Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

The ammonium nitrate and its mechanism of decomposition in the gas phase: a theoretical study and a DFT benchmark

Stefania Cagnina, Patricia Rotureau, Guillaume Fayet and Carlo Adamo

SUPPORTING INFORMATION

Table S1. Relative energies (kcal/mol) for the decomposition reaction of ammonium nitrate obtained using three different basis sets.

	B3LYP/6-31G(d)		B3LYP/6-31+G(d,p)		B3LYP/6-311+G(2d,2p)	
	ΔE	BSSE	ΔE	BSSE	ΔE	BSSE
NH_4NO_3	0.0	2.2	0.0	1.4	0	0.5
NH_3 + HNO_3	17.5		15.3		13.0	
°NO_2 + HO°	69.5		64.1		62.1	
TS_1	72.7		66.7		64.7	
°NH_2+H_2O	63.7		55.5		52.7	
NH_2NO_2	9.3		1.7		-0.1	
$TS_{2[A]}$	51.7		42.8		41.8	
HN=NO(OH)	20.9		12.3		10.3	
$TS_{3[A]}$	56.1		44.2		42.2	
N_20+H_2O	-16.2		-29.4		-34.2	
N_2 + °OOH	-39.1		-51.5		-57.1	
O_2 + 2°OH	-52.5		-63.2		-68.3	
H_2NONO	29.9		24.1		22.9	
H_2NO° + NO°	47.2		37.4		35.8	
H_2N-N=O	-4.8		-14.9		-14.0	
$TS_{2[B]}$	29.9		20.1		21.6	
HN=N-OH	0.0		-11.9		-12.2	
$TS_{3[B]}$	28.6		14.3		13.6	
N_2+H_2O	-62.4		-77.4		-81.9	
°N_2H + °OH	52.1		38.8		37.4	
$TS_{3[C]1}$	59.9		46.0		44.9	
H_2O + NO_3^-	-26.5		-63.0		-64.3	
$TS_{3[C]2}$	65.7		47.2		44.6	
HNO + H_2O	32.5		13.7		10.5	
$TS_{3[C]3}$	107.0		91.3		90.5	
H_2O + ½ O_2	49.3		33.4		31.2	
MAE CBS-QB3	16.4		5.7		4.5	

Table S2. Relative energies (kcal/mol) for the decomposition reaction of ammonium nitrate obtained using different DFT methods using B3LYP/6-311+G(2d,2p) geometries.

	B3LYP	X3LYP	O3LYP	PBE1PBE	M06	M06-HF	M06-2X	M06-L	MPW1PW	BMK	LC-wPBE	CAM-B3LYP	WB97	WB97X	MPW1K	B2PLYP	PBE0DH	CCSD(T)	CBS-QB3
	ΔE	ΔE	ΔE	ΔE	ΔE	ΔE	ΔE	ΔE	ΔE	ΔE	ΔE	ΔE	ΔE	ΔE	ΔE	ΔE	ΔE	ΔE	ΔE
NH_4NO_3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
NH_3 + HNO_3	13.0	13.6	10.3	14.5	13.7	17.7	15.2	13.0	13.9	13.6	13.9	14.6	15.0	15.0	14.4	13.3	14.7	13.2	13.8
$^{\circ}NO_2$ + HO°	62.1	63.2	60.8	67.9	69.5	75.7	70.3	64.6	65.5	66.0	66.9	66.2	68.8	68.5	63.5	62.0	66.3	61.4	67.8
TS_1	64.7	66.0	62.3	70.2	74.5	82.3	75.3	68.6	68.0	71.3	71.4	69.7	75.2	74.0	69.2	64.7	70.6	67.3	71.8
$^{\circ}NH_2$+H_2O	52.7	53.7	51.4	57.4	58.4	62.4	57.8	57.0	54.7	54.7	52.9	54.6	56.9	56.9	50.7	48.8	53.3	46.4	53.0
NH_2NO_2	-0.1	0.0	-1.0	-0.4	-0.9	-6.0	-3.1	3.7	-1.4	-4.3	-4.4	-1.7	-1.9	-1.7	-5.5	-3.7	-4.1	-5.5	-4.7
$TS_{2[A]}$	41.8	42.1	39.4	40.5	39.8	36.8	39.4	44.4	39.9	38.8	37.9	40.9	42.6	42.2	38.6	38.6	38.6	38.1	37.3
HN=NO(OH)	10.3	10.4	10.0	10.7	9.1	3.1	6.4	14.0	9.7	6.8	7.9	9.2	10.3	10.0	6.2	6.7	7.3	3.7	5.1
$TS_{3[A]}$	42.2	43.1	41.6	47.1	42.7	53.5	48.2	41.1	45.8	48.7	49.7	46.6	51.4	50.0	49.9	36.2	46.3	38.0	40.4
N_20+H_2O	-34.2	-33.5	-35.6	-29.6	-37.3	-35.1	-36.8	-32.4	-31.6	-34.0	-33.0	-32.8	-30.6	-31.6	-35.2	-42.2	-35.5	-45.9	-42.4
N_2 + $^{\circ}OOH$	-57.1	-58.6	-56.4	-51.3	-53.7	-75.8	-64.8	-46.2	-53.7	-62.6	-60.2	-60.7	-59.5	-59.3	-58.6	-66.3	-57.8	-74.8	-65.5
O_2 + $2^{\circ}OH$	-68.3	-70.1	-66.6	-63.2	-69.2	-91.2	-80.0	-61.0	-64.3	-73.6	-69.9	-72.2	-71.0	-70.9	-63.8	-79.4	-67.5	-89.9	-85.8
H_2NONO	22.9	23.3	24.6	26.3	24.2	15.9	19.8	26.8	25.0	19.4	22.1	22.3	22.1	22.8	22.8	19.0	23.2	13.5	16.7
H_2NO° + NO°	-35.8	-36.4	-38.2	-41.6	-44.4	-24.4	-34.6	-49.0	-38.7	-33.1	-32.8	-34.4	-35.9	-36.6	-31.0	-33.6	-36.2	-28.8	-35.1
H_2N-N=O	-14.0	-13.8	-13.9	-12.3	-11.4	-27.4	-17.4	-4.6	-13.2	-19.1	-17.9	-16.3	-16.1	-15.8	-17.1	-15.0	-14.8	-15.6	-16.5
$TS_{2[B]}$	21.6	21.9	20.7	22.3	23.0	9.1	18.4	29.8	21.8	17.7	17.5	19.6	20.8	20.9	20.7	19.7	21.0	19.3	17.9
HN=N-OH	-12.2	-12.0	-10.8	-9.7	-9.7	-28.8	-17.5	-2.2	-10.7	-17.6	-15.2	-14.6	-13.9	-13.8	-15.0	-13.4	-12.5	-16.9	-16.1
$TS_{3[B]}$	13.6	14.3	17.7	20.9	18.5	6.4	14.5	21.9	19.5	15.4	19.0	14.6	18.5	17.7	20.2	10.1	19.3	7.6	10.0
N_2+H_2O	-81.9	-81.2	-79.0	-74.8	-78.6	-105.7	-90.4	-68.5	-77.2	-87.7	-84.1	-84.2	-82.6	-82.8	-84.4	-88.4	-82.2	-95.5	-90.2
$^{\circ}N_2H$ + $^{\circ}OH$	37.4	37.9	41.5	43.5	45.4	24.9	36.1	51.0	40.7	35.6	37.2	36.4	40.3	39.7	31.8	36.9	38.3	32.2	38.8
$TS_{3[C]1}$	44.9	45.9	46.1	51.9	55.6	35.5	48.1	57.6	49.3	47.5	48.7	46.8	53.5	52.1	43.8	49.4	50.2	53.5	52.6
H_2O + NO_3^-	-64.3	-62.1	-59.2	-54.0	-55.8	-81.2	-64.9	-41.8	-58.2	-68.0	-66.5	-65.7	-59.9	-60.4	-66.1	-63.8	-60.0	-64.4	-65.5
$TS_{3[C]2}$	44.6	45.7	45.9	52.6	53.3	47.5	52.6	53.7	49.8	49.9	52.2	48.6	55.0	53.1	46.5	41.6	49.0	41.1	48.6

$HNO + H_2O$	10.5	11.5	12.3	18.6	16.1	-4.3	7.8	24.9	14.9	7.4	9.1	9.9	12.2	11.9	3.8	7.2	10.6	-0.7	8.2
$TS_{3[C]3}$	90.5	91.2	95.5	98.3	99.0	80.8	91.9	103.7	95.4	91.2	94.0	91.0	96.4	95.5	88.7	90.2	94.1	85.4	92.8
$H_2O + ½ O_2$	31.2	32.0	33.5	38.1	38.8	19.2	30.2	44.9	34.9	28.9	30.0	30.6	33.0	33.0	25.9	28.3	54.2	21.9	29.4
MAE CBS-QB3	4.5	4.5	5.5	7.9	6.3	8.7	2.5	11.0	5.7	2.9	3.3	3.4	4.8	4.5	4.8	2.5	4.7		
MAE CCSD(T)	6.7	7.1	8.0	10.7	9.9	7.7	5.9	14.0	8.9	5.9	6.9	6.5	8.4	8.2	5.9	3.6	8.1		

Figure S1 Energy profiles of the two lowest paths, obtained at CBS-QB3 level and selected DFT approaches.