	1.1	2.1
298	1.4	1.3	1.1	2.0
300	1.3	1.3	1.1	2.0
400	1.1	1.2	1.0	1.5

Table S16. CVT/SCT calculated unimolecular (s^{-1}) and bimolecular rate constants (cm^3 $molecule^{-1}$ s^{-1}) for the H_2CS + •OH reaction computed at the CCSD(T)/aug-cc-pVTZ//M06-2X/6-311++G(3df,3pd) level.

T (K)	Abstraction		Addition		$k_{OH} = k_{R1} + k_{R2}$ (cm^3 $molecule^{-1}$ s^{-1})
	k (s^{-1})	k_{R1} (cm^3 $molecule^{-1}$ s^{-1})	k (s^{-1})	k_{R2} (cm^3 $molecule^{-1}$ s^{-1})	
200	6.65×10^{8}	1.26×10^{-12}	5.19×10^{9}	9.82×10^{-12}	1.11×10^{-11}
210	9.85×10^{8}	1.27×10^{-12}	6.83×10^{9}	8.80×10^{-12}	1.10×10^{-11}
220	1.41×10^{9}	1.29×10^{-12}	8.75×10^{9}	7.98×10^{-12}	9.27×10^{-12}
230	1.96×10^{9}	1.31×10^{-12}	1.10×10^{10}	7.32×10^{-12}	8.62×10^{-12}
240	2.64×10^{9}	1.32×10^{-12}	1.35×10^{10}	6.77×10^{-12}	8.09×10^{-12}
250	3.49×10^{9}	1.35×10^{-12}	1.63×10^{10}	6.32×10^{-12}	7.67×10^{-12}
260	4.51×10^{9}	1.38×10^{-12}	1.94×10^{10}	5.93×10^{-12}	7.31×10^{-12}
270	5.72×10^{9}	1.41×10^{-12}	2.29×10^{10}	5.61×10^{-12}	7.02×10^{-12}
280	7.14×10^{9}	1.44×10^{-12}	2.65×10^{10}	5.34×10^{-12}	6.78×10^{-12}
290	8.77×10^{9}	1.47×10^{-12}	3.05×10^{10}	5.11×10^{-12}	6.58×10^{-12}
298	1.03×10^{10}	1.50×10^{-12}	3.39×10^{10}	4.94×10^{-12}	6.45×10^{-12}
300	1.06×10^{10}	1.50×10^{-12}	3.47×10^{10}	4.91×10^{-12}	6.41×10^{-12}
400	4.32×10^{10}	1.94×10^{-12}	8.78×10^{10}	3.95×10^{-12}	5.90×10^{-12}

Table S17. Bimolecular rate constants (cm^3 $molecules^{-1}$ s^{-1}) of $HC•S + 3H_2O$ formation by the $2\ H_2O••OH + H_2CS$ and $2H_2O••H_2CS + •OH$ reactions within the temperature range of 200–400 K.

T (K)	k_2 (s^{-1})	K_{eq4} $(H_2CS••OH••(H_2O)_2)$[a,b]	K_{eq5} $(H_2CS••OH\ ••(H_2O)_2)$[a,b]	k_7 (cm^3 $molecule^{-1}$ s^{-1})	k_8 (cm^3 $molecule^{-1}$ s^{-1})	$k_{total}=k_7+k_8$ (cm^3 $molecule^{-1}$ s^{-1})
200	8.07×10^{10}	1.37×10^{-22}	6.22×10^{-21}	1.10×10^{-11}	5.02×10^{-10}	5.13×10^{-10}
210	9.05×10^{10}	9.04×10^{-23}	3.34×10^{-21}	8.18×10^{-12}	3.02×10^{-10}	3.11×10^{-10}
220	1.01×10^{11}	6.24×10^{-23}	1.90×10^{-21}	6.30×10^{-12}	1.92×10^{-10}	1.98×10^{-10}
230	1.12×10^{11}	4.46×10^{-23}	1.14×10^{-21}	5.00×10^{-12}	1.27×10^{-10}	1.32×10^{-10}
240	1.23×10^{11}	3.30×10^{-23}	7.10×10^{-22}	4.06×10^{-12}	8.74×10^{-11}	9.14×10^{-11}
250	1.35×10^{11}	2.50×10^{-23}	4.61×10^{-22}	3.38×10^{-12}	6.22×10^{-11}	6.56×10^{-11}
260	1.48×10^{11}	1.95×10^{-23}	3.10×10^{-22}	2.88×10^{-12}	4.58×10^{-11}	4.87×10^{-11}
270	1.60×10^{11}	1.55×10^{-23}	2.14×10^{-22}	2.48×10^{-12}	3.43×10^{-11}	3.68×10^{-11}
280	1.74×10^{11}	1.26×10^{-23}	1.53×10^{-22}	2.19×10^{-12}	2.65×10^{-11}	2.87×10^{-11}
290	1.87×10^{11}	1.04×10^{-23}	1.11×10^{-22}	1.94×10^{-12}	2.08×10^{-11}	2.27×10^{-11}
298	1.98×10^{11}	8.97×10^{-24}	8.74×10^{-23}	1.78×10^{-12}	1.73×10^{-11}	1.91×10^{-11}
300	2.01×10^{11}	8.69×10^{-24}	8.29×10^{-23}	1.75×10^{-12}	1.67×10^{-11}	1.84×10^{-11}
400	3.51×10^{11}	2.67×10^{-24}	1.03×10^{-23}	9.38×10^{-13}	3.62×10^{-12}	4.56×10^{-12}

[a]Equilibrium constants in units of cm^3 $molecule^{-1}$. [b]All equilibrium constants were calculated by using energies computed at CCSD(T)/aug-cc-pVTZ level and partition functions obtained at M06-2X level.

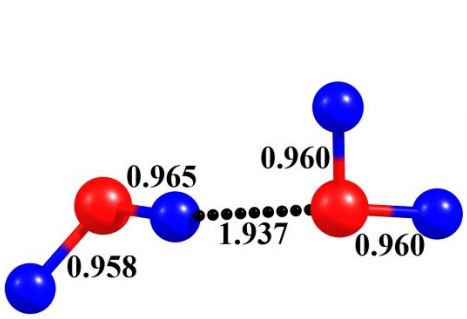
Table S18. Effective first order rate constants (s^{-1}) of HC•S + 3 H_2O formation from the 2 H_2O••OH + H_2CS and 2H_2O••H_2CS + •OH reaction pathways within the temperature range of 200–400 K.

T (K)	[H_2O••H_2O]	K_{eq6} (•OH••$(H_2O)_2$)[b,c]	K_{eq7} H_2CS••$(H_2O)_2$[b,c]	k_7^{eff} (s^{-1})	k_8^{eff} (s^{-1})	k_{total}^{eff} (s^{-1}) = k_7^{eff} + k_8^{eff}
200	4.74×10^{7}	3.74×10^{-18}	4.11×10^{-20}	1.96×10^{-15}	9.79×10^{-16}	2.94×10^{-15}
210	1.95×10^{9}	1.42×10^{-18}	1.92×10^{-20}	2.26×10^{-14}	1.13×10^{-14}	3.40×10^{-14}
220	2.50×10^{9}	5.87×10^{-19}	9.63×10^{-21}	9.25×10^{-15}	4.63×10^{-15}	1.39×10^{-14}
230	4.61×10^{10}	2.62×10^{-19}	5.15×10^{-21}	6.04×10^{-14}	3.02×10^{-14}	9.07×10^{-14}
240	7.04×10^{10}	1.25×10^{-19}	2.91×10^{-21}	3.57×10^{-14}	1.79×10^{-14}	5.36×10^{-14}
250	3.83×10^{11}	6.34×10^{-20}	1.72×10^{-21}	8.22×10^{-14}	4.11×10^{-14}	1.23×10^{-13}
260	2.22×10^{12}	3.39×10^{-20}	1.07×10^{-21}	2.17×10^{-13}	1.08×10^{-13}	3.25×10^{-13}
270	1.11×10^{13}	1.90×10^{-20}	6.86×10^{-22}	5.22×10^{-13}	2.61×10^{-13}	7.83×10^{-13}
280	2.94×10^{13}	1.11×10^{-20}	4.56×10^{-22}	7.11×10^{-13}	3.55×10^{-13}	1.07×10^{-12}
290	9.03×10^{13}	6.71×10^{-21}	3.13×10^{-22}	1.18×10^{-12}	5.88×10^{-13}	1.76×10^{-12}
298	1.69×10^{14}	4.58×10^{-21}	2.35×10^{-22}	1.38×10^{-12}	6.88×10^{-13}	2.06×10^{-12}
300	1.91×10^{14}	4.21×10^{-21}	2.21×10^{-22}	1.40×10^{-12}	7.02×10^{-13}	2.11×10^{-12}
400	2.90×10^{17}	1.48×10^{-22}	1.92×10^{-23}	4.02×10^{-11}	2.01×10^{-11}	6.03×10^{-11}

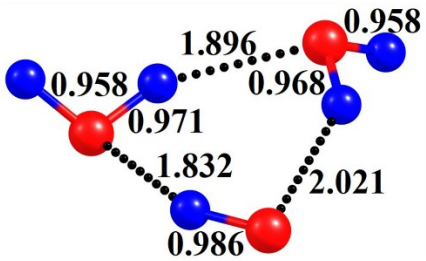
[a]Water dimer concentration in molecules cm^{-3}. [b]Equilibrium constants in units of cm^3 $molecule^{-1}$. [c]All equilibrium constants were calculated by using energies computed at CCSD(T)/aug-cc-pVTZ level and partition functions obtained at M06-2X level.

Table S19. T1 diagnostic values for the reactants, intermediates, transition states, and products involved in $H_2C(OH)S\bullet + {}^3O_2$ reaction calculated at CCSD(T)/aug-cc-pVTZ level of theory.

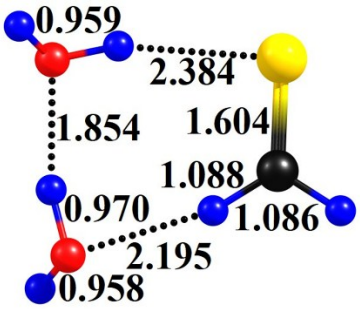
species	T1	species	T1
$H_2C(OH)S\bullet$	0.014	TS6	0.037
RO_2	0.029	TS7	0.041
HO_2	0.028	TS8	0.036
CH_2SO	0.013	TS9	0.035
CH_2O	0.015	TS10	0.039
SO_2H	0.027	PC5	0.024
HC(=S)OH	0.018	PC6	0.022
CH_2OH	0.016	PC7	0.025
SO_2	0.020	PC8	0.022
		PC9	0.021



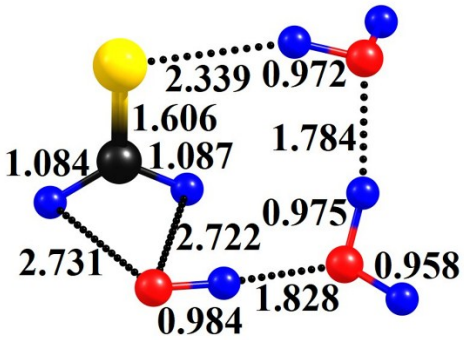
Water dimer



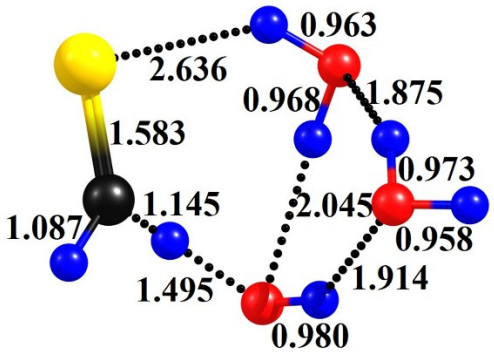
PRC4



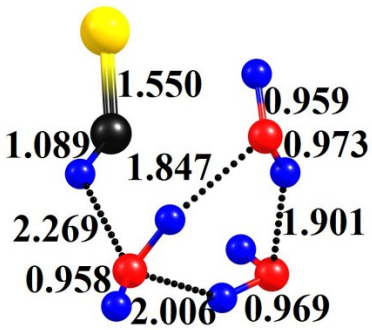
PRC5



RC4



TS6



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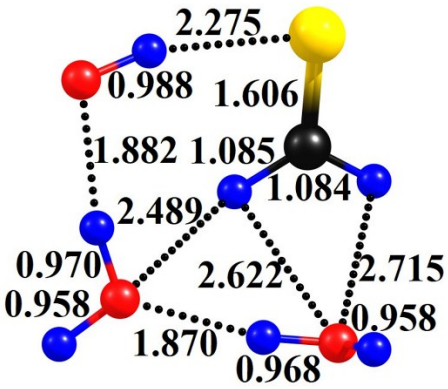

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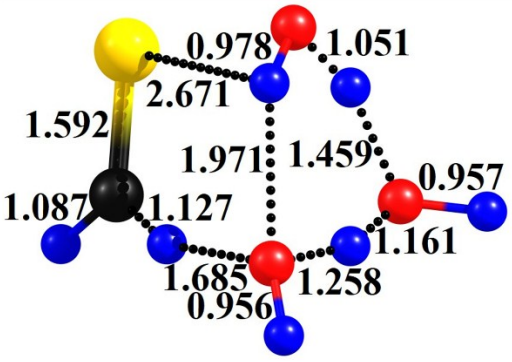

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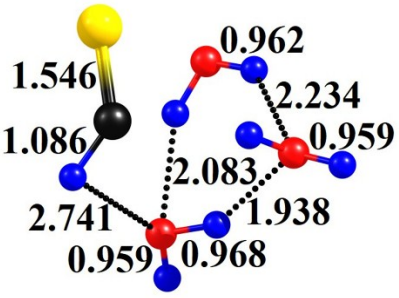

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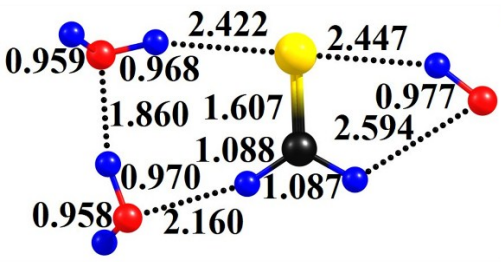

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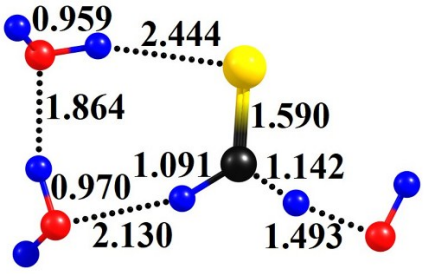

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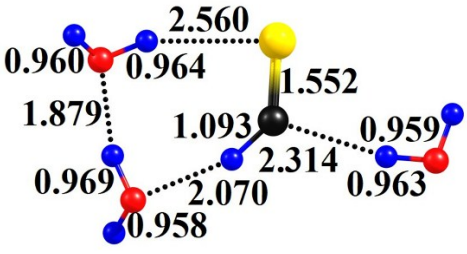

PC7

Figure S1. Optimized geometries of all the stationary points such as water dimers, and trimer complexes (PRCs), reactant complexes (RCs), transition states (TSs), and product complexes (PCs) for the H_2CS + •OH reaction assisted by water dimer molecule obtained at the M06-2X/6-311++G(3df,3pd) level of theory. The yellow, black, and blue colors denote sulfur, carbon, and hydrogen atoms, respectively.