

## Supplementary Material

### **Theoretical insight into the role of urea in the hydrolysis reaction of NO<sub>2</sub> as a source of HONO and aerosols**

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**Table S1:** Calculated total energies and  $T_1$  diagnostic values for all the species in the reactions  $2\text{NO}_2 + m\text{H}_2\text{O} + \text{NH}_2\text{CONH}_2$  ( $m=1, 2$ ), which obtained at CCSD(T)/6-311++G(d, p)//B3LYP/6-311G(d, p) level. Zero Point Energy (in kcal/mol) are calculated at the B3LYP/6-311G(d, p) level.

species	B3LYP	CCSD(T)	Zero Point Energy	$T_1$
$\text{NO}_2$	-205.132	-204.68430	5.53	0.025
$\text{H}_2\text{O}$	-76.447	-76.28660	13.37	0.010
$\text{NH}_2\text{CONH}_2$	-225.338	-224.80035	40.01	0.015
<i>c</i> -HONO	-205.762	-205.31319	12.71	0.022
<i>t</i> -HONO	-205.761	-205.31492	12.74	0.022
$\text{HNO}_2$	-205.751	-205.30014	13.78	0.021
$\text{HNO}_3$	-280.967	-280.35321	16.59	0.019
<i>t</i> -ONONO <sub>2</sub>	-410.269	-409.37684	13.37	0.023
<i>t</i> -ONONO <sub>2</sub> -U	-635.625	-634.18997	54.62	0.021
<i>t</i> -ONONO <sub>2</sub> -W	-486.730	-485.66969	29.35	0.022
UN-1	-506.326	-505.17213	58.09	0.017
UN-2	-506.334	-505.17793	57.60	0.017
UN-W	-582.782	-581.45964	73.56	0.017
<i>t</i> -HONO-U	-431.115	-430.12867	54.59	0.018
<i>c</i> -HONO-U	-431.115	-430.12663	54.37	0.018
$\text{HNO}_2$ -U	-431.107	-430.11572	55.37	0.018
<i>t</i> -ONONO <sub>2</sub> -1W-U	-712.094	-710.48482	71.19	0.020
TS1-1W-U	-712.090	-710.48556	68.99	0.019
<i>t</i> -HONO- $\text{HNO}_3$ -U	-712.105	-710.50332	70.98	0.019
<i>t</i> -ONONO <sub>2</sub> -2W-U	-788.560	-786.78654	86.76	0.019
TS2-2W-U	-788.557	-786.78811	84.61	0.018
<i>t</i> -HONO- $\text{HNO}_3$ -U-W	-788.571	-786.80367	86.37	0.018
<i>t</i> -ONONO <sub>2</sub> -3W-U	-865.028	-863.08965	102.67	0.018
TS3-3W-U	-865.025	-863.09144	100.61	0.017
<i>t</i> -HONO- $\text{HNO}_3$ -U-2W	-865.040	-863.10828	102.14	0.017
IM1	-712.101	-710.48417	71.46	0.019
TS1-1W-U-1	-712.083	-710.48434	68.75	0.019
<i>c</i> -HONO- $\text{HNO}_3$ -U	-712.098	-710.50318	71.23	0.019
IM2	-712.094	-710.49011	71.48	0.019
TS2-1W-U	-712.082	-710.47426	69.08	0.020
<i>c</i> -HONO-UN-1	-712.097	-710.49040	71.98	0.019

IM3	-712.096	-710.49471	71.87	0.019
TS3-1W-U	-712.079	-710.47229	68.85	0.019
HNO <sub>2</sub> -UN-1	-712.091	-710.47669	73.01	0.019
IM4	-712.090	-710.48397	72.43	0.019
TS4-1W-U	-712.079	-710.47208	68.94	0.019
<i>t</i> -HONO-UN-1	-712.097	-710.49314	72.25	0.019
IM5	-712.083	-710.48209	71.47	0.019
TS5-1W-U	-712.075	-710.46724	68.69	0.019
HNO <sub>2</sub> -UN-2	-712.100	-710.49235	71.70	0.019
IM6	-712.079	-710.47274	71.93	0.019
TS6-1W-U	-712.077	-710.46793	69.02	0.019
<i>t</i> -HONO -UN-2	-712.106	-710.50322	71.09	0.019
IM2-W	-788.561	-786.79497	87.52	0.019
TS1-2W-U	-788.553	-786.78186	84.57	0.019
<i>c</i> -HONO-UN-W	-788.567	-786.79532	87.87	0.019
IM3-W	-788.565	-786.79960	87.95	0.018
TS2-2W-U	-788.552	-786.78145	84.51	0.019
HNO <sub>2</sub> -UN-W	-788.562	-786.78882	88.91	0.019
IM4-W	-788.559	-786.78978	88.47	0.018
TS3-2W-U	-788.551	-786.77877	85.07	0.018
<i>t</i> -HONO-UN-W	-788.561	-786.78984	88.62	0.018

**Table S2.** The relative energies( $\Delta E$ ), reaction enthalpy ( $\Delta H$ ) and Gibbs free energies ( $\Delta G$ ) of main species involved in the title reactions at CCSD(T)/6-311++G(d, p)//B3LYP/6-311G(d, p) level of theory. (The unit of data is in hartree)

species	$\Delta E$	$\Delta H$	$\Delta G$
NO <sub>2</sub>	-204.6754835	-204.6716085	-204.64680
H <sub>2</sub> O	-76.2652848	-76.2615058	-76.282931
NH <sub>2</sub> CONH <sub>2</sub>	-224.7365876	-224.7312546	-224.81488
<i>c</i> -HONO	-205.2929326	-205.2904436	-205.31690
<i>t</i> -HONO	-224.7354513	-205.2888426	-205.31861
HNO <sub>2</sub>	-205.2781817	-205.2742847	-205.30196
HNO <sub>3</sub>	-280.3267611	-280.3222881	-280.35250
<i>t</i> -ONONO <sub>2</sub>	-409.3555317	-409.3486587	-409.38630
<i>t</i> -ONONO <sub>2</sub> -U	-485.6229135	-634.0903104	-634.14278
<i>t</i> -ONONO <sub>2</sub> -W	-634.1029194	-485.6134815	-485.65651
UN-1	-505.0795549	-505.0697522	-205.30196
UN-2	-505.0861327	-505.0581354	-505.10247
UN-W	-581.3569929	-505.0697496	-581.38146
<i>t</i> -HONO-U	-430.0416706	-430.0322336	-430.07588
<i>c</i> -HONO-U	-430.0399788	-430.0306068	-430.07413
HNO <sub>2</sub> -U	-430.0274802	-430.0182392	-430.06160
<i>t</i> -ONONO <sub>2</sub> -1W-U	-710.3713698	-710.3568148	-710.41419
TS1-1W-U	-710.3756118	-710.3618708	-710.41720
<i>t</i> -HONO-HNO <sub>3</sub> -U	-710.3901976	-710.3751366	-710.43631
<i>t</i> -ONONO <sub>2</sub> -2W-U	-786.6532795	-786.6308777	-786.69507
TS2-2W-U	-786.6482757	-786.6365265	-786.69916
<i>t</i> -HONO-HNO <sub>3</sub> -U-W	-786.6660254	-786.6479334	-786.71614
<i>t</i> -ONONO <sub>2</sub> -3W-U	-862.9260388	-862.9059648	-862.976594
TS3-3W-U	-862.9310898	-862.9116188	-862.98100
<i>t</i> -HONO-HNO <sub>3</sub> -U-2W	-862.9455111	-862.9248061	-862.997694
IM1	-710.3867301	-710.3719231	-710.432164
TS1-1W-U-1	-710.3665509	-710.3531569	-710.408454
<i>c</i> -HONO-HNO <sub>3</sub> -U	-710.3826603	-710.3678003	-710.427495
IM2	-710.3761913	-710.3614163	-710.42092
TS2-1W-U	-710.3641607	-710.3510427	-710.40464
<i>c</i> -HONO-UN-1	-710.3756863	-710.3621833	-710.41666

IM3	-710.3801784	-710.3655564	-710.42446
TS3-1W-U	-710.3625651	-710.3497831	-710.40238
HNO <sub>2</sub> -UN-1	-710.3603292	-710.3470362	-710.40111
IM4	-710.3685486	-710.3540756	-710.41290
TS4-1W-U	-710.3622114	-710.3493624	-710.40203
<i>t</i> -HONO-UN-1	-710.3779909	-710.3645499	-710.41880
IM5	-710.3681827	-710.3539247	-710.41085
TS5-1W-U	-710.3577749	-710.3442349	-710.40061
HNO <sub>2</sub> -UN-2	-710.3780779	-710.3635739	-710.42145
IM6	-710.3579424	-710.3441720	-710.40062
TS6-1W-U	-710.3579424	-710.3445134	-710.39941
<i>t</i> -HONO -UN-2	-710.389922	-710.3752920	-710.43312
IM2-W	-786.6554889	-786.6382119	-786.70255
TS1-2W-U	-786.6470933	-786.6307093	-786.69220
<i>c</i> -HONO-UN-W	-786.6552883	-786.6390143	-786.70028
IM3-W	-786.6594465	-786.6423235	-786.70634
TS2-2W-U	-786.6467761	-786.6308681	-786.69094
HNO <sub>2</sub> -UN-W	-786.647134	-786.631064	-786.69169
IM4-W	-786.6487867	-786.6319047	-786.69535
TS3-2W-U	-786.6431901	-786.6276741	-786.68710
<i>t</i> -HONO-UN-W	-786.6486117	-786.6325667	-786.69373

**Table S3:** The harmonic vibrational frequencies (imaginary frequency is suffixed with i) of all the species in the reactions  $2\text{NO}_2 + m\text{H}_2\text{O} + \text{NH}_2\text{CONH}_2$  ( $m=1, 2$ ) were obtained at B3LYP/6-311G(d, p) level.

Species	B3LYP /6-311G(d, p)
$\text{NO}_2$	766, 1399, 1706
$\text{H}_2\text{O}$	1638, 3810, 3907
$\text{NH}_2\text{CONH}_2$	383, 446, 475, 545, 582, 584, 786, 949, 1048, 1184, 1411, 1634, 1636, 1816, 3567, 3573, 3681, 3682
<i>c</i> -HONO	590, 620, 835, 1298, 1791, 3776
<i>t</i> -HONO	638, 717, 892, 1338, 1720, 3584
$\text{HNO}_2$	800, 1068, 1407, 1542, 1677, 3145
$\text{HNO}_3$	481, 589, 654, 775, 911, 1327, 1358, 1778, 3736
<i>t</i> -ONONO <sub>2</sub>	35, 126, 210, 307, 491, 641, 768, 811, 943, 1337, 1735, 1944
<i>t</i> -ONONO <sub>2</sub> -U	33, 37, 63, 85, 106, 129, 159, 170, 280, 313, 356, 445, 500, 510, 528, 598, 704, 711, 759, 780, 808, 991, 997, 1069, 1181, 1306, 1469, 1611, 1637, 1657, 1732, 2067, 3457, 3585, 3662, 3700
<i>t</i> -ONONO <sub>2</sub> -W	60, 90, 122, 184, 196, 272, 304, 327, 379, 533, 686, 698, 756, 810, 969, 1303, 1635, 1657, 2054, 3649, 3841
UN-1	52, 58, 93, 126, 130, 218, 454, 499, 521, 564, 593, 656, 694, 706, 789, 862, 938, 963, 1023, 1080, 1200, 1328, 1391, 1496, 1626, 1637, 1751, 1841, 2981, 3506, 3555, 3603, 3602
UN-2	31, 52, 95, 137, 155, 200, 355, 431, 500, 521, 597, 646, 654, 709, 776, 788, 966, 987, 1000, 1066, 1181, 1338, 1467, 1500, 1630, 1649, 1738, 1746, 2868, 3523, 3591, 3677, 3706
UN-W	33, 37, 71, 73, 90, 172, 204, 260, 273, 301, 459, 494, 521, 558, 564, 652, 711, 739, 752, 805, 812, 812, 826, 1048, 1099, 1186, 1224, 1285, 1342, 1571, 1580, 161, 1638, 1662, 1714, 1893, 2421, 2803, 3419, 3455, 3527, 3673, 3878
<i>t</i> -HONO-U	56, 74, 94, 138, 188, 208, 453, 489, 544, 568, 586, 702, 710, 862, 922, 930, 964, 1085, 1201, 1388, 1478, 1629, 1647, 1759, 1836, 3330, 3514, 3540, 3610, 3673
<i>c</i> -HONO-U	49, 67, 114, 133, 191, 228, 459, 497, 549, 554, 585, 709, 715, 864, 933, 1003, 1028, 1082, 1200, 1388, 1449, 1627, 1642, 1658, 1836, 3105, 3513, 3552, 3610, 3683
$\text{HNO}_2$ -U	49, 67, 121, 133, 169, 259, 463, 499, 555, 585, 587, 724, 792, 876, 934, 1090, 1192, 1205, 1368, 1406, 1565, 1628, 1648, 1668, 1834, 2975, 3511, 3530, 3611, 3677
<i>t</i> -ONONO <sub>2</sub> -1W-U	30, 53, 66, 72, 80, 114, 119, 146, 180, 226, 246, 304, 342, 397, 492, 500, 501, 551, 576, 585, 662, 708, 722, 795, 820, 911, 965, 990, 1052, 1066, 1189, 1299, 1462, 1514, 1647, 1651, 1678, 1738, 2081, 3283, 3347, 3572, 3585, 3689, 3694
TS1-1W-U	485i, 21, 50, 74, 75, 91, 99, 127, 149, 198, 238, 274, 285, 471,

	481, 495, 544, 569, 586, 608, 713, 735, 779, 813, 827, 979, 995, 1064, 1095, 1150, 1186, 1416, 1464, 1542, 1582, 1635, 1650, 1656, 1741, 2026, 3176, 3574, 3591, 3684, 3703
<i>t</i> -HONO-HNO <sub>3</sub> -U	14, 19, 32, 43, 71, 77, 95, 103, 138, 157, 174, 260, 337, 423, 495, 508, 583, 618, 631, 654, 673, 770, 781, 829, 864, 920, 974, 993, 1055, 1171, 1347, 1409, 1420, 1471, 1636, 1663, 1750, 1760, 1781, 3111, 3302, 3545, 3590, 3681, 3706
<i>t</i> -ONONO <sub>2</sub> -2W-U	21, 28, 49, 53, 67, 80, 84, 91, 138, 174, 196, 217, 236, 267, 303, 322, 355, 386, 390, 456, 507, 520, 531, 583, 659, 670, 707, 734, 775, 819, 853, 993, 1012, 1055, 1062, 1066, 1170, 1290, 1468, 1524, 1639, 1668, 1673, 1700, 1744, 2082, 3210, 3215, 3344, 3588, 3661, 3681, 3704, 3844
TS2-2W-U	388i, 22, 31, 56, 63, 76, 85, 87, 100, 143, 174, 205, 215, 215, 236, 249, 288, 314, 398, 447, 485, 507, 530, 585, 621, 661, 711, 755, 771, 814, 843, 850, 964, 998, 1055, 1123, 1170, 1222, 1430, 1473, 1530, 1594, 1633, 1641, 1679, 1704, 1745, 2018, 3026, 3335, 3591, 3663, 3696, 3708, 3839
<i>t</i> -HONO-HNO <sub>3</sub> -U-W	13, 16, 33, 43, 49, 67, 72, 79, 99, 118, 157, 163, 182, 209, 255, 288, 310, 331, 434, 501, 515, 532, 589, 629, 648, 685, 771, 781, 803, 853, 888, 931, 996, 1010, 1052, 1169, 1346, 1419, 1459, 1481, 1638, 1661, 1682, 1736, 1754, 1763, 2929, 3249, 3402, 3593, 3664, 3710, 3765, 3869
<i>t</i> -ONONO <sub>2</sub> -3W-U	19, 29, 37, 42, 54, 63, 73, 83, 112, 120, 133, 157, 178, 211, 217, 267, 275, 297, 337, 339, 361, 373, 431, 462, 488, 509, 538, 544, 585, 652, 713, 721, 739, 774, 814, 841, 921, 996, 1052, 1056, 1069, 1081, 1166, 1313, 1471, 1505, 1639, 1646, 1668, 1674, 1704, 1736, 2079, 3102, 3165, 3342, 3520, 3588, 3645, 3664, 3703, 3838, 3859
TS3-3W-U	305i, 20, 25, 37, 51, 57, 67, 78, 94, 121, 128, 136, 162, 175, 206, 222, 229, 276, 279, 326, 359, 431, 458, 470, 483, 512, 537, 587, 641, 656, 715, 757, 770, 813, 848, 919, 935, 993, 997, 1054, 1160, 1178, 1243, 1415, 1476, 1561, 1595, 1622, 1645, 1669, 1673, 1704, 1740, 2011, 2864, 3330, 3524, 3590, 3659, 3668, 3706, 3833, 3860
<i>t</i> -HONO-HNO <sub>3</sub> -U-2W	20, 26, 32, 45, 48, 67, 74, 77, 87, 102, 110, 129, 148, 173, 179, 185, 206, 262, 294, 321, 329, 373, 428, 450, 488, 513, 533, 596, 633, 682, 697, 747, 771, 790, 856, 892, 932, 953, 1006, 1063, 1095, 1168, 1348, 1433, 1479, 1497, 1635, 1646, 1660, 1681, 1727, 1738, 1761, 2706, 3142, 3304, 3590, 3607, 3672, 3705, 3787, 3843, 3878
IM1	15, 24, 43, 55, 60, 85, 91, 105, 120, 153, 179, 257, 405, 457, 508, 562, 597, 626, 676, 695, 712, 778, 814, 831, 870, 936, 968, 1015, 1068, 1198, 1341, 1385, 1423, 1486, 1630, 1644, 1750, 1785, 1835, 3103, 3290, 3508, 3568, 3607, 3706

TS1-1W-U-1	518i, 21, 40, 50, 77, 98, 111, 139, 170, 179, 189, 366, 440, 465, 512, 527, 580, 622, 685, 712, 734, 774, 800, 816, 948, 1065, 1077, 1106, 1201, 1252, 1344, 1391, 1556, 1583, 1589, 1641, 1647, 1661, 1784, 1904, 2211, 3343, 3537, 3680
<i>c</i> -HONO-HNO <sub>3</sub> -U	28, 36, 44, 52, 58, 71, 87, 111, 119, 157, 186, 229, 342, 469, 522, 572, 579, 607, 652, 699, 742, 785, 805, 854, 871, 951, 979, 1038, 1079, 1204, 1303, 1348, 1391, 1486, 1627, 1646, 1736, 1762, 1838, 2881, 3479, 3497, 3568, 3597, 3717
IM2	25, 32, 46, 53, 59, 75, 81, 111, 124, 182, 216, 248, 307, 465, 516, 568, 598, 614, 664, 727, 729, 745, 781, 861, 898, 945, 1049, 1062, 1074, 1203,
TS2-1W-U	714i, 36, 58, 65, 78, 95, 118, 144, 167, 177, 285, 360, 429, 466, 484, 576, 617, 638, 663, 692, 746, 785, 817, 855, 940, 1063, 1081, 1155, 1203, 1286, 1324, 1389, 1447, 1515, 1531, 1624, 1644, 1676, 1707, 1881, 2370, 3358, 3528, 3538, 3698
<i>c</i> -HONO-UN-1	46, 47, 65, 69, 96, 130, 149, 161, 180, 221, 246, 281, 479, 521, 545, 560, 660, 713, 719, 728, 786, 792, 829, 1042, 1060, 1065, 1081, 1132, 1198, 1242, 1351, 1417, 1560, 1576, 1617, 1629, 1636, 1705, 1904, 2250, 3006, 3258, 3379, 3526, 3675
IM3	25, 36, 46, 54, 61, 87, 90, 115, 135, 179, 215, 242, 355, 462, 518, 567, 604, 628, 666, 726, 742, 770, 830, 858, 902, 941, 984, 1029, 1067, 1201, 1344, 1385, 1404, 1505, 1629, 1643, 1759, 1775, 1837, 3131, 3309, 3502, 3577, 3600, 3715
TS3-1W-U	863i, 44, 61, 69, 84, 104, 133, 143, 173, 190, 340, 410, 441, 490, 496, 575, 639, 646, 684, 712, 756, 796, 827, 876, 962, 1084, 1099, 1197, 1211, 1293, 1371, 1404, 1480, 1552, 1567, 1629, 1645, 1664, 1697, 1740, 1884, 3269, 3489, 3527, 3688
HNO <sub>2</sub> -UN-1	42, 47, 68, 80, 92, 130, 154, 171, 195, 207, 262, 312, 500, 528, 556, 565, 665, 712, 731, 792, 795, 803, 834, 1047, 1086, 1152, 1201, 1225, 1242, 1343, 1380, 1539, 1565, 1585, 1640, 1646, 1671, 1713, 1903, 2343, 2887, 3094, 3355, 3523, 3673
IM4	25, 35, 42, 51, 66, 82, 91, 111, 116, 185, 223, 303, 356, 463, 521, 575, 610, 631, 674, 743, 771, 801, 840, 875, 908, 949, 1070, 1202, 1245, 1336, 1357, 1397, 1401, 1596, 1629, 1644, 1693, 1769, 1836, 2775, 3258, 3499, 3572, 3599, 3715
TS4-1W-U	977i, 53, 57, 72, 74, 117, 125, 151, 166, 177, 332, 382, 441, 481, 492, 568, 638, 663, 674, 706, 762, 791, 832, 853, 968, 1084, 1115, 1167, 1211, 1292, 1348, 1389, 1519, 1566, 1614, 1625, 1647, 1655, 1695, 1779, 1876, 3319, 3507, 3534, 3693
<i>t</i> -HONO-UN-1	44, 50, 68, 81, 99, 129, 145, 166, 173, 232, 239, 281, 498, 531, 555, 572, 667, 714, 730, 734, 786, 796, 830, 975, 985, 1051, 1085, 1144, 1200, 1235, 1352, 1452, 1567, 1580, 1634, 1642, 1709, 1746, 1902, 2168, 3155, 3258, 3367, 3523, 3672
IM5	29, 42, 47, 77, 86, 98, 124, 153, 174, 188, 205, 233, 291, 431,



	530, 588, 647, 692, 702, 736, 740, 771, 798, 927, 979, 1005, 1051, 1092, 1119, 1239, 1323, 1338, 1479, 1494, 1525, 1636, 1710, 1734, 1745, 2640, 3080, 3534, 3593, 3615, 3740
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<i>c</i> -HONO -UN-W	29, 46, 50, 65, 68, 85, 104, 114, 138, 172, 184, 225, 241, 252, 268, 339, 452, 494, 530, 556, 603, 659, 709, 731, 749, 783, 788, 830, 864, 1040, 1079, 1090, 1102, 1168, 1205, 1308, 1347, 1467, 1549, 1578, 1621, 1635, 1657, 1670, 1717, 1902, 2510, 2818, 3209, 3258, 3314, 3521, 3669, 3877
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HNO <sub>2</sub> -UN-W	32, 47, 56, 64, 76, 88, 102, 111, 159, 168, 193, 216, 237, 278, 305, 331, 478, 496, 526, 562, 582, 664, 714, 734, 779, 800, 804, 830, 887, 1051, 1089, 1179, 1205, 1242, 1300, 1337, 1374, 1524, 1554, 1595, 1641, 1662, 1674, 1680, 1711, 1903, 2629, 2787, 3038, 3287, 3323, 3517, 3670, 3878
IM4-W	23, 34, 50, 55, 63, 76, 91, 107, 126, 139, 157, 205, 208, 243, 269, 321, 373, 476, 506, 555, 577, 642, 644, 680, 696, 774, 784, 801, 885, 921, 959, 986, 1095, 1233, 1277, 1321, 1355, 1398, 1441, 1605, 1635, 1641, 1676, 1696, 1729, 1828, 2635, 3093, 3427, 3516, 3582, 3675, 3698, 3882
TS3-2W-U	640i, 34, 44, 58, 74, 80, 91, 107, 120, 139, 175, 181, 218, 244, 326, 358, 419, 449, 493, 516, 583, 620, 640, 684, 702, 727, 758, 798, 842, 877, 983, 1092, 1152, 1211, 1238, 1297, 1340, 1414, 1454, 1558, 1598, 1644, 1659, 1661, 1678, 1737, 1795, 1875, 3099, 3521, 3526, 3624, 3696, 3886
<i>t</i> -HONO-UN-W	32, 47, 56, 64, 76, 88, 102, 111, 159, 168, 193, 216, 237, 278, 305, 331, 478, 496, 526, 562, 582, 664, 714, 734, 779, 800, 804, 830, 887, 1051, 1089, 1179, 1205, 1242, 1300, 1337, 1374, 1524, 1554, 1595, 1641, 1662, 1674, 1680, 1711, 1903, 2629, 2787, 3038, 3287, 3323, 3517, 3670, 3878

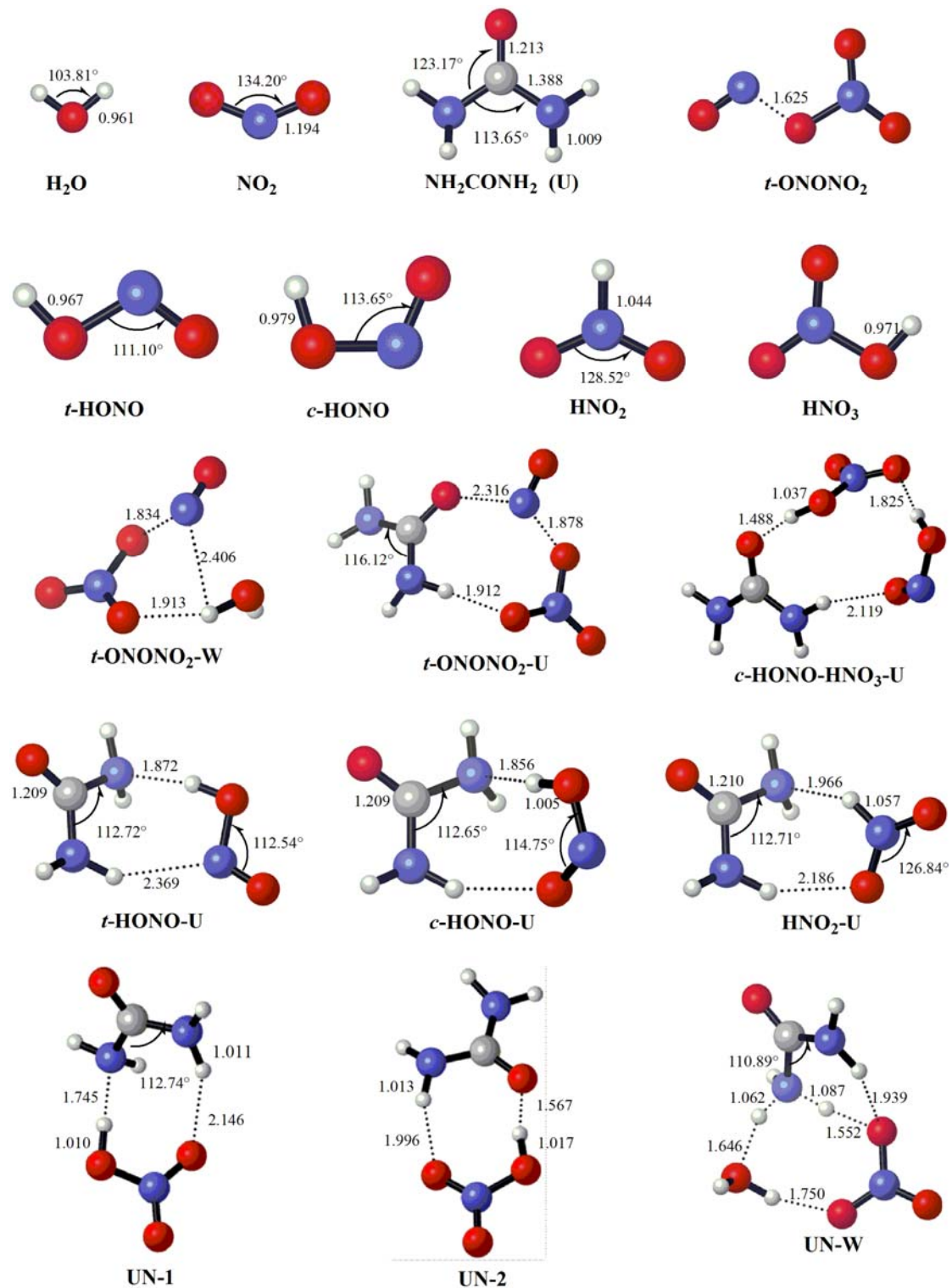
**Table S4.** The relative energies  $\Delta E$ , enthalpies  $\Delta H$ , and Gibbs free energies  $\Delta G$  of the complexes obtained at CCSD(T)/6-311++G(d, p)//B3LYP/6-311G(d, p) + ZPE level, and compared with the data in parentheses obtained at CCSD(T)/6-311++G(d, p)//MP2/6-311G(d, p) + ZPE level. (in kcal/mol)

	Reactant Complexes			Product Complexes		
	$\Delta E$	$\Delta H$	$\Delta G$	$\Delta E$	$\Delta H$	$\Delta G$
2NO <sub>2</sub> +H <sub>2</sub> O+NH <sub>2</sub> CONH <sub>2</sub>						
Pathway1	-11.62 (-19.45)	-13.07 (-17.30)	-14.28 (-19.44)	-23.63 (-25.67)	-24.57 (-23.85)	-28.16 (-26.21)
Pathway2	-14.65 (-17.14)	-15.96 (-15.50)	-18.50 (-16.78)	-14.33 (-20.34)	-16.44 (-18.72)	-15.83 (-20.59)
Pathway3	-17.15 (-18.89)	-18.56 (-17.31)	-20.73 (-18.48)	-4.70 (-10.53)	-6.94 (-9.57)	-6.07 (-8.93)
Pathway4	-9.63 (-11.83)	-11.26 (-10.35)	-12.18 (-11.53)	-15.83 (-18.00)	-17.32 (-16.94)	-18.84 (-16.50)

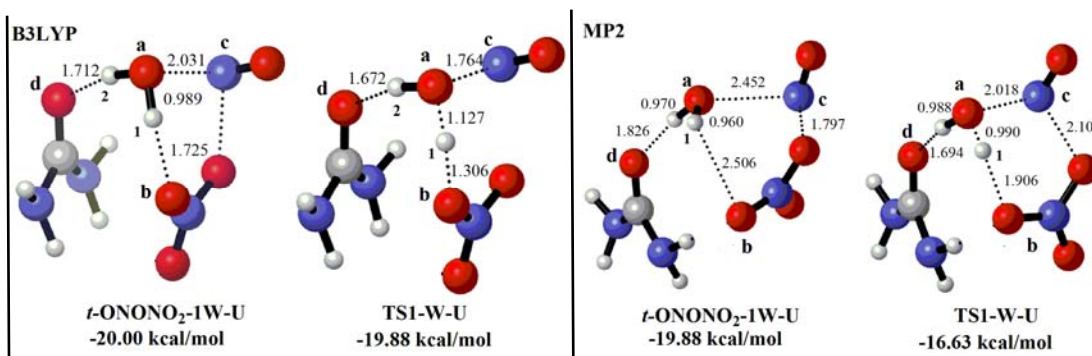
**Table S5.** Comparing the relative energies  $\Delta E$ , enthalpies  $\Delta H$ , and Gibbs free energies  $\Delta G$  (in kcal/mol) of the complexes. The data is obtained at CCSD(T)/6-311++G(d, p)//B3LYP/6-311G(d, p) + ZPE level at non-solvent and solvent (solvent=water) conditions. (The unit is kcal/mol)

	Reactant Complexes			Product Complexes		
	$\Delta E$	$\Delta H$	$\Delta G$	$\Delta E$	$\Delta H$	$\Delta G$
2NO <sub>2</sub> +H <sub>2</sub> O+NH <sub>2</sub> CONH <sub>2</sub>						
Pathway1 (non-solvent)	-11.62	-13.07	-14.28	-23.63	-24.57	-28.16
Pathway1 (solvent)	-12.57	-13.89	17.01	-20.01	-21.26	8.97
Pathway4 (non-solvent)	-9.63	-11.26	-12.18	-15.83	-17.32	-18.84
Pathway4 (solvent)	-8.15	-9.85	21.15	-13.09	-15.24	17.44

**Fig S1.** Reactants, complexes and products for the reactions  $2\text{NO}_2 + m\text{H}_2\text{O} + \text{NH}_2\text{CONH}_2$  ( $m=1, 2$ ) at the B3LYP/6-311G (d, p) level.

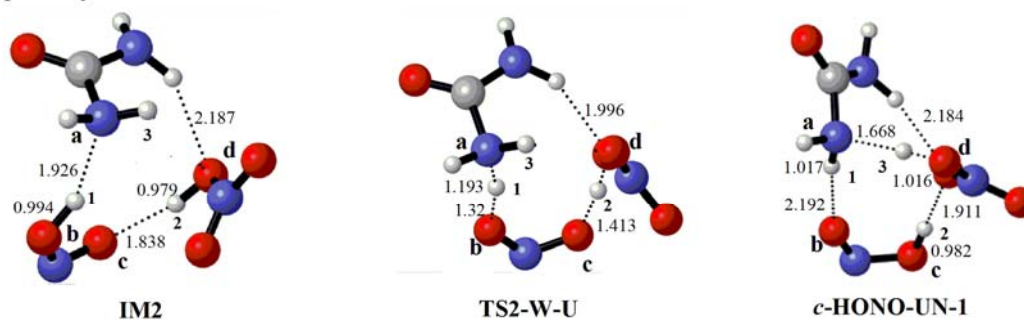


**Fig S2.** The transition state TS1-W-U and reactant complex *t*-ONONO<sub>2</sub>-1W-U configurations of hydrolysis reaction optimized at the B3LYP/6-311G(d, p) level and MP2/6-311G(d, p) level.

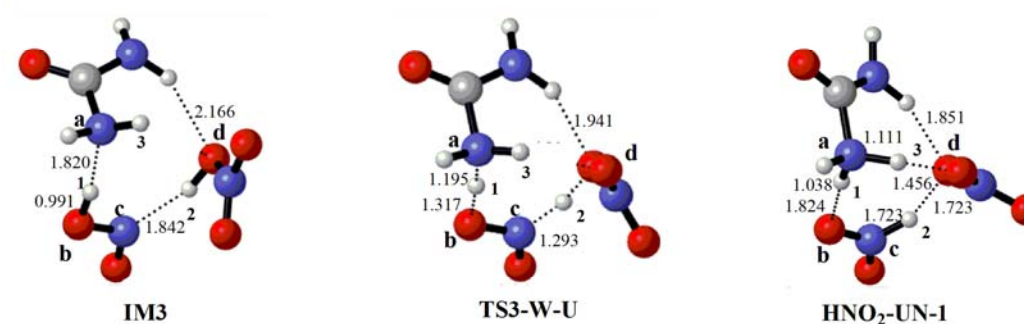


**Fig S3.** Transition states and complexes of urea nitrate formation mechanism obtained under the MP2 method

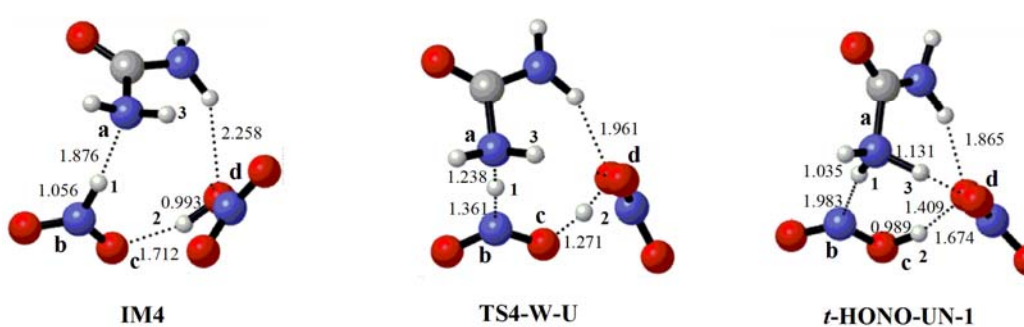
pathway2



pathway3

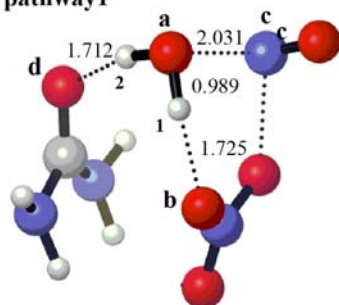


pathway4

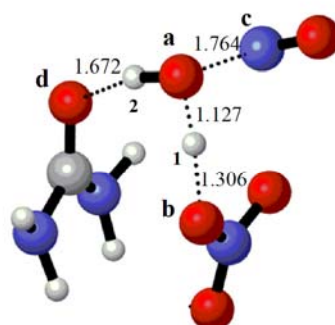


**Fig S4.** Transition states and complexes for the reaction  $2\text{NO}_2 + \text{H}_2\text{O} + \text{NH}_2\text{CONH}_2$  at the B3LYP/6-311G (d, p) level at non-solvent and solvent (solvent=water) conditions.

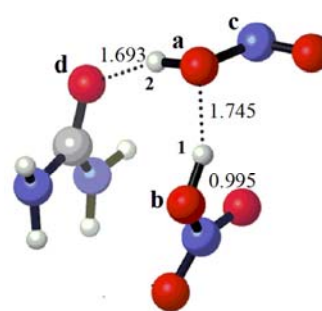
**non-solvent  
pathway1**



*t*-ONONO<sub>2</sub>-1W-U

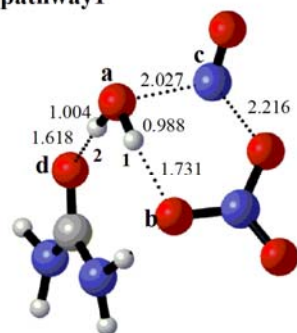


TS1-W-U

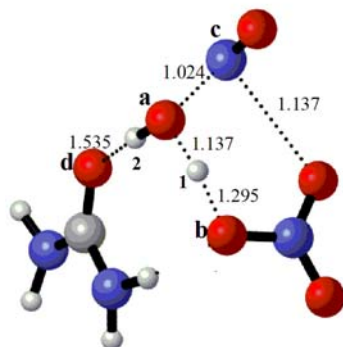


*t*-HONO-HNO<sub>3</sub>-U

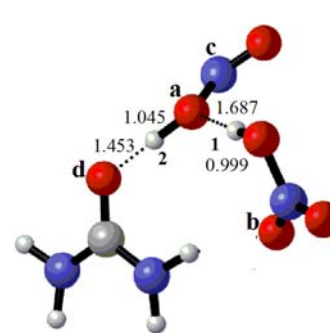
**solvent (solvent=water)  
pathway1**



*t*-ONONO<sub>2</sub>-1W-U

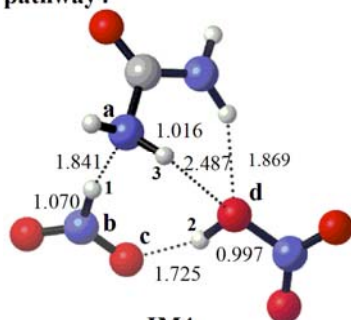


TS1-W-U

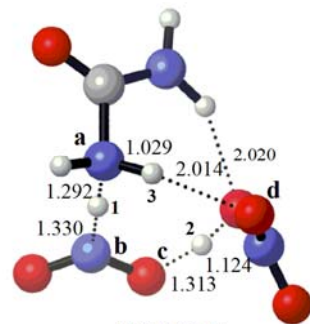


*t*-HONO-HNO<sub>3</sub>-U

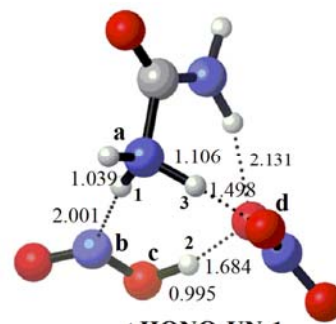
**non-solvent  
pathway4**



IM4

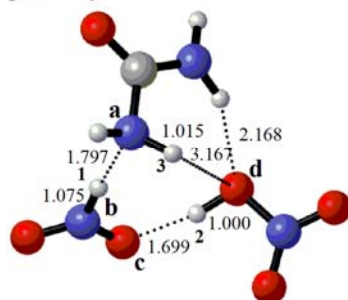


TS4-W-U

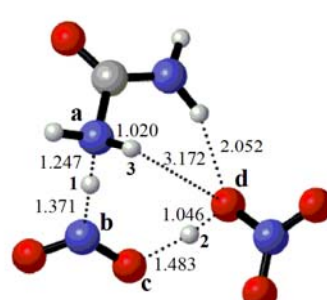


*t*-HONO-UN-1

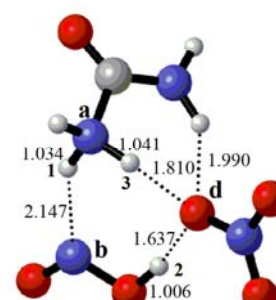
**solvent (solvent=water)  
pathway4**



IM4



TS4-W-U



*t*-HONO-UN-1