

Fig. S1. The geometries of reactants, products, and the corresponding bimolecular geometries involved in the title reaction are optimized at B3LYP/6-311++G(2df,2pd) level. (values in parentheses from Harmony *et al.*^[47]; bond distances in angstroms; bond angles in degree).

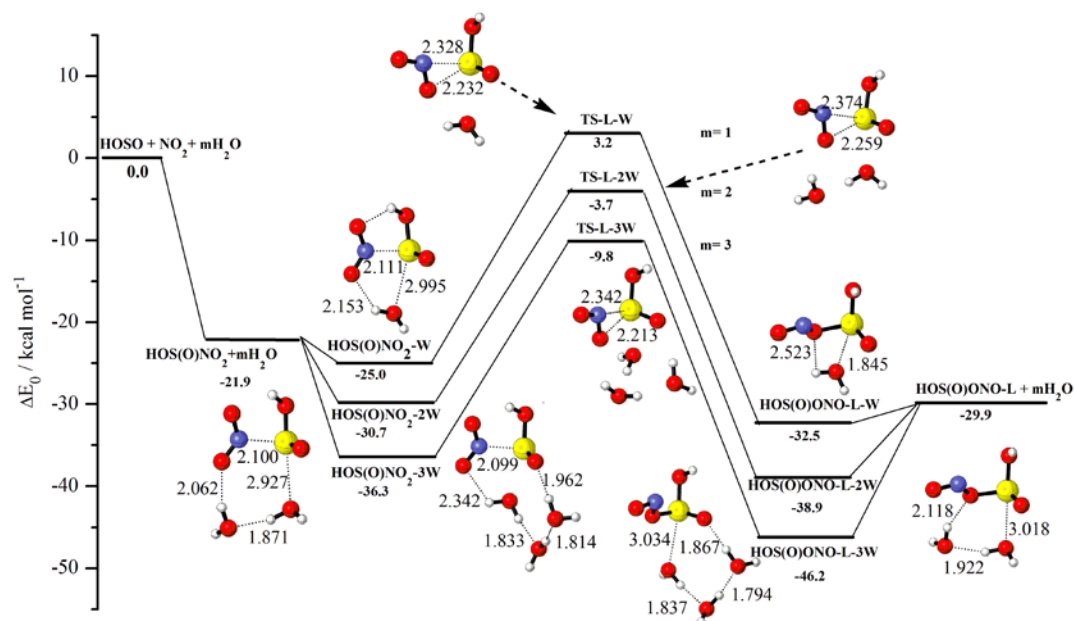


Fig. S2. Effect of water molecules on the isomerization of the HOS(O)NO₂ to the HOS(O)ONO-L: B3LYP/6-311++G(2df, 2pd) optimized structures of the relevant intermediates and transition states. Selected bond distances are given in Angstrom (Å).

Table S1. Zero point corrected relative energies (ΔE_0), and relative enthalpies (ΔH^0) and Gibbs free energies (ΔG^0) at 298 K for the reactants, intermediates, transition states, and products are involved in the HOSO + NO₂ reaction

The energies are in kcal mol⁻¹

species	ΔE_0				$\Delta H_{298.15}^0$	$\Delta G_{298.15}^0$
	B3LYP	CCSD(T)	CBS-QB3	G2MP2	CBS-QB3	CBS-QB3
HOSO + NO ₂	0.0	0.0	0.0	0.0	0.0	0.0
HOS(O)NO ₂	-16.2	-15.4	-21.9	-23.8	-22.8	-9.8
HOS(O)ONO-L	-19.5	-9.4	-29.5		-30.4	-18.4
TS-PC	-15.6	-11.9	-20.8	-22.6	-22.6	-8.4
TS-L	12.0	23.4	7.7		6.8	19.6
<i>t</i> -HONO-SO ₂	-30.1	-28.9	-41.5		-41.4	-33.4
<i>t</i> -HONO + SO ₂	-27.6	-24.5	-37.3	-39.1	-42.9	-36.9

Table S2. Optimized geometries of *cis*-HOSO in this work at the B3LYP/6-311++G(2df, 2pd) level^a

Geometry parameters	H-O	O-S	S-O	∠HOS	∠OSO	∠HOSO
this work	0.970	1.652	1.478	109.4	109.1	26.31
Ref.13	0.969	1.655	1.475	106.3	109.0	0.10
Ref.14	0.957	1.657	1.443	106.9	108.8	11.10
Ref.14	0.950	1.657	1.442	108.3	108.8	planar
Ref.16	0.969	1.640	1.473	107.2	108.8	24.20

^aThe bond distances are in angstroms and bond angles in degrees.

Table S3. Experimental and calculated vibrational frequencies (in cm⁻¹) of *cis*-HOSO at the B3LYP/6-311++G(2df, 2pd) level

<i>cis</i> -HOSO						
Vibrational frequencies	torsional mode ν ₁	OSO bend ν ₂	OS stretch ν ₃	HOS bend ν ₄	SO stretch ν ₅	OH stretch ν ₆
this work	106	394	753 (3.0 ^a /2.6 ^b /1.8 ^c)	1067	1168 (0.0 ^a /0.3 ^b /0.9 ^c)	3745 (5.7 ^a /5.7 ^b /6.9 ^c)
Ref.13			776 ^A 773 ^B 767 ^C		1168 ^A /1164 ^B /1158 ^C	3544 ^A /3525 ^B /3504 ^C
Ref.16		392	798 (2.8 ^a /3.2 ^b /4.0 ^c)	1085	1202 (2.9 ^a /3.3 ^b /3.8 ^c)	

Superscripts A, B, and C refer to experimental values obtained in matrices of Ar, Kr, and Xe respectively; superscripts a, b, and c refer to percentual differences respect to experimental values [Exp] in Ar, Kr, and Xe matrices, respectively.

Table S4. Vibrational frequencies (cm⁻¹) of intermediates and transition states involved in the reaction of HOSO + NO₂ + H₂O

Species	Values (Vibrational Frequencies, cm ⁻¹)
HOS(O)NO ₂ -W-1	42,64,93,108,167,194,241,255,293,381,416,465,517,581,818,827,1164,1245, 1373,1612,1639,3402,3779,3894
HOS(O)NO ₂ -W-2	37,72,125,176,201,238,244,278,397,440,511,563,583,825,884,1057,1223,1339,1374, 1612,1644,2789,3700,3861
HOS(O)ONO-L-W-1	41,90,103,143,162,193,203,295,314,380,405,429,495,614,702,709,869,1099,1158,1654,2043, 3555,3787,3872
HOS(O)ONO-L-W-2	42,79,90,134,160,183,200,213,322,368,383,422,481,623,655,731,841,1074,1177,1650,2023, 3620,3750,3878
<i>t</i> -HONO-SO ₂ -W-1	28,58,86,110,121,149,153,166,219,282,397,524,607,708,783,919,1160,1328,1412,1838, 1744,3538,3658,3864
<i>t</i> -HONO-SO ₂ -W-2	25,56,68,89,114,132,181,202,226,236,374,516,549,735,944,965,1157,1334,1482,1639,1732, 3266,3724,3881
<i>t</i> -HONO-H ₂ SO ₃ -1	36,65,122,155,191,199,228,378,450,505,666,722,759,807,872,941,1079,1146,1264,1468, 1747,3332,3411,3718
<i>t</i> -HONO-H ₂ SO ₃ -2	59,63,114,133,152,202,306,390,411,505,616,661,702,786,800,915,1092,1200,1272,1422,1754, 3455,3553,3765
<i>t</i> -HONO-H ₂ SO ₃ -3	38,64,121,141,161,210,264,389,427,510,615,661,704,801,829,920,1115,1213,1254,1452, 1760,3403,3502,3770
<i>t</i> -HONO-H ₂ SO ₃ -4	6,14,36,87,125,148,154,324,375,431,464,644,673,731,917,858,1069,1095,1220,1395,1757, 3595,3709,3721
<i>t</i> -HONO-H ₂ SO ₃ -5	26,48,68,110,129,182,222,363,447,493,534,624,744,779,792,817,1085,1134,1205,1317,1778, 3550,3586,3718
HNO ₃ - <i>t</i> -S(OH) ₂	21,42,60,74,108,209,349,526,545,630,680,751,759,795,929,1159,1189,1334,1448,1738, 3384,3749,3760
<i>c</i> -HONO-H ₂ SO ₃	20,41,63,108,153,185,219,363,445,489,531,598,745,781,795,851,1083,1135,1224, 1727,3476,3580,3718
TS1	811 <i>i</i> ,48,90,105,117,151,180,260,301,395,423,437,523,668,858,1031,1091,1262,1335,1623, 1651,1802,3776,3896
TS2	1704 <i>i</i> ,51,69,114,141,166,212,288,470,537,665,713,749,801,928,1006,1037,1225,1284,1432, 1748,1937,3452,3510
TS3	870 <i>i</i> ,79,102,116,159,252,280,338,398,465,540,611,636,776,823,846,1131,1286,1309,1457, 1569,1722,3504,3803
TS4	415 <i>i</i> ,47,102,144,203,271,301,343,422,461,522,582,674,734,812,1005,1044,1227,1338,1472, 1629,1954,3715,3791
TS5	524 <i>i</i> ,66,83,157,197,220,414,456,470,487,530,594,658,843,1032,1181,1242,1338,1448,1587, 1646,1734,2593,3808
TS6	625 <i>i</i> ,20,89,140,185,230,256,321,397,423,433,641,730,757,814,902,1077,1230,1299,1587, 1613,1682,3690,3785

TS7	821i,47,54,141,192,201,327,381,400,421,506,528,606,703,732,817,971,1107,1129,1319,1578, 2045,3732,3797
TS8	644i,32,59,68,124,165,231,309,353,357,407,521,670,731,783,860,1104,1118,1191,1341,1616, 1839,3751,3817
TS9	849i,56,63,165,198,206,331,372,401,414,531,549,612,689,730,849,973,1099,1142,1450,1480, 2010,3736,3780

Table S5. Vibrational frequencies (cm⁻¹) of intermediates and the transition states involved in the reaction of HOSO + NO₂ + 2H₂O

Species	Values(Vibrational Frequencies, cm ⁻¹)
HOS(O)NO ₂ -2W	28,46,77,103,117,124,175,183,199,246,270,287,322,374,406,470,483,518,595, 739,813,825,1163,1208,1366,1632,1637,1656,3449,3637,3753,3866,3893
HOS(O)ONO-L-2W-1	47,53,88,131,160,165,191,238,247,276,282,344,368,399,413,477,515,562,632, 686,780,885,915,1084,1166,1643,1693,2067,3505,3541,3637,3783,3880
HOS(O)ONO-L-2W-2	55,57,87,120,138,157,167,170,200,216,279,343,353,405,430,464,482,570,596, 697,742,805,887,1093,1153,1628,1679,2064,3572,3632,3695,3785,3890
<i>t</i> -HONO-SO ₂ -2W	19,32,59,94,108,123,148,168,178,186,198,227,289,304,427,523,533,684,706, 777,865,912,1153,1300,1411,1626,1651,1746,3504,3546,3686,3761,3892
W--H ₂ SO ₃ - <i>t</i> -HONO	19,41,66,73,113,145,169,184,207,229,314,354,414,423,535,629,723,727,792, 854,873,951,1142,1266,1320,1470,1619,1740,3226,3333,3481,3787,3895
W- <i>t</i> -HONO-H ₂ SO ₃	22,26,68,83,105,130,141,155,184,226,168,363,387,434,500,590,619,661,754, 823,835,983,1109,1177,1246,1391,1633,1769,3312,3395,3660,3880
W- <i>c</i> -HONO-H ₂ SO ₃	8,28,46,78,87,130,163,181,233,254,273,402,414,448,507,620,633,658,754,790, 920,958,1118,1185,1245,1638,1710,3068,3469,3633,3706,3881
TS1-W	884 <i>i</i> ,33,69,71,104,109,126,162,178,194,264,283,314,365,420,446,458,536,651, 727,856,1033,1096,1228,1322,1631,1655,1661,1818,3648,3761,3862,3895
TS2-W	753 <i>i</i> ,33,56,84,107,147,180,217,332,366,493,505,545,575,606,633,726,759,869, 947,1032,1111,1204,1359,1445,1464,1629,1738,1773,2240,3349,3536,3816
TS7-W	642 <i>i</i> ,50,72,100,140,155,192,222,238,244,296,379,413,439,488,529,592,642, 716,776,935,1071,1098,1149,1231,1410,1614,1649,2035,3275,3531,3784,3875
TS9-W	689 <i>i</i> ,54,80,93,114,139,170,183,217,248,261,399,412,425,469,524,625,725,762, 881,1004,1086,1123,1200,1432,1588,1633,2002,3347,3555,3735,3886

Table S6. Vibrational frequency (cm⁻¹) of intermediates and the transition states involved in the reaction of HOSO + NO₂ + H₂O + NH₃

Species	Values(vibrational Frequencies, cm ⁻¹)
HOS(O)NO ₂ -W-A	24,46,70,86,102,111,121,178,215,240,248,282,292,331,401,476,509,538,801, 821,827,1092,1160,1222,1368,1626,1661,1671,1678,3439,3458,3476,3589,3600, 3860
HOS(O)ONO-L-W-A-1	45,53,74,108,132,146,165,200,231,255,291,295,360,385,396,427,487,568,638, 647,814,911,964,1081,1120,1163,1659,1679,1709,2048,3299,3455,3515,3569, 3600,3783
HOS(O)ONO-L-W-A-2	42,50,60,81,122,132,137,160,176,230,274,286,320,360,405,431,481,599,609, 697,757,888,915,1083,1103,1155,1662,1674,1700,2033,3360,3472,3584,3598, 3625,3787
<i>t</i> -HONO-SO ₂ -W-A	24,32,59,81,93,96,115,162,167,183,192,256,298,327,355,525,611,711,718,812, 980,1124,1150,1298,1424,1659,1667,1681,1739,3182,3471,3490,3583,3597, 3699
<i>t</i> -HONO-A-H ₂ SO ₃	19,32,54,68,73,104,146,190,197,268,331,374,407,443,549,582,728,734,898,911, 943,1086,1113,1153,1235,1422,1483,1660,1666,1738,2541,3272,3475,3550, 3589,3596
A- <i>t</i> -HONO-H ₂ SO ₃	28,38,54,61,88,100,140,149,165,226,257,350,394,398,451,500,601,682, 748,812,866,1107,1116,1145,1177,1246,1495,1663,1677,1748,2872,3433, 3462,3573,3596,3741
A- <i>c</i> -HONO-H ₂ SO ₃	21,40,44,79,98,127,149,155,176,221,286,371,372,443,476,503,680,693,742, 816,943,1086,1152,1165,1192,1261,1487,1657,1676,1678,2470,3378,3450, 3467,3598,3723
TS1-A	858 <i>i</i> ,29,62,79,103,110,117,160,209,234,271,295,325,414,437,523,656,809,857, 1028,1091,1095,1241,1323,1650,1662,1671,1680,1811,3455,3477,3589,3600, 3856
TS2-A	277 <i>i</i> ,36,39,74,91,142,193,200,212,261,308,424,433,487,518,560,712,735,932, 951,1003,1072,1129,1204,1418,1482,1576,1604,1697,1729,1818,3225,3263, 3524,3593,3638
TS7-A	525 <i>i</i> ,36,77,89,135,150,178,232,247,389,426,461,513,552,611,651,817,999,1076, 1159,1249,1308,1416,1631,1670,1681,2011,2870,3423,3553,3599,3787,
TS9-A	634 <i>i</i> ,55,69,82,111,134,156,174,202,249,277,360,397,408,436,499,527,623,711, 806,989,1035,1106,1142,1198,1301,1464,1615,1659,1682,1944,2823,3448,3564, 3597,3741