Electronic Supplementary Material (ESI) for New Journal of Chemistry.

A combined experimental and theoretical study of the thermal decomposition mechanism and kinetics of ammonium dinitramide (ADN)

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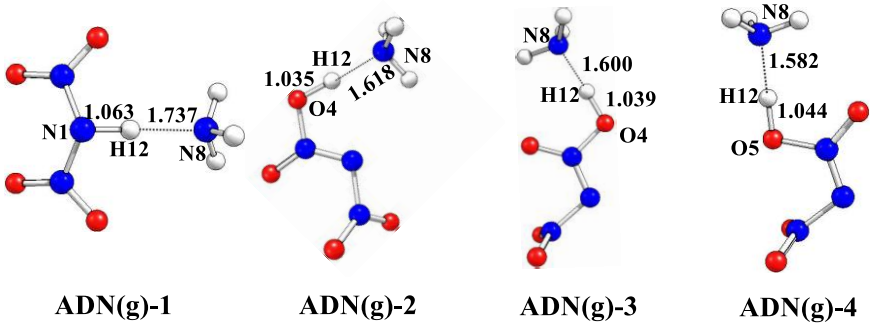

Fig. S1 Four optimized structures of gaseous ADN.

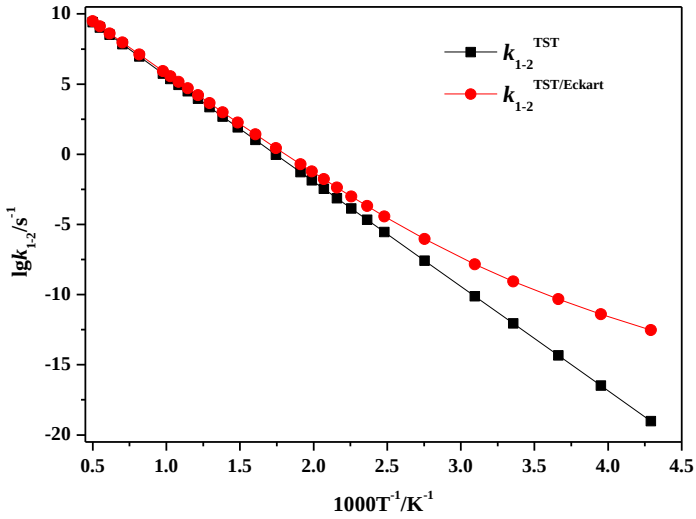

Fig. S2 Arrhenius plots of rate coefficients (k^{TST} and $k^{TST/Eckart}$) of the most favorable decomposition path D3 calculated at the B3LYP-D3 level of theory.

Table S1 Bond dissociation energies (kcal/mol) for the NH_3 elimination reaction of gaseous ADN (four structures).

Reaction	B3LYP-D3[a]	CCSD(T)//B3LYP-D3[b]	Ref.
ADN(g)-1→HDN-1+NH_3	13.0	12.5	12.4[c]
ADN(g)-2--HDN-2+NH_3	15.7	13.7	14.1[c], 13.9[d]
ADN(g)-3--HDN-3+NH_3	16.2	13.7	-
ADN(g)-4--HDN-4+NH_3	16.5	14.2	-

[a]The dissociation energies include zero-point corrections at the B3LYP-D3/6-311G(2d,p), which is denoted as B3LYP-D3；[b]CCSD(T)/6-311+G(3d,2p)//B3LYP-D3/6-311G(2d,p) is denoted as CCSD(T)//B3LYP-D3；[c]Reference 32, MP4(SDQ)/6-31+G(d,p)；[d]Reference 41, Generalized gradient approximation (GGA) with PW91 exchange-correlation functional via the Vienna Ab-initio Simulation Package (VASP).

Table S2 The relative energies (∆*E*, kcal/mol) of species involved in the proton transfer reactions of HDN.

Species	B3LYP-D3[a]	M062X-D3[b]	CCSD(T) //B3LYP-D3[c]	Ref.B3LYP[d]	Ref.G2M[e]
HDN-1	0.0	0.0	0.0	0.0	0.0
TS1	33.6	33.9	35.6	33.7	34.3
HDN-2	7.1	5.7	3.9	7.2	4.0
TS2	11.6	10.3	7.4	13.0	7.7
HDN-3	6.4	4.8	3.1	6.8	3.1
TS3	34.5	33.1	33.4	39.0	32.3
HDN-4	7.5	7.0	5.2	9.1	5.4
TS4	12.6	11.6	9.5	-	-
HDN-5	3.6	2.1	4.5	-	-

[a]The relative energies (∆*E*) include zero-point corrections at the B3LYP-D3/6-311G(2d,p), which is denoted as B3LYP-D3; [b]M062X-D3/6-311G(2d,p) is denoted as B3LYP-D3;[c]CCSD(T)/6-311+G(3d,2p)//B3LYP-D3/6-311G(2d,p) is denoted as CCSD(T)//B3LYP-D3; [d]Reference 33, B3LYP/6-311G(d,p); [e]Reference 33, G2M(RCC,MP2).

Table S3 Relative Energies (Δ*E*), Enthalpies (Δ*H*), and Gibbs free energies (Δ*G*) of all the species for the initial decomposition pathways of HDN. (Δ*H* and Δ*G* Values are given at 1.0 atm and 298.15 K).

Species	Δ*H* (kcal/mol)[a]	Δ*E* (kcal/mol)[b]	Δ*G* (kcal/mol)[b]
HDN-1	0.0	0.0	0.0
A1-TS1	73.5	69.4	69.7
A1-IM1	7.3	3.0	3.0
7+NO	18.0	15.5	4.8
A2-TS1	31.9	36.4	37.3
A2-IM1	17.8	17.4	17.2
6+NO	39.1	41.0	4.8
HDN-2	0.0	0.0	0.0
B1-TS1	69.5	62.2	62.7
B1-IM1	16.4	6.1	6.3
NOOH+2NO	-2.7	-16.2	-36.5
B2-TS1	34.9	38.6	39.5
B2-IM2	17.3	17.7	19.1
NO_3+N_2+OH	-2.8	-13.1	-31.8
B3-TS1	44.4	41.5	41.5
B3-IM1	-0.7	2.0	2.4
NO_2+N_2O+OH	5.6	-0.9	-20.1
HDN-3	0.0	0.0	0.0
C1-TS1	57.5	42.3	41.7
C1-IM1	9.4	7.8	7.5
NOOH+2NO	-2.1	-15.5	-36.1
C2-TS1	44.6	38.9	39.4
C2-IM1	19.1	12.2	10.9
NO_3+N_2+OH	-2.1	-12.4	-31.4
HDN-4	0.0	0.0	0.0
D1-TS1	55.8	40.3	39.6
D1-IM1	6.4	3.5	3.1
NOOH+2NO	-3.7	-17.6	-38.3
D2-TS1	50.1	50.6	51.4
HNO_3+N_2O	-43.4	-45.0	-55.1
D3-TS1	29.1	33.3	33.5
HNO_3+N_2O	-43.4	-45.0	-55.1
HDN-5	0.0	0.0	0.0
E1-TS1	61.0	42.3	41.0
E1-IM1	12.4	5.6	4.4
NOOH+2NO	1.2	-16.8	-38.1
E2-TS2	55.2	51.4	51.5
HNO_3+N_2O	-38.6	-44.2	-54.9

[a] Calculated by B3LYP-D3/6-311G(2d,p); [b] Calculated by CCSD(T)/6-311+G(3d,2p) //B3LYP-D3/6-311G(2d,p).

Table S4 The theoretical rate coefficients expression of the corresponding molecular and radical reaction from the NIST Chemical Kinetics Database.[a]

No.	Reaction	A	n	E_a	order
1	$NOOH \rightarrow NO + OH$	1.09×10^{16}	-1.23	208	1
2	$H + NO \rightarrow HNO$	1.47×10^{14}	-0.41	0	2
3	$HNO + OH \rightarrow H_2O + NO$	4.82×10^{13}	0	4.16	2
4	$HNO + NO_2 \rightarrow NOOH + NO$	6.02×10^{11}	0	8.31	2
5	$H + NO_2 \rightarrow OH + NO$	1.32×10^{14}	0	1.51	2
6	$H + OH \rightarrow H_2O$	2.09×10^{17}	0	0	3

[a]The units of rate constants are s^{-1} for first-order reactions, $m^3\cdot mol^{-1}\cdot s^{-1}$ for second-order reactions, and $m^6\cdot mol^{-2}\cdot s^{-1}$ for second-order reactions. *Ea* is in kJ/mol.