Decomposition of Condensed Phase Energetic Materials: Interplay between Uni- and Bimolecular Mechanisms– Supporting Information

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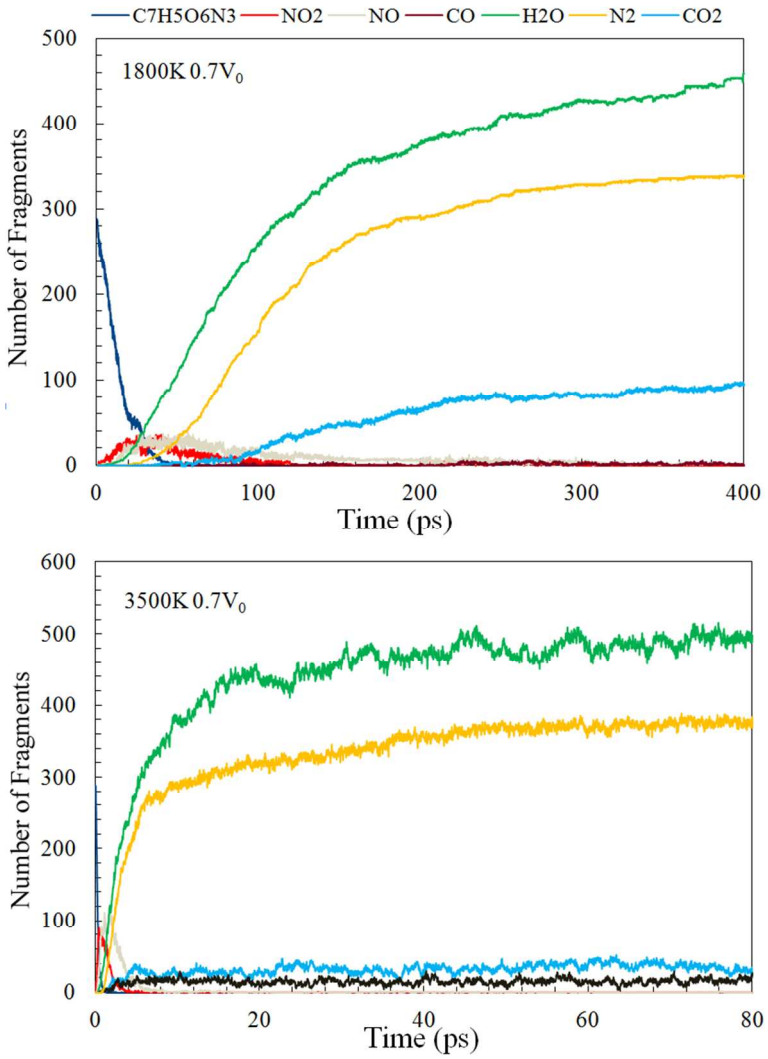
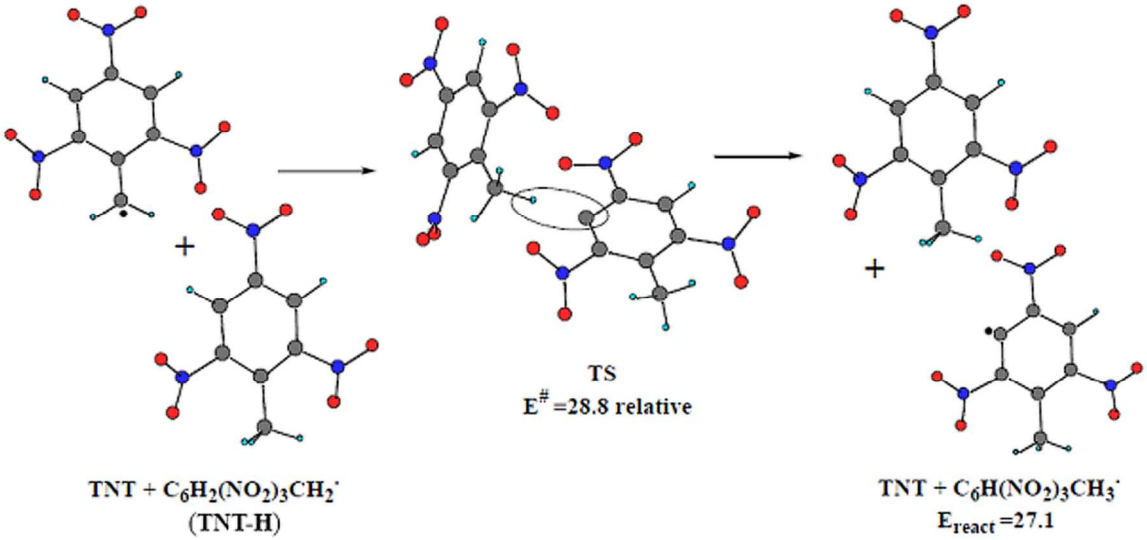


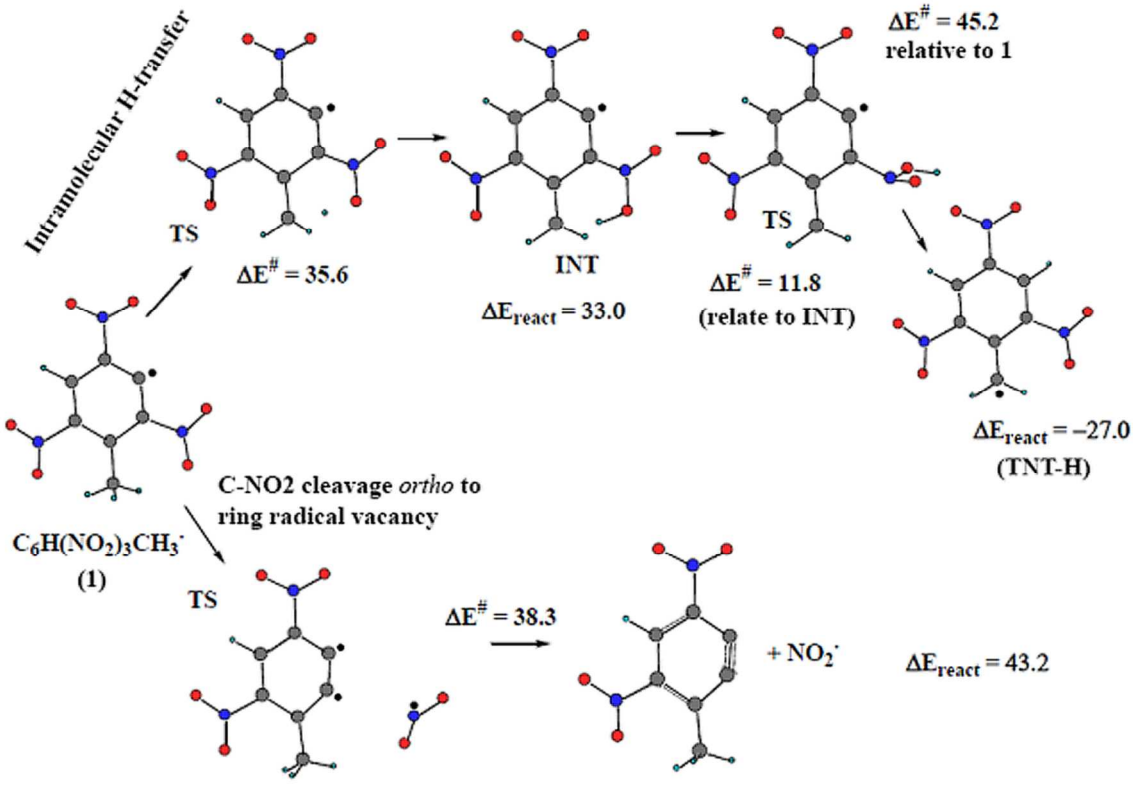
Figure S1: Time evolution of main species for 1800K and 3500K at 0.7V0

Table S1: Parameters obtained by fitting an exponential function to the Potential energy time evolution curve for second stage decomposition (exothermic decay phase) and 1st order rate model to TNT decomposition curves (endothermic step)

T (K)	Super cell volume	τ_{exo} (ps)	ΔQ (cal/g)	t_{max} (ps)	U_0 (kcal/mol)	τ_{endo} (ps)
1800		256.0	-1304.0	49.8	-2688.4	42.9
2250		41.3	-1144.0	8.0	-2580.1	7.1
2500	V_0	22.0	-1092.58	5.3	-2553.3	3.0
3000		10.3	-1091.7	1.7	-2508.0	0.9
3500		5.6	-1095.8	0.7	-2459.5	0.4
1800		165.1	-1280.8	21.2	-2658.0	30.0
2250		34.2	-1191.4	5.2	-2589.4	6.8
2500	0.9 V_0	17.7	-1125.8	3.2	-2555.1	2.3
3000		8.6	-1129.4	1.3	-2513.8	0.9
3500		5.0	-1121.2	0.7	-2465.1	0.4
1800		101.0	-1266.6	11.8	-2639.3	21.5
2250		25.6	-1274.9	3.4	-2597.4	3.7
2500	0.8 V_0	13.3	-1170.1	2.8	-2561.3	1.9
3000		7.4	-1184.9	0.8	-2520.7	0.7
3500		4.3	-1119.9	0.5	-2467.5	0.3
1800		60.9	-1250.42	8.4	-2629.4	11.4
2250		18.4	-1370.2	2.4	-2591.1	3.0
2500	0.7 V_0	10.1	-1244.0	2.3	-2560.9	1.4
3000		5.6	-1514.8	0.8	-2517.3	0.5
3500		3.8	-1606.7	0.04	-2466.2	0.3

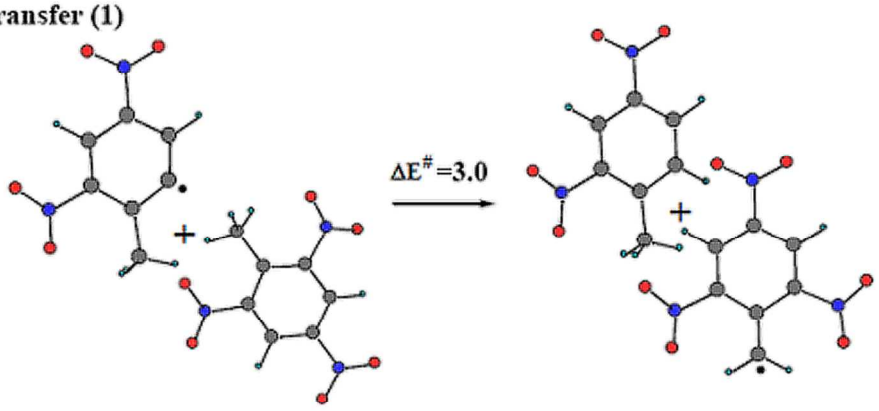
Scheme S1: Hydrogen transfer routes between TNT and TNT-H and the cleavage of C-NO_2 from TNT molecule missing a ring bound hydrogen. Units: kcal/mol.





Scheme S2: Reactions of TNT radical missing a NO_2 group (TNT-NO_2). Units: kcal/mol.

Intermolecular H-transfer (1)

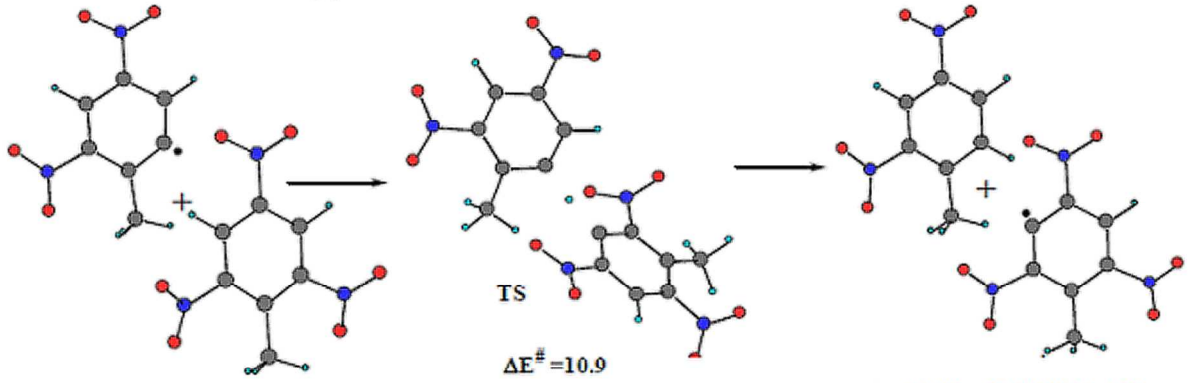


TNT + $C_6H_2(NO_2)_2CH_3$·

2,4-DNT + $C_6H_2(NO_2)_3CH_2$·
(TNT-H)

E_{react} =−22.3

Intermolecular H-transfer (2)

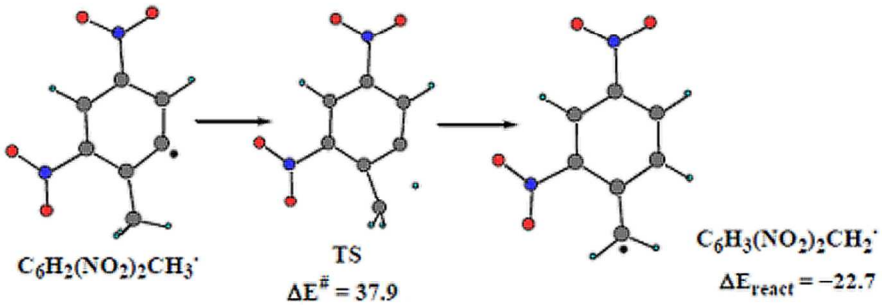


TNT + $C_6H_2(NO_2)_2CH_3$·

2,4-DNT + $C_6H(NO_2)_3CH_3$

ΔE_{react} =4.8

Intramolecular H-transfer



$C_6H_2(NO_2)_2CH_3$·

$C_6H_3(NO_2)_2CH_2$·

ΔE_{react} = −22.7

Scheme S3. Total energies for *ortho* hydrogen transfer (top part) and further decomposition routes (bottom part). Units: kcal/mol.

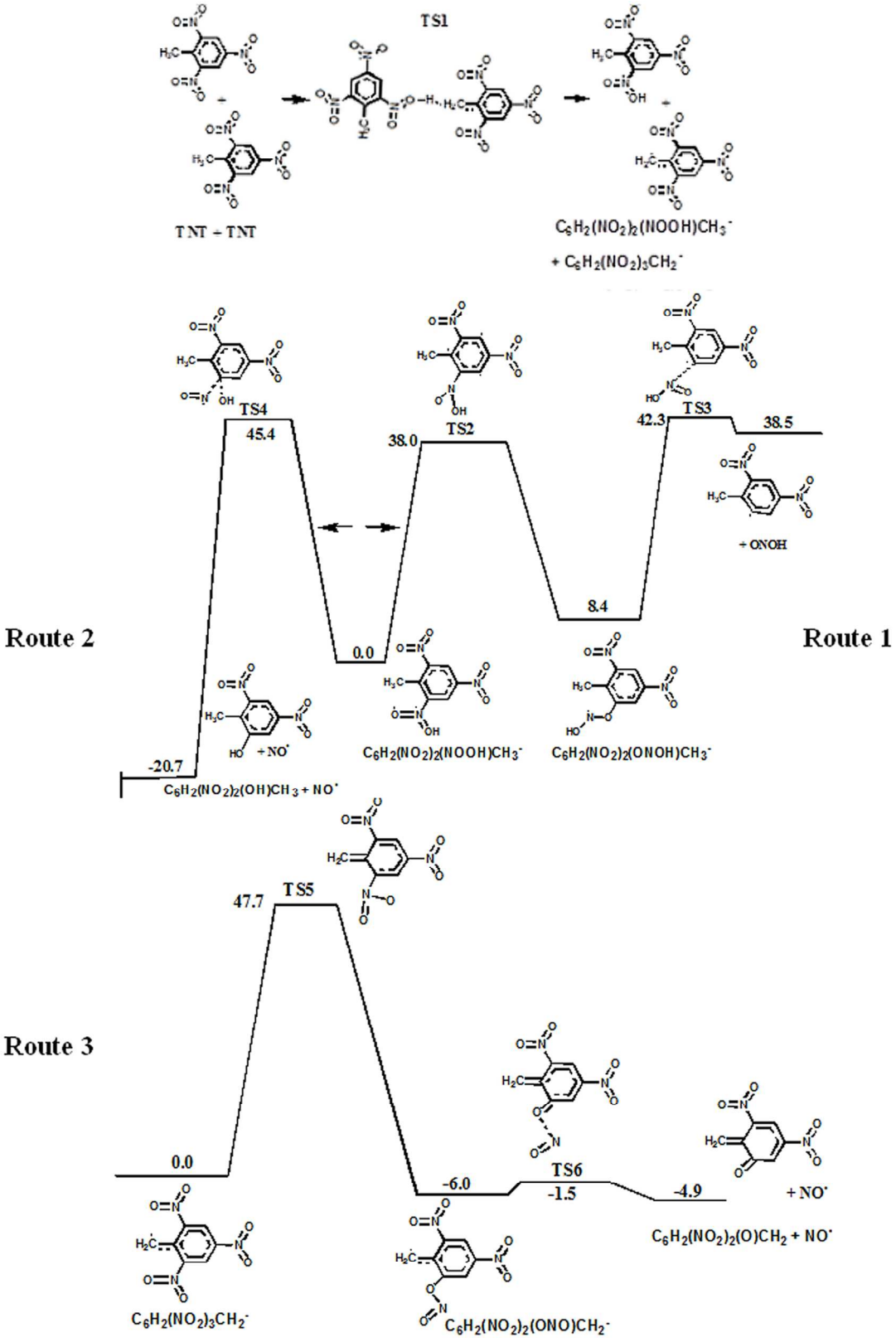


Table S2. Energy barriers and reaction energies, Functional: PBE1PBE, basis set: cc-pVDz, energy values in kcal/mol

Reaction	**$\Delta E^{\#}$ / ΔE_{react}**
TNT…TNT → TS1 → $C_6H_2(NO_2)_2$ (NOOH)$CH_3^{\bullet}$ (TNT_{+H})+ $C_6H_2(NO_2)_3CH_2^{\bullet}$ (TNT_{-H})	43.0 / 43.6
$C_6H_2(NO_2)_2$ (NOOH)$CH_3^{\bullet}$ (ortho)	
$C_6H_2(NO_2)_2$ (NOOH)$CH_3^{\bullet}$ → TS2 → $C_6H_2(NO_2)_2$ (ONOH)$CH_3^{\bullet}$	38.0 / 8.4
$C_6H_2(NO_2)_2$ (ONOH)$CH_3^{\bullet}$ → TS3 → $C_6H_2(NO_2)_2CH_3^{\bullet}$ + ONOH	33.9 / 30.1
$C_6H_2(NO_2)_2$ (NOOH)$CH_3^{\bullet}$ → TS4 → $C_6H_2(NO_2)_2$ (OH)CH_3 +$NO^{\bullet}$	45.4 / -20.7
$C_6H_2(NO_2)_2$ (NOOH)$CH_3^{\bullet}$ (para)	
$C_6H_2(NO_2)_2$ (NOOH)$CH_3^{\bullet}$ → TS2 → $C_6H_2(NO_2)_2$ (ONOH)$CH_3^{\bullet}$	44.2 / 10.2
$C_6H_2(NO_2)_2$ (ONOH)$CH_3^{\bullet}$ → TS3 → $C_6H_2(NO_2)_2CH_3^{\bullet}$ + ONOH	35.1 / 34.3
$C_6H_2(NO_2)_2$ (NOOH)$CH_3^{\bullet}$ → TS4 → $C_6H_2(NO_2)_2$ (OH)CH_3 +$NO^{\bullet}$	47.8 / -15.8
$C_6H_2(NO_2)_3CH_2^{\bullet}$ (ortho)	
$C_6H_2(NO_2)_3CH_2^{\bullet}$ → TS5 → $C_6H_2(NO_2)_2$(ONO)$CH_2^{\bullet}$	47.7 / -6.0
$C_6H_2(NO_2)_2$(ONO)$CH_2^{\bullet}$ → TS6 → $C_6H_2(NO_2)_2$(O)CH_2 + $NO^{\bullet}$	4.4 / 1.1
$C_6H_2(NO_2)_3CH_2^{\bullet}$ (para)	
$C_6H_2(NO_2)_3CH_2^{\bullet}$ → TS5 → $C_6H_2(NO_2)_2$(O)CH_2 + $NO^{\bullet}$	54.3 / -0.4

Scheme S4: Total energy changes of RDX decomposition routes. Units: kcal/mol.

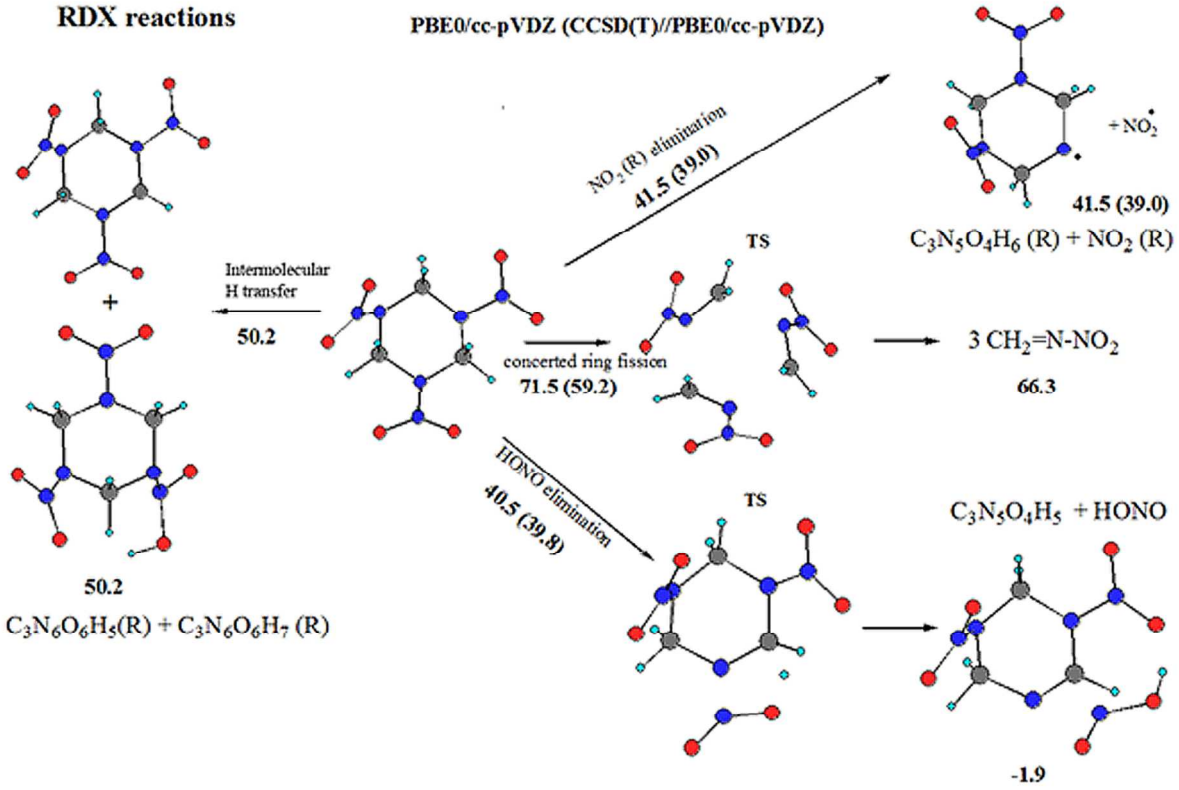


Table S3. DFT values of activation energies of NO_2 cleavage from TNT, RDX and PETN. For TNT *ortho* and *para* positions of NO_2 group are with respect to CH_3 group. For RDX the positions are with respect to removed H atom. Asterisk denotes a change in total energy (=bond dissociation energy) in cases where no transition state was found. - No $H^{m/ar}$ indicates a methylic/aromatic hydrogen deficient molecule

Case		**$\Delta E^{\ddagger}$ (kcal/mol)** ***ortho / para***
#1	TNT → TNT• + NO_2•	61.7* / 67.8*
#2	TNT•$^+$ → TNT$^+$ + NO_2•	34.4 / 42.1
#3	TNT•$^-$ → TNT$^-$ + NO_2•	59.2 / 66.4
#4	TNT-noH^m → TNT + •TNT_noH^m + NO_2•	59.0 / 89.4*
#5	TNT-noH^{ar} → TNT + •TNT_noH^{ar} + NO_2•	38.3 / 44.8
#6	RDX → RDX• + NO_2•	41.5*
#7	RDX•$^+$ → RDX$^+$ + NO_2•	19.4
#8	RDX•$^-$ → RDX$^-$ + NO_2•	-0.1
#9	RDX•-noH → RDX-noH + NO_2•	2.1 / 29.4
#10	RDX + RDX → RDX+H ($C_3N_6O_6H_7$) + RDX-H ($C_3N_6O_6H_5$)	50.2
#11	RDX → 3 (CH2=N-NO2)	71.5
#12	RDX → $C_3N_5O_4H_5$ + HONO	40.5
#13	PETN →PETN• + NO_2•	46.5*
#14	PETN•$^+$ → PETN$^+$ + NO_2•	0.1
#15	PETN•$^-$ → PETN$^-$ + NO_2•	0.3
#16	PETN•-noH →PETN•-noH (A) + NO_2•	-0.3
#17	PETN•-noH →PETN•-noH (B) + NO_2•	20.9

For cases #13 and #14: (A) refers to NO_2 cleavage from the same chain where H is absent and (B) refers to a cleavage from a different chain

ReaxFF-lg force field parameters used in this study:

```
39      ! Number of general parameters
  50.0000 !Overcoordination parameter
   9.4514 !Overcoordination parameter
  30.0000 !Valency angle conjugation parameter
 216.4305 !Triple bond stabilisation parameter
  12.4838 !Triple bond stabilisation parameter
   0.0000 !C2-correction
   1.0701 !Undercoordination parameter
   7.5000 !Triple bond stabilisation parameter
  11.9083 !Undercoordination parameter
  13.3822 !Undercoordination parameter
 -10.4637 !Triple bond stabilization energy
   0.0000 !Lower Taper-radius
  10.0000 !Upper Taper-radius
   2.8793 !Not used
  33.8667 !Valency undercoordination
   3.5895 !Valency angle/lone pair parameter
   1.0563 !Valency angle
   2.0384 !Valency angle parameter
   6.1431 !Not used
   6.9290 !Double bond/angle parameter
   0.0283 !Double bond/angle parameter: overcoord
   0.0570 !Double bond/angle parameter: overcoord
  -2.4837 !Not used
   5.8374 !Torsion/BO parameter
  10.0000 !Torsion overcoordination
   1.8820 !Torsion overcoordination
  -1.2327 !Conjugation 0 (not used)
   2.1861 !Conjugation
   1.5591 !vdWaals shielding
   0.0100 !Cutoff for bond order (*100)
   5.2216 !Valency angle conjugation parameter
   3.4021 !Overcoordination parameter
  38.5241 !Overcoordination parameter
   2.1533 !Valency/lone pair parameter
   0.5000 !Not used
  20.0000 !Not used
   5.0000 !Molecular energy (not used)
   2.0000 !Version number
   6.5560 !Valency angle conjugation parameter
 4    ! Nr of atoms; cov.r; valency;a.m;Rvdw;Evdw;gammaEEM;cov.r2;#
        alfa;gammavdW;valency;Eunder;Eover;chiEEM;etaEEM;n.u.
        cov r3;Elp;Heat inc.;n.u.;n.u.;n.u.;n.u.
        ov/un;val1;n.u.;val3,vval4
 C    1.3742   4.0000  12.0000   1.9684   0.1723   0.8712   1.2385   4.0000
      9.4606   2.1346   4.0000  31.0823  79.5548   5.7254   6.9235   0.0000
      1.2104   0.0000 183.7012   5.7419  33.3951  11.9957   0.8563   0.0000
     -2.8983   2.5000   1.0564   4.0000   2.9663   0.0000   0.0000   0.0000
      0.0001   1.9255
```

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H    0.6867   1.0000   1.0080   1.3525   0.0616   0.8910  -0.1000   1.0000
     9.3858   5.0013   1.0000   0.0000 121.1250   3.8446  10.0839   1.0000
    -0.1000   0.0000  58.4228   3.8461   3.2540   1.0000   1.0698   0.0000
   -15.7683   2.1504   1.0338   1.0000   2.8793   0.0000   0.0000   0.0000
     0.0001   1.4430
O    1.3142   2.0000  15.9990   1.9741   0.0880   0.8712   1.1139   6.0000
    10.2186   7.7719   4.0000  29.5271 116.0768   8.5000   7.1412   2.0000
     0.9909  14.9473  69.2812   9.1371   1.6258   0.1863   0.9745   0.0000
    -3.5965   2.5000   1.0493   4.0000   2.9225   0.0000   0.0000   0.0000
   623.8417   1.7500
N    1.2450   3.0000  14.0000   1.9951   0.1088   1.0512   1.1911   5.0000
     9.9303   7.8431   4.0000  32.4758 100.0000   6.7768   6.8035   2.0000
     1.0636   0.1045 128.0119   2.1604   2.9464   2.5181   0.9745   0.0000
    -4.0959   2.0047   1.0183   4.0000   2.8793   0.0000   0.0000   0.0000
  1240.001   1.8300
 10      ! Nr of bonds; Edis1;LPpen;n.u.;pbe1;pbo5;13corr;pbo6
                    pbe2;pbo3;pbo4;Etrip;pbo1;pbo2;ovcorr
 1  1 141.9346 113.4487  67.6027   0.1554  -0.3045   1.0000  30.4515   0.4283
       0.0801  -0.2113   8.5395   1.0000  -0.0933   6.6967   1.0000   0.0000
 1  2 163.6889   0.0000   0.0000  -0.4525   0.0000   1.0000   6.0000   0.5921
      12.1053   1.0000   0.0000   1.0000  -0.0097   8.6351   0.0000   0.0000
 2  2 169.8421   0.0000   0.0000  -0.3591   0.0000   1.0000   6.0000   0.7503
       9.3119   1.0000   0.0000   1.0000  -0.0169   5.9406   0.0000   0.0000
 1  3 164.0476 117.4881  72.1261  -0.6031  -0.1795   1.0000  14.9755   0.5413
       1.2626  -0.3063   7.0000   1.0000  -0.1588   4.5000   0.0000   0.0000
 3  3 110.4748 155.6441  40.0000   0.1150  -0.1054   1.0000  28.5221   0.2000
       0.9590  -0.2635   8.5715   1.0000  -0.1007   6.8548   1.0000   0.0000
 1  4 130.7147 175.2276  97.2523  -0.0368  -0.4942   1.0000  26.7545   0.5133
       0.3296  -0.3653   7.0000   1.0000  -0.1171   5.1025   1.0000   0.0000
 3  4  85.4950 114.0081  70.1453   0.5778  -0.1070   1.0000  16.6611   0.2339
       0.3474  -0.1948   8.3762   1.0000  -0.1089   5.8148   1.0000   0.0000
 4  4 157.7518  67.1322 160.9732  -0.5869  -0.1824   1.0000  12.0000   0.7136
       0.8204  -0.1657  10.6490   1.0000  -0.0967   4.5976   1.0000   0.0000
 2  3 224.3076   0.0000   0.0000  -0.6280   0.0000   1.0000   6.0000   1.0000
       5.0050   1.0000   0.0000   1.0000  -0.0512   5.1982   0.0000   0.0000
 2  4 212.1772   0.0000   0.0000  -0.3585   0.0000   1.0000   6.0000   0.3316
      10.4316   1.0000   0.0000   1.0000  -0.0658   6.4545   0.0000   0.0000
 6    ! Nr of off-diagonal terms; Ediss;Ro;gamma;rsigma;rpi;rpi2
 1  2   0.0464   1.8296  10.1311   1.0029  -1.0000  -1.0000
 2  3   0.0375   1.7275  10.8037   0.8813  -1.0000  -1.0000
 2  4   0.0509   1.7672  10.4261   0.9990  -1.0000  -1.0000
 1  3   0.1036   1.8869   9.5668   1.3590   1.1099   1.1534
 1  4   0.1971   1.7356  10.0734   1.2754   1.2113   1.1172
 3  4   0.0535   1.6709  10.8180   1.2968   1.1416   1.0167
42    ! Nr of angles;at1;at2;at3;Thetao,o;ka;kb;pv1;pv2
 1  1  1  74.0317  32.2712   0.9501   0.0000   0.1780  10.5736   1.0400
 1  1  2  70.6558  14.3658   5.3224   0.0000   0.0058   0.0000   1.0400
 2  1  2  76.7339  14.4217   3.3631   0.0000   0.0127   0.0000   1.0400
 1  2  2   0.0000   0.0000   6.0000   0.0000   0.0000   0.0000   1.0400
 1  2  1   0.0000   3.4110   7.7350   0.0000   0.0000   0.0000   1.0400
 2  2  2   0.0000  27.9213   5.8635   0.0000   0.0000   0.0000   1.0400
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 1  1  3  65.3104   6.3897   7.5000   0.0000   0.2000  10.0000   1.8525
 3  1  3  71.9855  28.5708   6.4252   0.0000   0.2000   0.0000   1.8525
 1  1  4  65.8892  45.0000   1.6598   0.0000   0.2000  10.0000   1.8525
 3  1  4  73.1057  25.8227   4.2145   0.0000   0.2000   0.0000   1.8525
 4  1  4  65.8759  40.9838   2.4369   0.0000   0.2000   0.0000   1.8525
 2  1  3  56.3039  17.3681   5.3095   0.0000   0.9110   0.0000   1.0400
 2  1  4  71.5505  11.1820   3.7129   0.0000   0.9110   0.0000   1.0400
 1  2  4   0.0000   0.0019   6.3000   0.0000   0.0000   0.0000   1.0400
 1  3  1  72.3642  37.8942   1.1566   0.0000   0.7472   0.0000   1.2639
 1  3  3  90.0000  45.0000   0.5719   0.0000   0.7472   0.0000   1.2639
 1  3  4  70.4313  14.4055   7.1593   0.0000   0.7472   0.0000   1.2639
 3  3  3  83.8833  23.3345   2.3433 -10.0000   0.7472   0.0000   1.2639
 3  3  4  84.0407  45.0000   1.0695   0.0000   0.7472   0.0000   1.2639
 4  3  4  73.9966  24.4410   5.2760   0.0000   0.7472   0.0000   1.2639
 1  3  2  89.1394  37.0874   0.3849   0.0000   3.0000   0.0000   1.2618
 2  3  3  80.7068   5.0854   5.7151   0.0000   3.0000   0.0000   1.2618
 2  3  4  76.0238  45.0000   0.8637   0.0000   3.0000   0.0000   1.2618
 2  3  2  82.3474  13.5165   3.4896   0.0000   0.3596   0.0000   1.3307
 1  4  1  68.4330  19.3525   2.1625   0.0000   1.7325   0.0000   1.0440
 1  4  3  86.2893  37.5587   1.2660   0.0000   1.7325   0.0000   1.0440
 1  4  4  74.2404  12.0547   7.5000   0.0000   1.7325   0.0000   1.0440
 3  4  3  78.5566  43.8492   1.3351 -26.1471   1.7325  40.0000   1.0440
 3  4  4  77.4239  33.7297   1.7944  -0.9193   1.7325   0.0000   1.0440
 4  4  4  64.9107  17.5558   7.5000   0.0000   1.7325   0.0000   1.0440
 1  4  2  90.0000  32.0540   0.7195   0.0000   0.5355   0.0000   2.5279
 2  4  3  84.1185  45.0000   1.3826   0.0000   0.5355   0.0000   2.5279
 2  4  4  78.7133  24.6250   3.8202   0.0000   0.5355   0.0000   2.5279
 2  4  2  56.3036  14.1532   3.3914   0.0000   0.2000   0.0000   2.1689
 1  2  3   0.0000   0.0019   6.0000   0.0000   0.0000   0.0000   1.0400
 1  2  4   0.0000   0.0019   6.0000   0.0000   0.0000   0.0000   1.0400
 1  2  5   0.0000   0.0019   6.0000   0.0000   0.0000   0.0000   1.0400
 3  2  3   0.0000   0.0019   6.0000   0.0000   0.0000   0.0000   1.0400
 3  2  4   0.0000   0.0019   6.0000   0.0000   0.0000   0.0000   1.0400
 4  2  4   0.0000   0.0019   6.0000   0.0000   0.0000   0.0000   1.0400
 2  2  3   0.0000   0.0019   6.0000   0.0000   0.0000   0.0000   1.0400
 2  2  4   0.0000   0.0019   6.0000   0.0000   0.0000   0.0000   1.0400
17    ! Nr of torsions;at1;at2;at3;at4;;V1;V2;V3;V2(BO);vconj;n.u;n
 1  1  1  1   0.0000  48.4194   0.3163  -8.6506  -1.7255   0.0000   0.0000
 1  1  1  2   0.0000  63.3484   0.2210  -8.8401  -1.8081   0.0000   0.0000
 2  1  1  2   0.0000  45.2741   0.4171  -6.9800  -1.2359   0.0000   0.0000
 0  1  2  0   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000
 0  2  2  0   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000
 0  1  3  0  -0.0002  85.8794   0.3236  -3.8134  -2.0000   0.0000   0.0000
 0  2  3  0   0.0000   0.1000   0.0200  -2.5415   0.0000   0.0000   0.0000
 0  3  3  0  -0.9667 116.4743   0.0002  -4.9422   0.0000   0.0000   0.0000
 0  1  4  0  -0.0069 150.0000   0.4891  -7.4921  -2.0000   0.0000   0.0000
 0  2  4  0   0.0000   0.1000   0.0200  -2.5415   0.0000   0.0000   0.0000
 0  3  4  0   1.6745  56.6301  -0.0008  -4.5064  -2.0000   0.0000   0.0000
 0  4  4  0   1.1253  75.3447   0.0080  -9.0000  -2.0000   0.0000   0.0000
 0  1  1  0   0.0930  18.5962   0.0002  -9.0000  -1.0000   0.0000   0.0000
 4  1  4  4  -2.0000  20.8732  -1.5000  -9.0000  -2.0000   0.0000   0.0000
```

```
 1  1  3  3  -0.0002  21.5452   0.1727  -9.0000  -2.0000   0.0000   0.0000
 1  3  3  1   0.0002  79.3777  -1.5000  -5.2139  -2.0000   0.0000   0.0000
 3  1  3  3  -1.3476  22.4932   1.5000  -9.0000  -2.0000   0.0000   0.0000
 4    ! Nr of hydrogen bonds;at1;at2;at3;Rhb;Dehb;vhb1
 3  2  3   2.0000  -5.0000   3.0000   3.0000
 3  2  4   1.7753  -5.0000   3.0000   3.0000
 4  2  3   1.3884  -5.0000   3.0000   3.0000
 4  2  4   1.6953  -4.0695   3.0000   3.0000
```

Cutoff of bond orders used for post-analysis of molecular species:

C	N	0.3
C	C	0.55
C	O	0.65
C	H	0.4
O	O	0.65
N	O	0.40
O	H	0.4
H	H	0.55
H	N	0.55
N	N	0.55