Environ. Chem. **2016**
doi:10.1071/EN16080_AC

Supplementary material

Theoretical study of the hydrolysis of HOSO + NO_2 as a source of atmospheric HONO: effects of H_2O or NH_3

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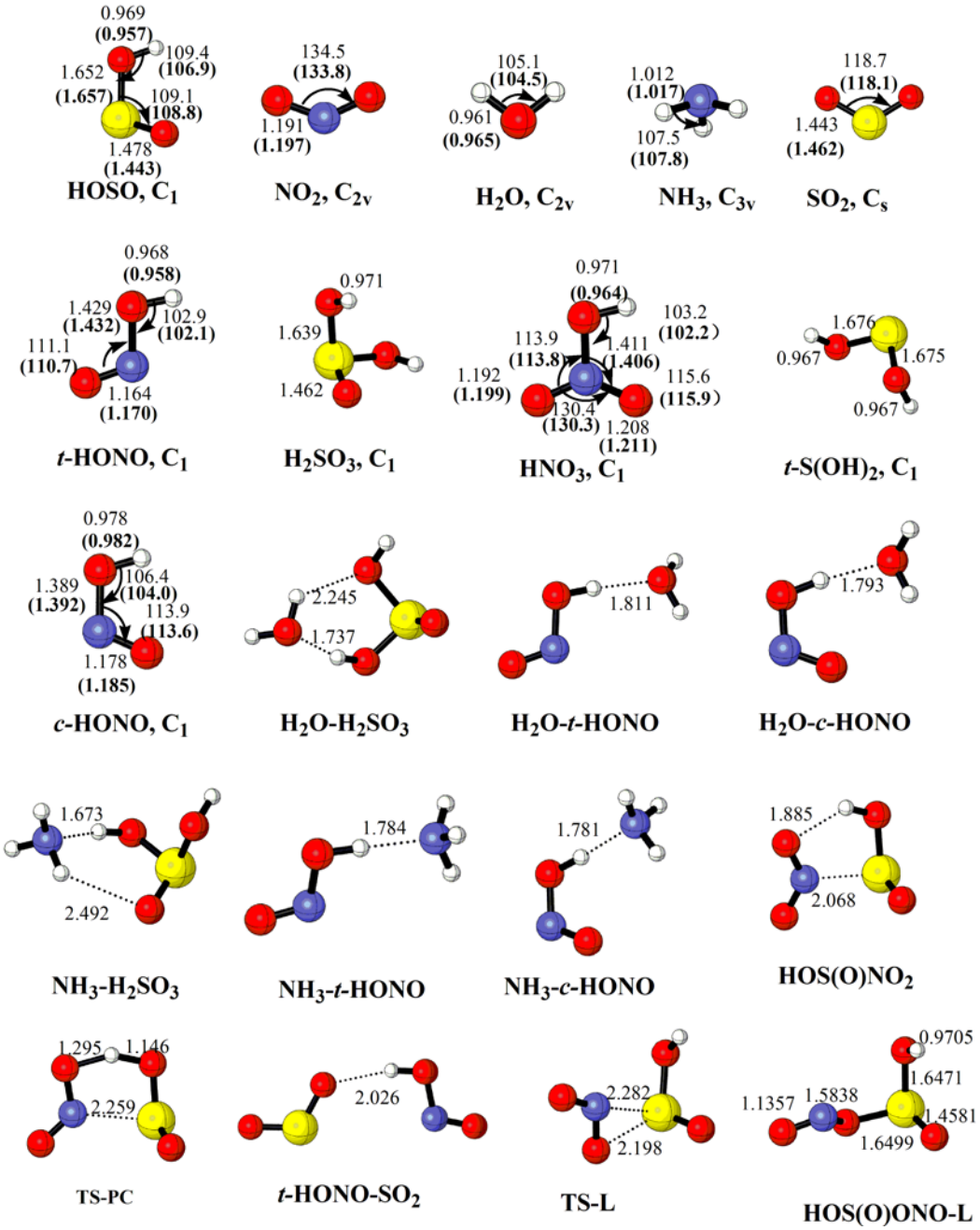

Fig. S1. The geometries of reactants, products, and the corresponding bimolecular geometries involved in the title reaction are optimized at B3LYP/6-311++G(2df,2pd) level. (values in parentheses from Harmony *et al*.[47]; bond distances in angstroms; bond angels in degree).

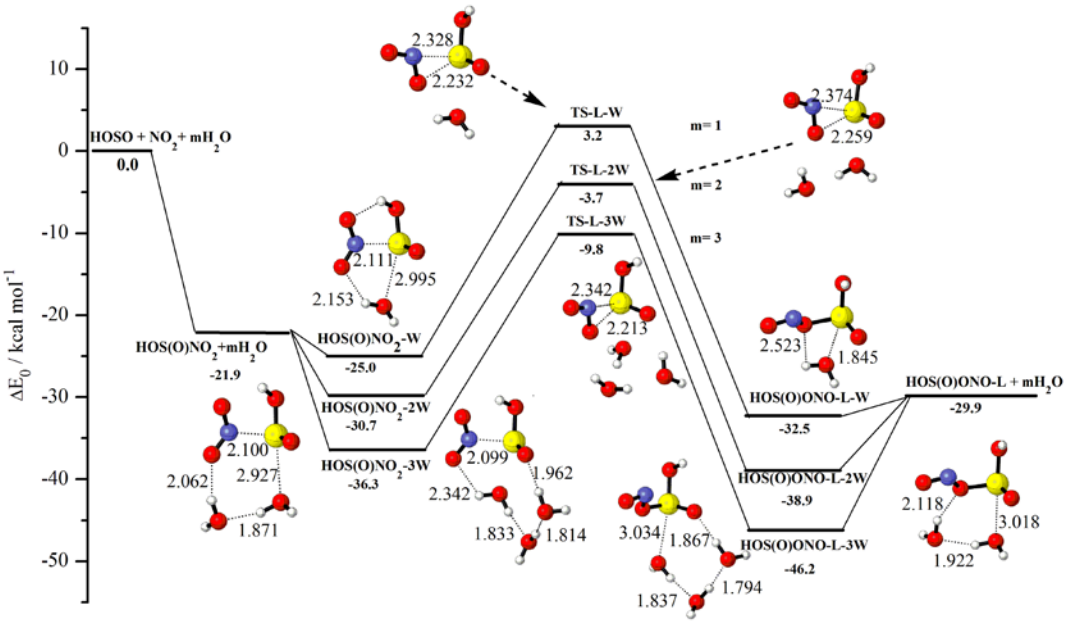

Fig. S2. Effect of water molecules on the isomerization of the $HOS(O)NO_2$ to the HOS(O)ONO-L: B3LYP/6-311++G(2df, 2pd) optimized structures of the relevant intermediates and transition states. Selected bond distances are given in Angstrom (Å).

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 + NO_2 reaction

The energies are in kcal mol^{-1}

species	ΔE_0				$\Delta H^0_{298.15}$	$\Delta G^0_{298.15}$
	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
t-HONO-SO_2	-30.1	-28.9	-41.5		-41.4	-33.4
t-HONO + SO_2	-27.6	-24.5	-37.3	-39.1	-42.9	-36.9

doi:10.1071/EN16080_AC

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

[a] The 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

***cis*-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.

doi:10.1071/EN16080_AC

Table S4. Vibrational frequencies (cm^{-1}) of intermediates and transition states involved in the reaction of HOSO + NO_2 + H_2O

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
t-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
t-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
t-HONO-H_2SO_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
t-HONO-H_2SO_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
t-HONO-H_2SO_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
t-HONO-H_2SO_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
t-HONO-H_2SO_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-*t*-$S(OH)_2$	21,42,60,74,108,209,349,526,545,630,680,751,759,795,929,1159,1189,1334,1448,1738, 3384,3749,3760
c-HONO-H_2SO_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*,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*,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*,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*,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*,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*,20,89,140,185,230,256,321,397,423,433,641,730,757,814,902,1077,1230,1299,1587, 1613,1682,3690,3785

TS7	821*i*,47,54,141,192,201,327,381,400,421,506,528,606,703,732,817,971,1107,1129,1319,1578, 2045,3732,3797
TS8	644*i*,32,59,68,124,165,231,309,353,357,407,521,670,731,783,860,1104,1118,1191,1341,1616, 1839,3751,3817
TS9	849*i*,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 + NO_2 + $2H_2O$

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
t-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_2SO_3-*t*-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-*t*-HONO-H_2SO_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-*c*-HONO-H_2SO_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*,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*,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*,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*,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 + NO_2 +H_2O + NH_3

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
t-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
t-HONO-A-H_2SO_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-*t*-HONO-H_2SO_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-*c*-HONO-H_2SO_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*,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*,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*,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*,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