Supplementary Material

Theoretical study of the reaction of NO_3(radical) with CH_2ClBr, CH_2ICl, CH_2BrI, $CHCl_2Br$, and $CHClBr_2$

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Index:

Table S1. Benchmark calculation of the NO_3+ CH_3I → NO_3H + CH_2I. Relative energies (kcal/mol)

Stationary species	*B3LYP*[a]	*CCSD(T)//B3LYP*[a]	M08HX[b]	DLPNO//M08HX[c]
CH_3I + NO_3	*0.0*	*0.00*	0.00	0.00
TS1a	*6.52*	*10.54*	4.11	7.88
EP1a	*0.03*	*-3.43*	-11.50	-8.46
TS2a	*7.00*	*10.33*	3.94	8.01
EP2a	*0.61*	*-2.97*	-11.79	-7.99
CH_2I+ HNO_3	*1.79*	*-0.70*	-8.24	-6.84
TS3a	*17.41*	*23.00*	14.83	18.17
EP3a	*-16.42*	*-19.49*	-30.10	-26.02
CH_3NO_3+I	*-16.27*	*-18.44*	-29.05	-26.29

[a] Taken from F.-Y. Bai, X. Wang, Y.-Q. Sun and X.-M. Pan, *RSC Advances*, 2015, **5**, 88087 (Table 1)

[b] M08HX/6-311+G(2df,2p)/def2-TZVP.

[c] DLPNO/CCSD(T)/def2-TZVP//M08HX6-311+G(2df,2p)/def2-TZVP

There are two pathways yielding CH_2I + HNO_3 with barriers, calculated at the DLPNO//M08HX and M08HX levels of theory used here, that are 2.7, 2.3 kcal mol^{-1} and 6.43, 6.39 kcal mol^{-1}, respectively, lower than the corresponding barriers calculated by Bai et al. (2015) at the CCSD(T)//B3LYP level of theory. In that study, the estimated rate coefficient for NO_3 + CH_3I was a factor of 2 smaller than the measurement by Nakano et al (2005) at 298 K. Thus, the lower barriers calculated at the DLPNO//M08HX and M08HX levels would allow an improved match to the experimental rate coefficient using a Master Equation treatment like MESMER

Table S2. Energetics of the exit channel with respect to the entrance channel, kJ mol^{-1}.

Exit Channel	Electronic Energy	G (298 K)
NO_3H + CHClBr	-58.2	-54.8
NO_3Cl + CH2Cl	140.5	133.9
NO_3Br + CH2Br	118.5	113.5
O_2NOCH_2Br + Cl	-39.6	-9.8
O_2NOCH_2Cl + Br	-84.4	-53.0
NO3H + CHClI	-57.1	-53.9
NO3Cl + CH2I	140.2	134.4
NO3I + CH2Cl	60.0	55.5
O_2NOCH_2I + Cl	-37.2	-7.5
O_2NOCH_2Cl + I	-151.6	-136.7
NO3H + CHBrI	-53.6	-50.0
NO3Br + CH2I	121.7	116.4
NO3I + CH2Br	63.7	57.9
O_2NOCH_2I + Br	-80.9	-49.9
O_2NOCH_2Br + I	-150.4	-117.4
NO3H + CCl2Br	-74.0	-68.4
NO3Cl + CHClBr	113.7	112.3
NO3Br + CHCl2	91.4	89.9
$O_2NOCHClBr$ + Cl	-37.5	-9.0
$O_2NOCHCl_2$ + Br	-84.9	-54.7
NO3H + CClBr2	-73.4	-67.9
NO3Cl + CHBr2	114.7	113.3
NO3Br + CHClBr	92.4	91.2
$O_2NOCHBr_2$ + Cl	-32.8	-3.2
$O_2NOCHClBr$ + Br	-4.4	-54.4

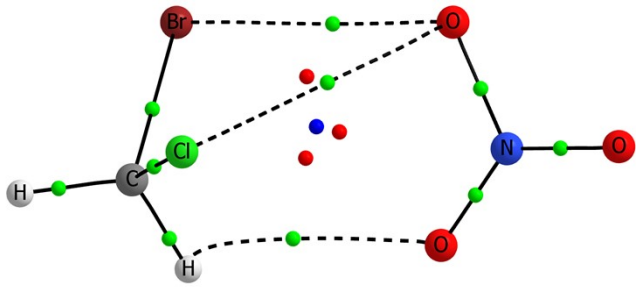
Table S3. Available experimental bond dissociation energies, BDE, (kJ mol^{-1}) of the molecules studied.[a] The bond measured is indicated in bold.

Molecule	BDE	Molecule	BDE
H-CHClBr	406.0 ± 2.4	**H-O**NO_2	426.8
Cl-CH_2Br	332.8 ± 4.6	**Cl-O**NO_2	172.0
Cl-CHBr_2	299		
Cl-CH_2I	328.2 ± 6.9		
Br-CH_2Cl	277.3 ± 3.6	**Br-O**NO_2	143.1 ± 6.3
Br-CHCl_2	248 ± 21		
Br-CHClBr	241 ± 21		
Br-CH_2I	274.5 ± 7.5		
I-CH_2Cl	221.8 ± 4.2	**I-O**NO_2	140.6
I-CH_2Br	219.2 ± 5.4		

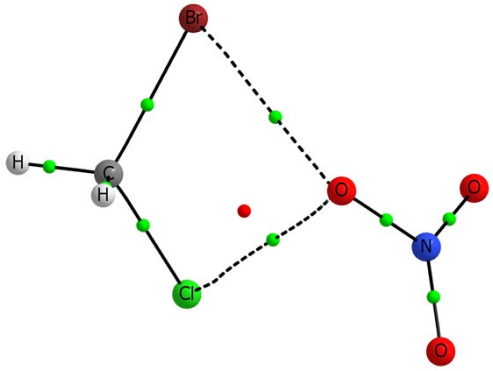
[a] Taken from Y. R. Luo, Comprehensive handbook of chemical bond energies, 2007, CRC Press-Taylor & Francis Group, Boca Raton (FL).

Table S4. Molecular structures and energetics of the different conformation minima found for the pre-reactive complexes.

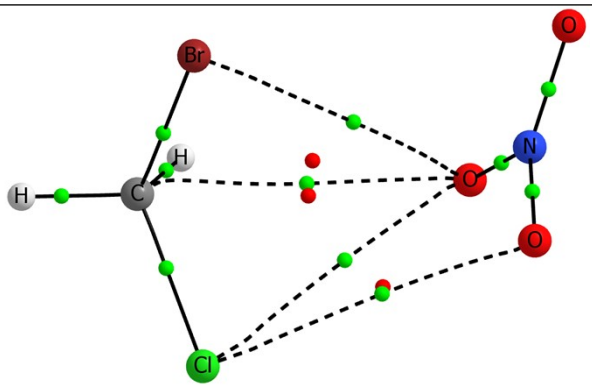
$CH_2ClBr:NO_3$



Erel = 0.00 kJ mol-1 , Eb= -21.7 kJ mol-1



Erel = 4.01 kJ mol-1 , Eb= -17.7 kJ mol-1



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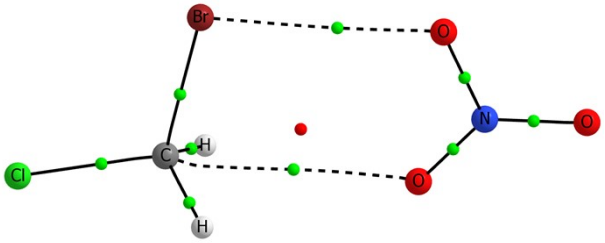
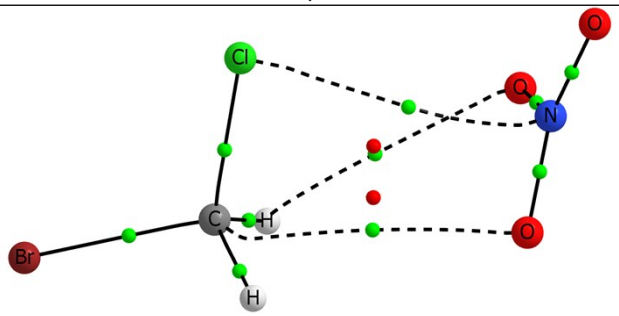
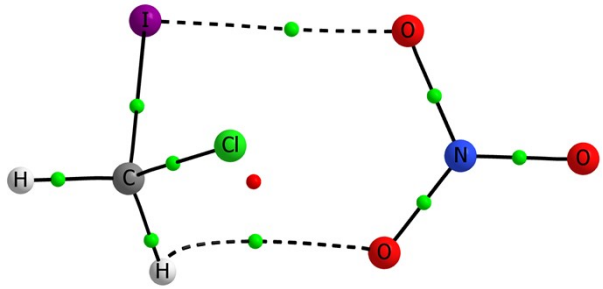


Erel = 5.40 kJ mol-1 , Eb= -16.3 kJ mol-1

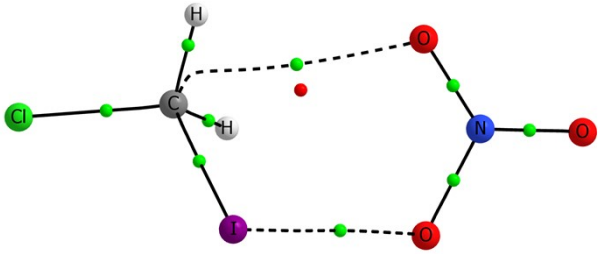


Erel = 6.89 kJ mol-1 , Eb= -14.8 kJ mol-1

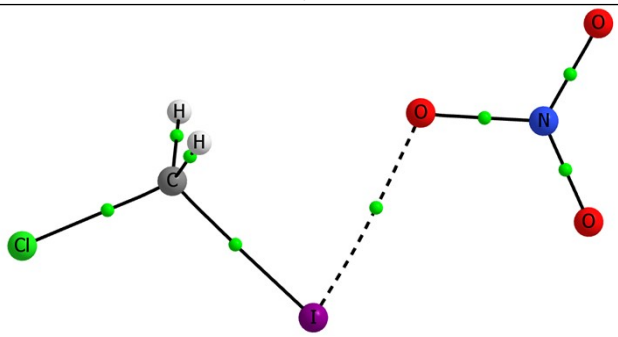
$CH_2ClI{:}NO_3$



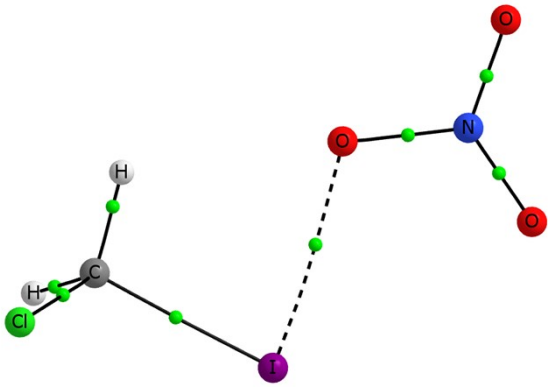
Erel= 0.00 kJ mol-1, Eb = -32.6 kJ mol-1



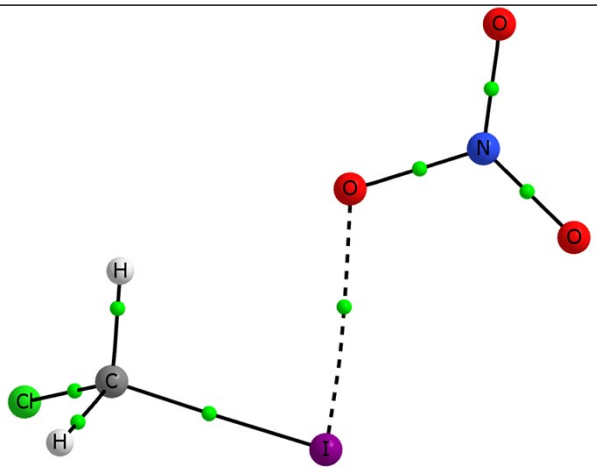
Erel= 0.20 kJ mol-1, Eb = -32.4 kJ mol-1



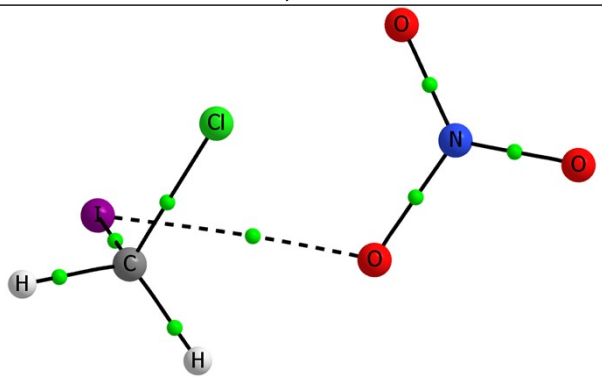
Erel= 3.79 kJ mol-1, Eb = -28.9 kJ mol-1



Erel= 3.79 kJ mol-1, Eb = -28.9 kJ mol-1

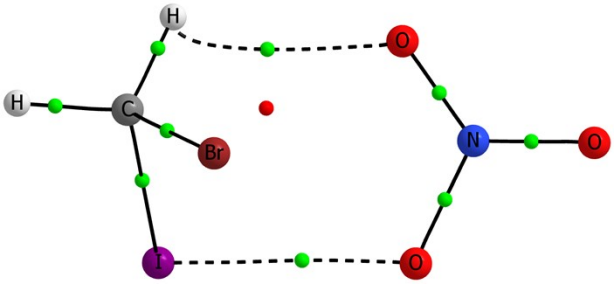


Erel= 3.87 kJ mol-1, Eb = -28.8 kJ mol-1

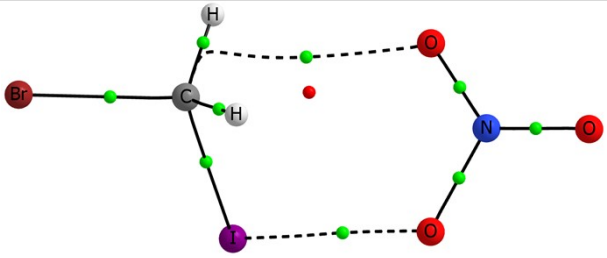


Erel= 6.42 kJ mol-1, Eb = -26.2 kJ mol-1

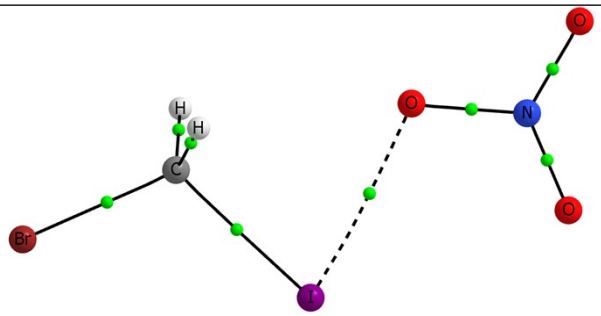
$CH_2BrI{:}NO_3$



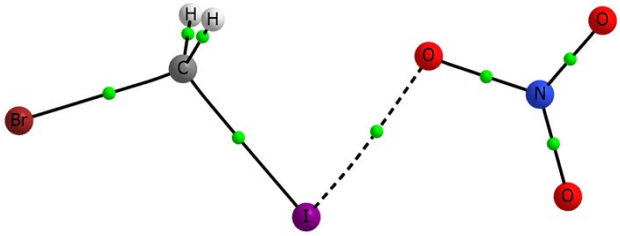
Erel = 0.00 kJ mol-1 , Eb= -32.71 kJ mol-1



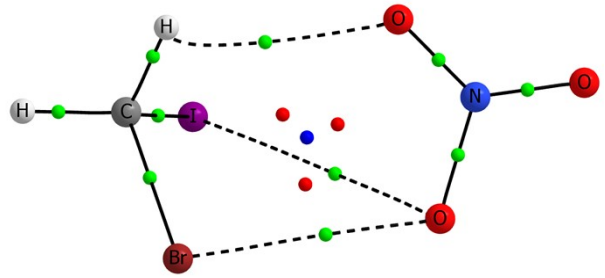
Erel = 0.40 kJ mol-1 , Eb= -32.31 kJ mol-1



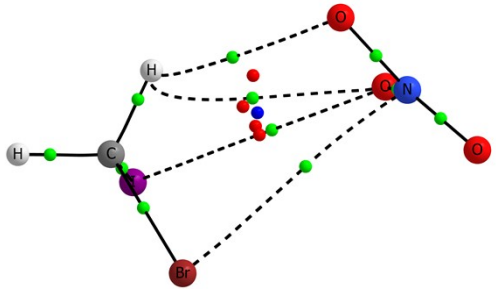
Erel = 3.82 kJ mol-1 , Eb= -28.89 kJ mol-1



Erel = 4.17 kJ mol-1 , Eb= -28.54 kJ mol-1

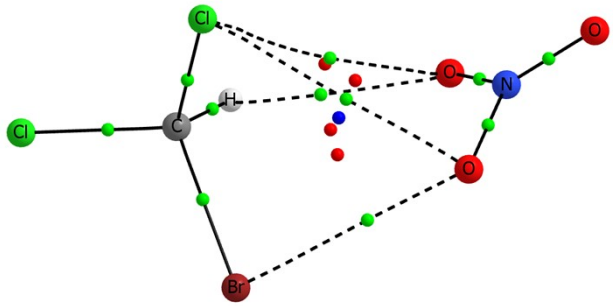


Erel = 10.24 kJ mol-1 , Eb= -22.47 kJ mol-1

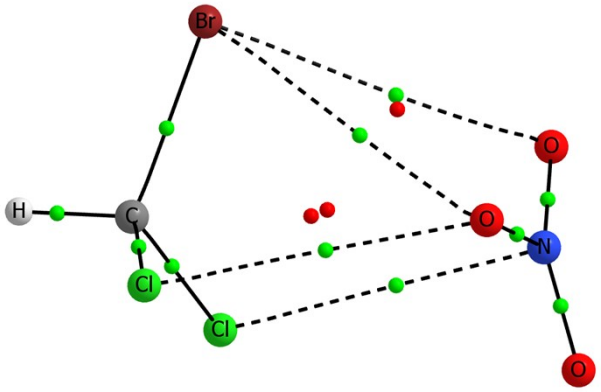


Erel = 15.52 kJ mol-1 , Eb= -17.19 kJ mol-1

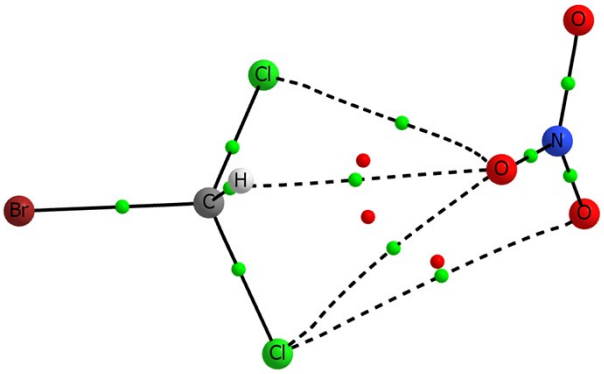
$CHCl_2Br:NO_3$



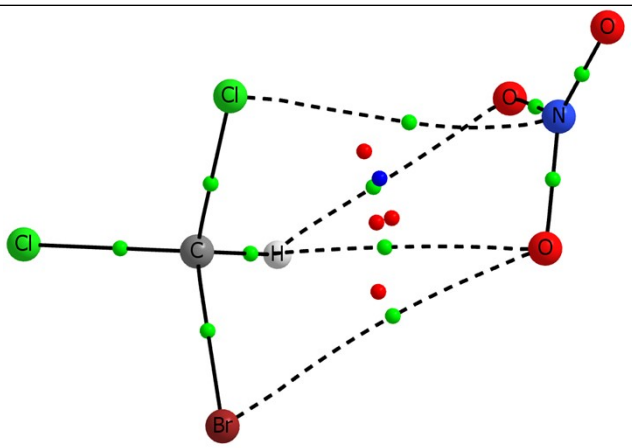
Erel = 0.00 kJ mol-1 , Eb= -20.25 kJ mol-1



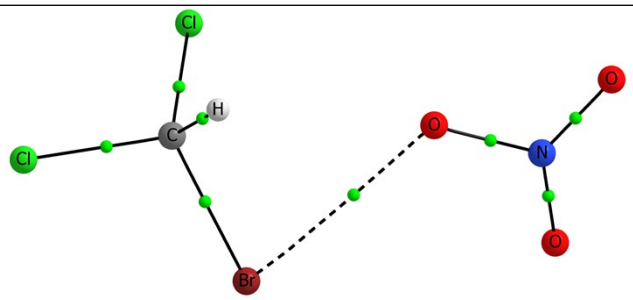
Erel = 2.78 kJ mol-1 , Eb= -17.48 kJ mol-1



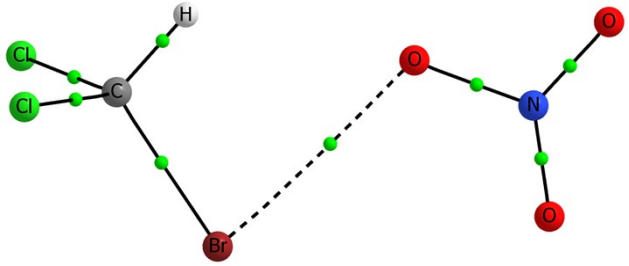
Erel = 3.76 kJ mol-1 , Eb= -16.49 kJ mol-1



Erel = 4.38 kJ mol-1 , Eb= -15.88 kJ mol-1

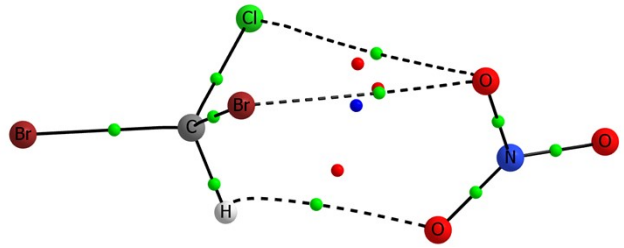


Erel = 8.09 kJ mol-1 , Eb= -12.16 kJ mol-1

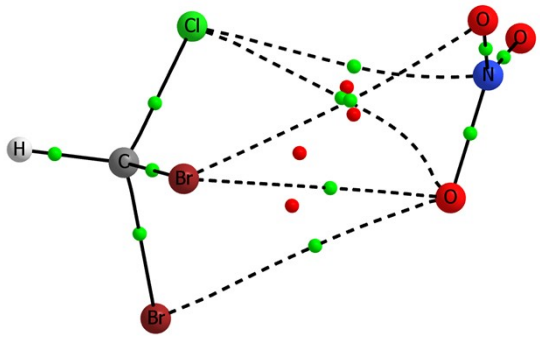


Erel = 9.50 kJ mol-1 , Eb= -10.75 kJ mol-1

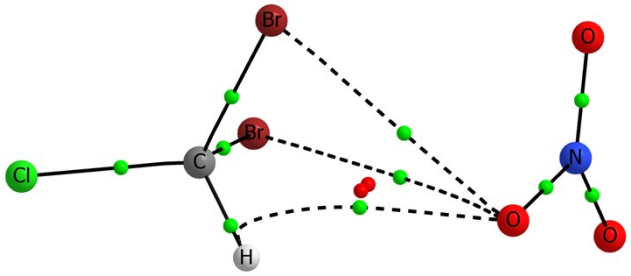
$CHClBr_2$:NO_3



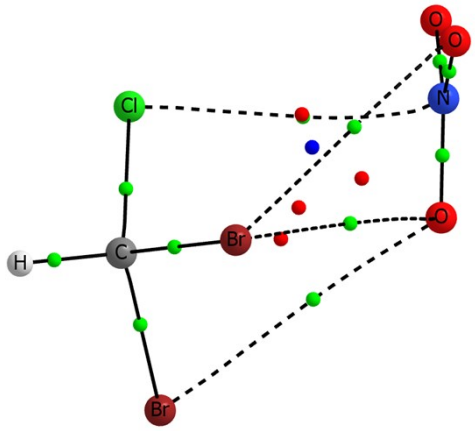
Erel = 0.00 kJ mol-1 , Eb= -20.29 kJ mol-1



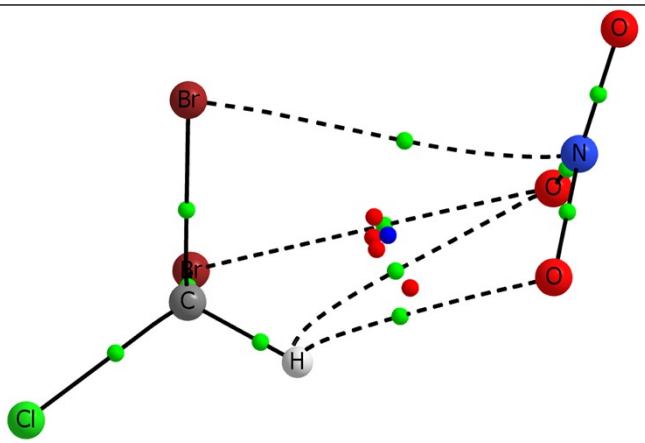
Erel = 2.73 kJ mol-1 , Eb= -17.56 kJ mol-1



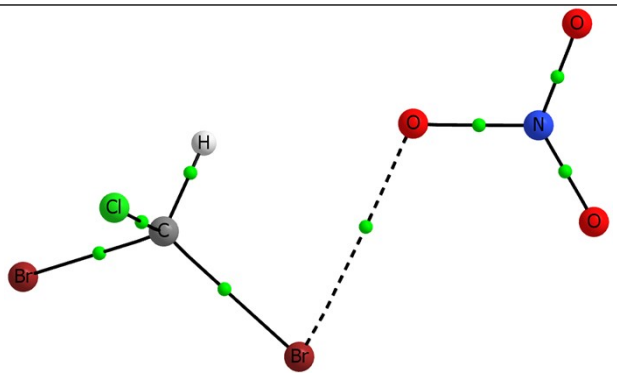
Erel = 3.01 kJ mol-1 , Eb= -17.29 kJ mol-1



Erel = 3.38 kJ mol-1 , Eb= -16.91 kJ mol-1



Erel = 3.69 kJ mol-1 , Eb= -16.61 kJ mol-1



Erel = 8.05 kJ mol-1 , Eb= -12.24 kJ mol-1

Table S5. Relative energy of the different stationary points in the hydrogen transfer reaction with respect to the corresponding entrance channel, kJ mol^{-1}.

	Electronic Energy	G (298 K)
NO3:CH_2ClBr*	-21.7	25.9
NO3/CH_2ClBr (TS-A)	17.3	56.7
NO3/CH_2ClBr (TS-B)	17.2	56.1
NO3/CH_2ClBr (TS-C)	16.7	56.6
NO3H:CHClBr*	-81.3	-34.2
NO3H + CHClBr	-58.2	-54.8
NO3:$CHCl_2Br$*	-20.3	25.0
NO3/$CHCl_2Br$ (TS-A)	13.8	55.0
NO3/$CHCl_2Br$ (TS-B)	13.7	55.0
NO_3H:CCl_2Br*	-96.2	-45.7
NO3H + CCl_2Br	-74.0	-68.4
NO_3:$CHClBr_2$*	-20.3	25.5
NO_3/$CHClBr_2$ (TS-A)	11.7	53.3
NO_3/$CHClBr_2$ (TS-B)	11.7	53.7
NO_3H:$CClBr_2$*	-96.2	-45.1
NO_3H + $CClBr_2$	-73.4	-67.9
NO_3:CH_2ClI*	-32.6	20.9
NO_3/CH_2ClI (TS-A)	16.0	54.8
NO_3/CH_2ClI (TS-B)	15.2	54.9
NO_3/CH_2ClI (TS-C)	14.7	54.5
NO_3H:CHClI*	-79.5	-33.9
NO_3H + CHClI	-57.1	-53.9
NO_3:CH_2BrI*	-32.7	20.7
NO_3/CH_2BrI (TS-A)	14.8	54.3
NO_3/CH_2BrI (TS-B)	14.2	54.6
NO_3/CH_2BrI (TS-C)	13.3	53.8
NO_3H:CHBrI*	-77.4	-30.0
NO_3H + CHBrI	-53.6	-50.0

* Most stable conformation.

Table S6. Molecular structures and energetics of the different hydrogen transfer TSs.

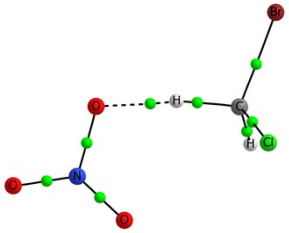
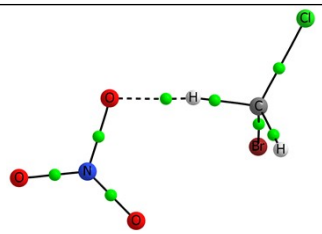
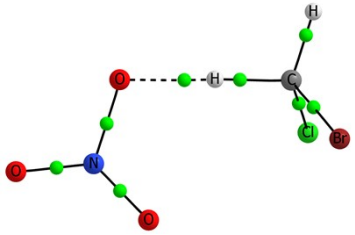
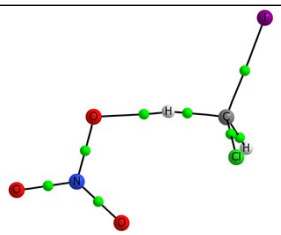
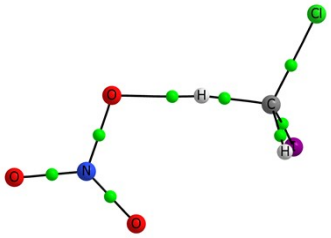
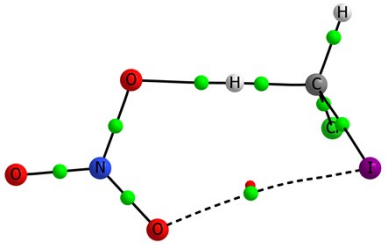
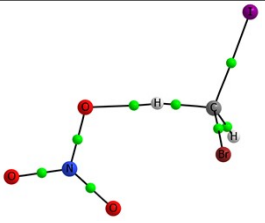
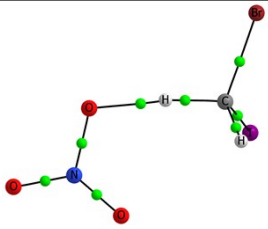
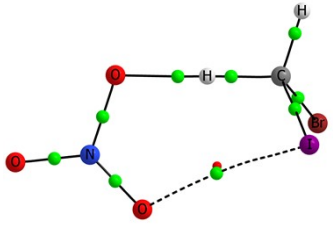
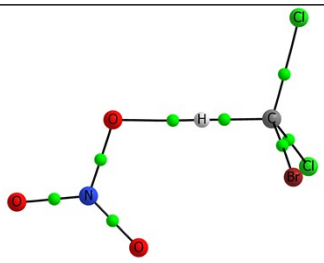
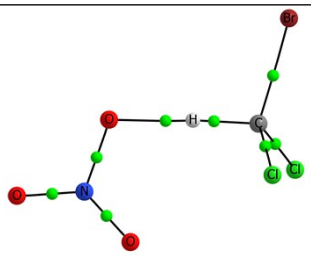
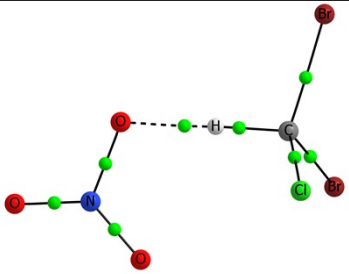
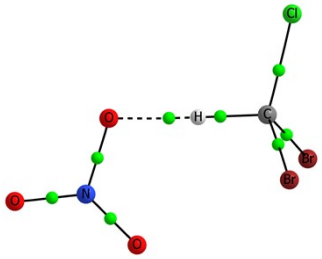
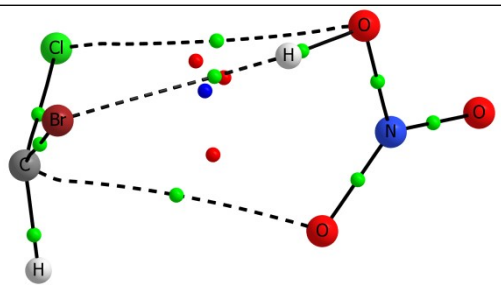
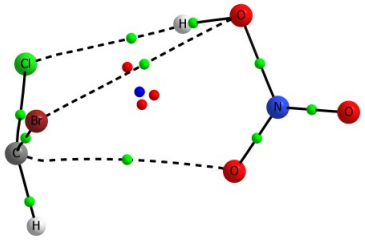
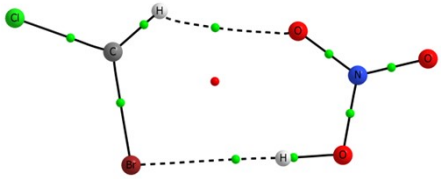
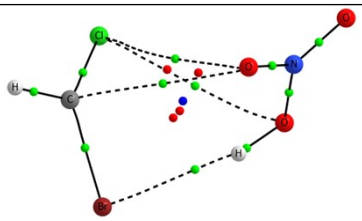
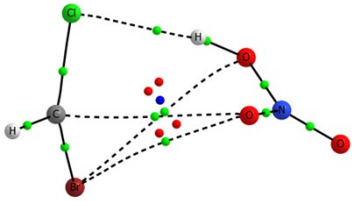
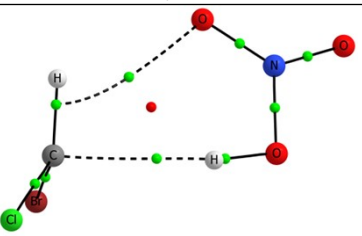
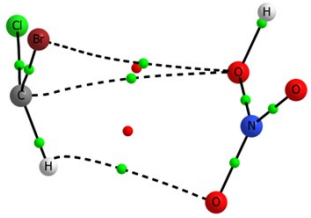
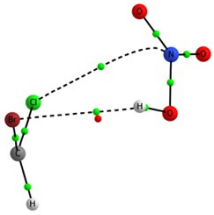
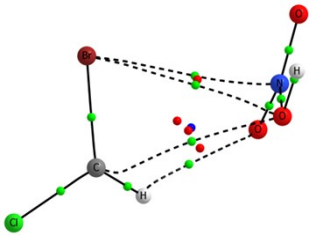
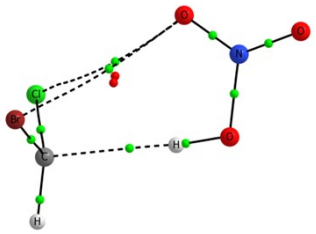
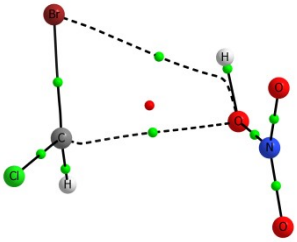
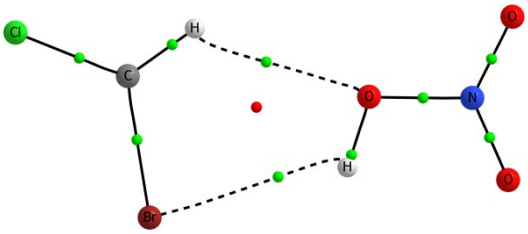
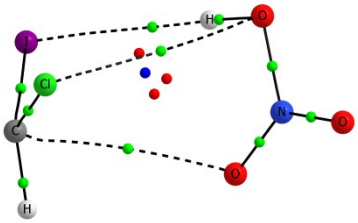
	TS-A	TS-B	TS-C
$CH_2ClBr:NO_3$	 Total Energy= -3353.850025 Hartree	 Total Energy= -3353.850072 Hartree	 Total Energy= -3353.850252 Hartree
$CH_2ClI:NO_3$	 Total Energy= -1077.282571 Hartree	 Total Energy= -1077.282941 Hartree	 Total Energy= -1077.28319503 Hartree
$CH_2BrI:NO_3$	 Total Energy= -3191.260401 Hartree	 Total Energy= -3191.260677 Hartree	 Total Energy= -3191.261113 Hartree
$CHCl_2Br:NO_3$	 Total Energy= -3813.436626 Hartree	 Total Energy= -3813.436652 Hartree	
$CHClBr_2:NO_3$	 Total Energy= -5927.413609 Hartree	 Total Energy= -5927.413629 Hartree	

Table S7. Molecular structures and energetics of the most stable conformation minima found for the hydrogen transfer post-reaction complexes.

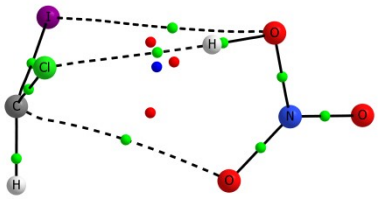
CHClBr:NO_3H

 Erel= 0.0 kJ mol-1, Eb= -23.0 kJ mol-1	 Erel= 0.9 kJ mol-1, Eb= -22.1 kJ mol-1
 Erel= 1.4 kJ mol-1, Eb= -21.6 kJ mol-1	 Erel= 2.5 kJ mol-1, Eb= -20.5 kJ mol-1
 Erel= 3.2 kJ mol-1, Eb= -19.8 kJ mol-1	 Erel= 4.2 kJ mol-1, Eb= -18.8 kJ mol-1
 Erel= 4.8 kJ mol-1, Eb= -18.2 kJ mol-1	 Erel= 5.3 kJ mol-1, Eb= -17.7 kJ mol-1
 Erel= 6.4 kJ mol-1, Eb= -16.6 kJ mol-1	 Erel= 6.9 kJ mol-1, Eb= -16.1 kJ mol-1
 Erel= 7.0 kJ mol-1, Eb= -16.1 kJ mol-1	 Erel= 9.3 kJ mol-1, Eb= -13.7 kJ mol-1

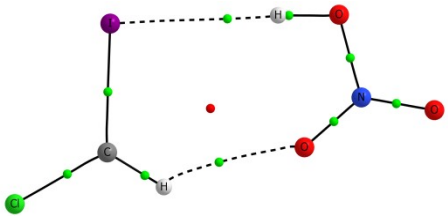
CHClI: NO_3H



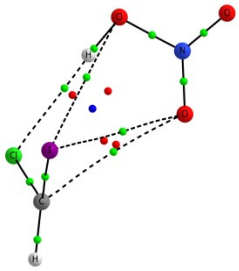
Erel= 0.0 kJ mol-1, Eb= -22.4 kJ mol-1



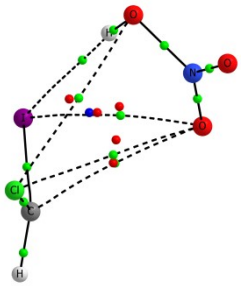
Erel= 0.1 kJ mol-1, Eb= -22.3 kJ mol-1



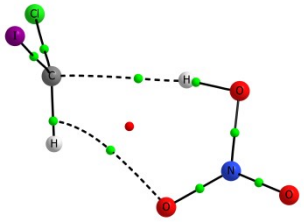
Erel= 1.0 kJ mol-1, Eb= -21.4 kJ mol-1



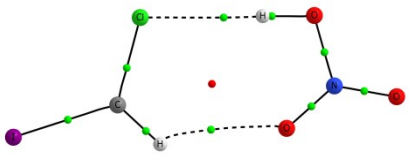
Erel= 1.9 kJ mol-1, Eb= -20.5 kJ mol-1



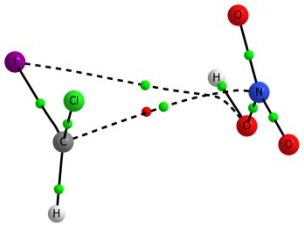
Erel= 2.1 kJ mol-1, Eb= -20.4 kJ mol-1



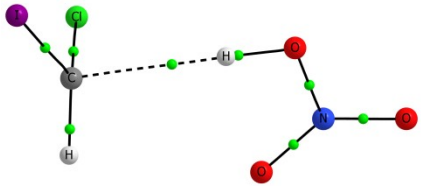
Erel= 2.3 kJ mol-1, Eb= -20.1 kJ mol-1



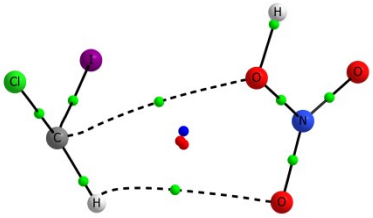
Erel= 2.4 kJ mol-1, Eb= -20.0 kJ mol-1



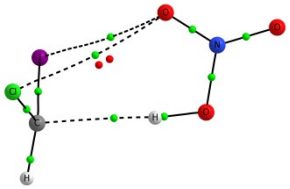
Erel= 3.7 kJ mol-1, Eb= -18.7 kJ mol-1



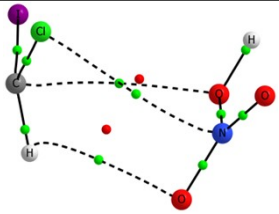
Erel= 4.0 kJ mol-1, Eb= -18.4 kJ mol-1



Erel= 4.6 kJ mol-1, Eb= -17.8 kJ mol-1

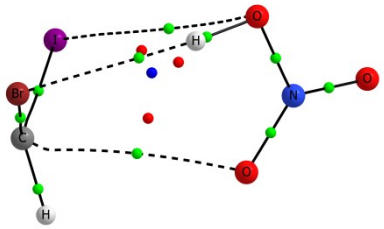


Erel= 4.8 kJ mol-1, Eb= -17.6 kJ mol-1

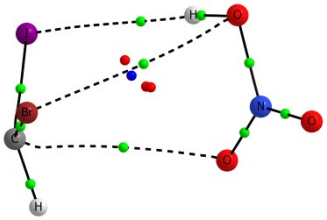


Erel= 5.02 kJ mol-1, Eb= -17.4 kJ mol-1

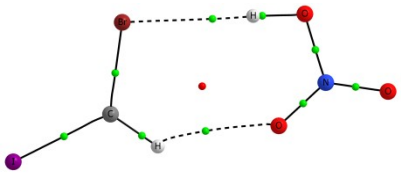
CHBrI:NO_3H



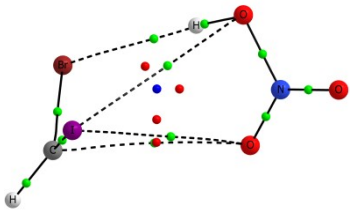
Erel= 0.0 kJ mol-1, Eb= -23.5 kJ mol-1



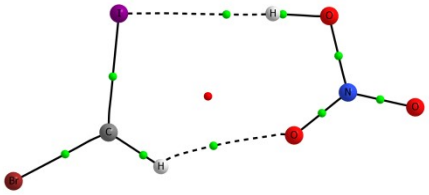
Erel= 0.6 kJ mol-1, Eb= -22.9 kJ mol-1



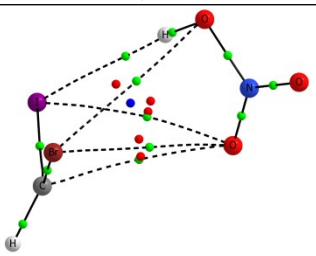
Erel= 2.3 kJ mol-1, Eb= -21.3 kJ mol-1



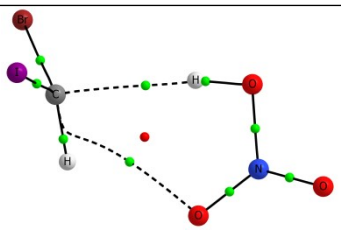
Erel= 2.3 kJ mol-1, Eb= -21.2 kJ mol-1



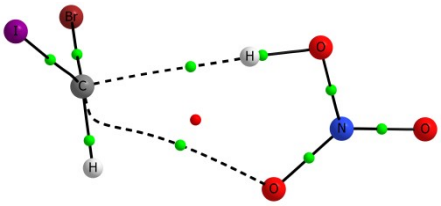
Erel= 2.6 kJ mol-1, Eb= -20.9 kJ mol-1



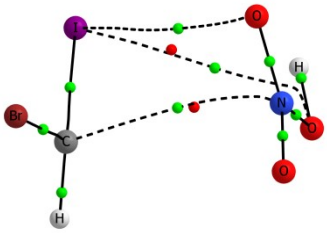
Erel= 3.1 kJ mol-1, Eb= -20.5 kJ mol-1



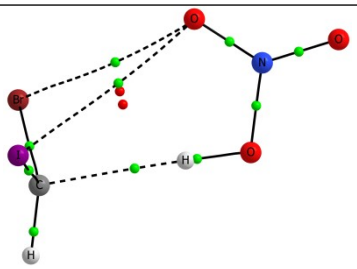
Erel= 3.2 kJ mol-1, Eb= -20.3 kJ mol-1



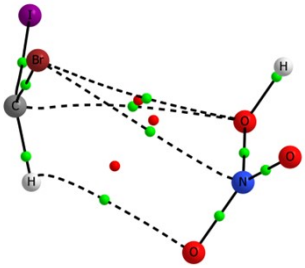
Erel= 3.9 kJ mol-1, Eb= -19.6 kJ mol-1



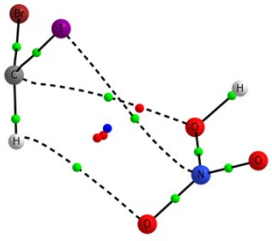
Erel= 4.8 kJ mol-1, Eb= -18.8 kJ mol-1



Erel= 5.2 kJ mol-1, Eb= -18.3 kJ mol-1

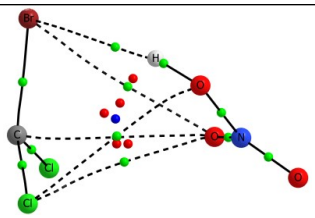


Erel= 5.5 kJ mol-1, Eb= -18.1 kJ mol-1

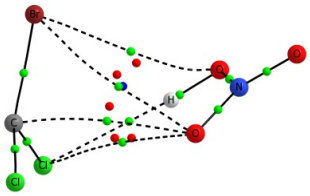


Erel= 5.6 kJ mol-1, Eb= -18.0 kJ mol-1

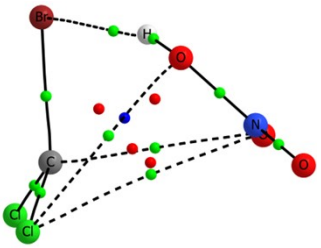
$CCl_2Br:NO_3H$



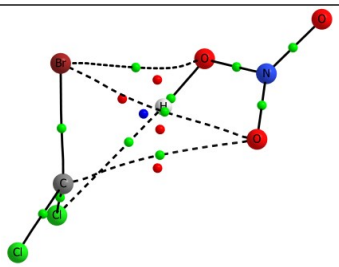
Erel= 0.0 kJ mol-1, Eb= -22.2 kJ mol-1



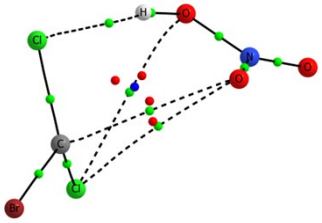
Erel= 0.9 kJ mol-1, Eb= -21.3 kJ mol-1



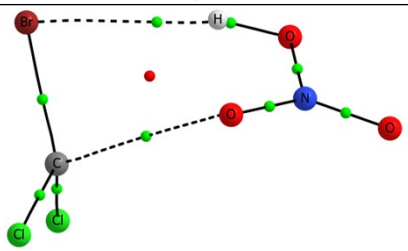
Erel= 3.4 kJ mol-1, Eb= -18.9 kJ mol-1



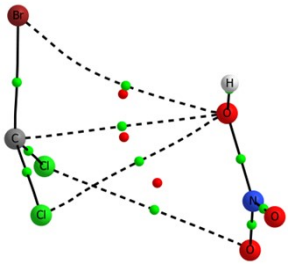
Erel= 4.3 kJ mol-1, Eb= -18.0 kJ mol-1



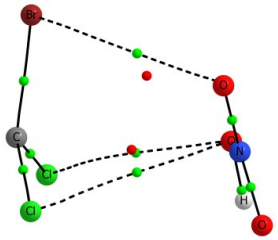
Erel= 4.8 kJ mol-1, Eb= -17.4 kJ mol-1



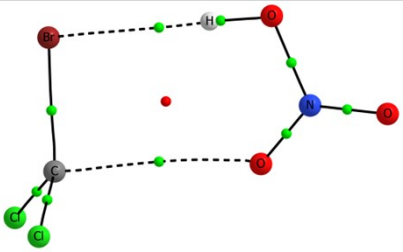
Erel= 4.9 kJ mol-1, Eb= -17.4 kJ mol-1



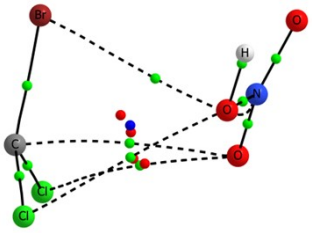
Erel= 4.9 kJ mol-1, Eb= -17.3 kJ mol-1



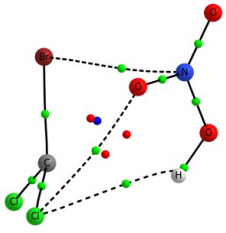
Erel= 5.5 kJ mol-1, Eb= -16.8 kJ mol-1



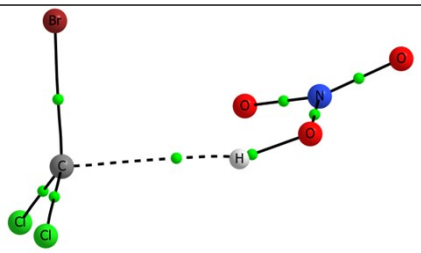
Erel= 5.6 kJ mol-1, Eb= -16.6 kJ mol-1



Erel= 5.8 kJ mol-1, Eb= -16.4 kJ mol-1

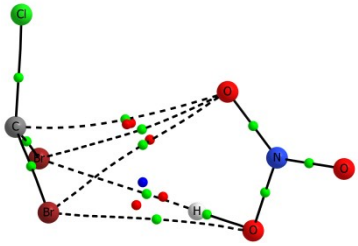


Erel= 6.2 kJ mol-1, Eb= -16.1 kJ mol-1

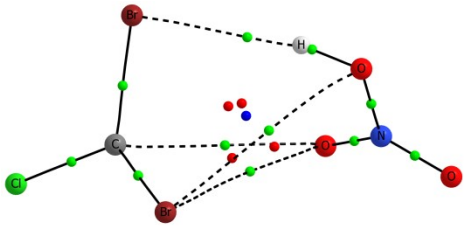


Erel= 6.5 kJ mol-1, Eb= -15.7 kJ mol-1

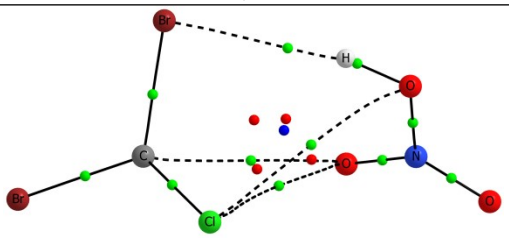
CClBr2:NO3H



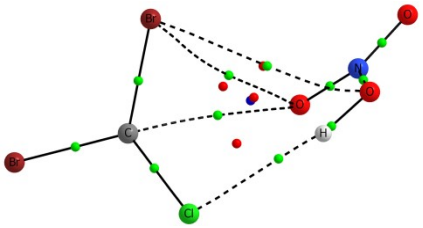
Erel= 0.0 kJ mol-1, Eb= -22.8 kJ mol-1



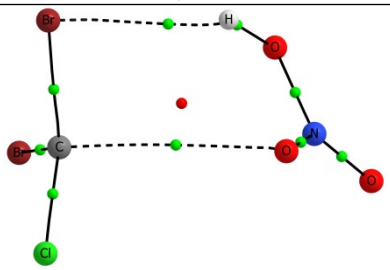
Erel= 3.4 kJ mol-1, Eb= -19.4 kJ mol-1



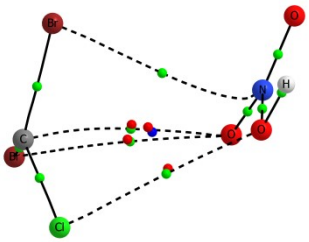
Erel= 4.0 kJ mol-1, Eb= -18.7 kJ mol-1



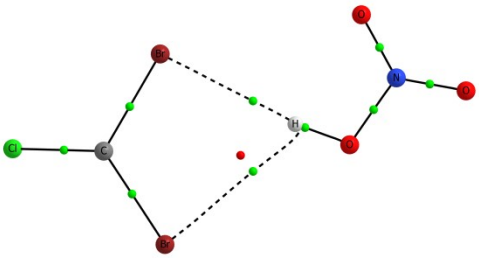
Erel= 4.9 kJ mol-1, Eb= -17.8 kJ mol-1



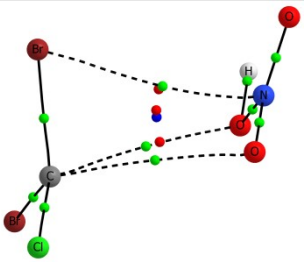
Erel= 5.0 kJ mol-1, Eb= -17.8 kJ mol-1



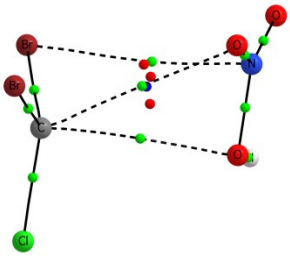
Erel= 6.6 kJ mol-1, Eb= -16.2 kJ mol-1



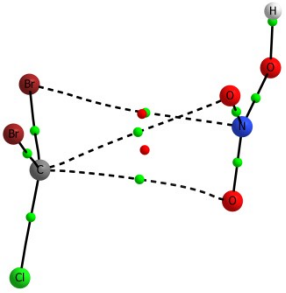
Erel= 6.6 kJ mol-1, Eb= -16.1 kJ mol-1



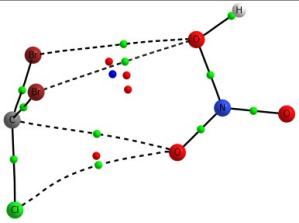
Erel= 6.9 kJ mol-1, Eb= -15.9 kJ mol-1



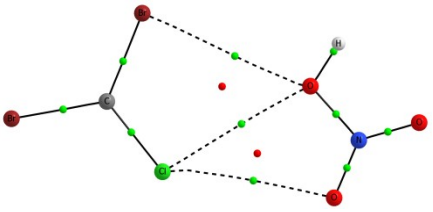
Erel= 7.1 kJ mol-1, Eb= -15.6 kJ mol-1



Erel= 7.5 kJ mol-1, Eb= -15.2 kJ mol-1

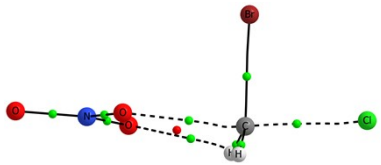
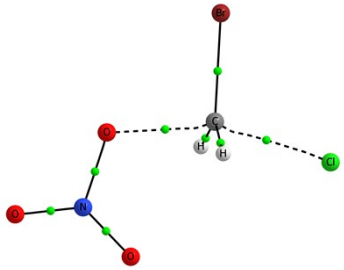
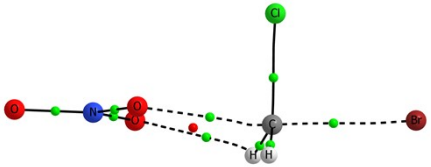
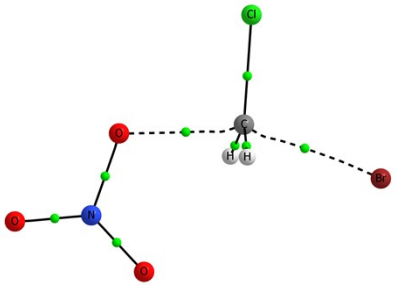
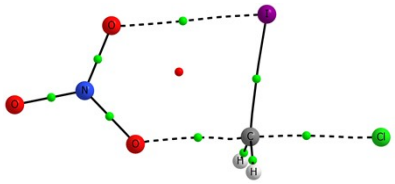
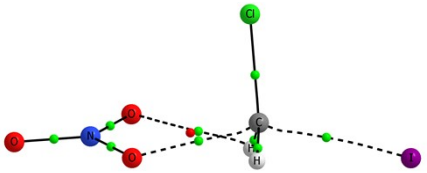
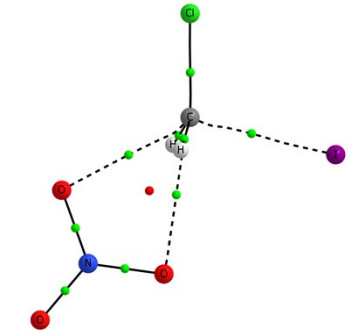
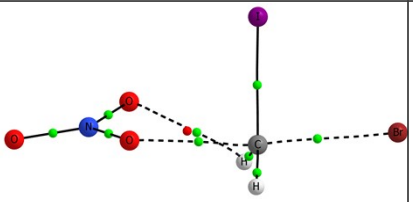
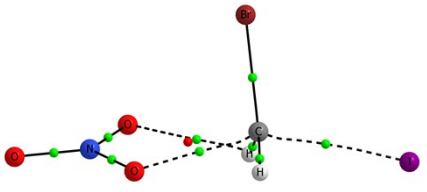
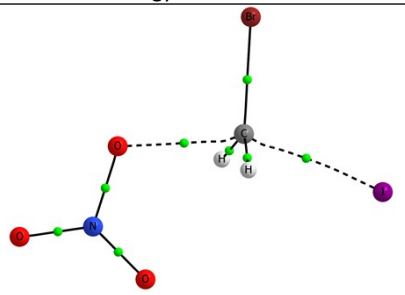


Erel= 8.6 kJ mol-1, Eb= -14.2 kJ mol-1



Erel= 15.3 kJ mol-1, Eb= -7.44 kJ mol-1

Table S8. Molecular structures and energetics (hartree) of the different S_N2 conformation TSs.

	III-A	III-B	III'-A	III'-B
$CH_2ClBr:NO_3$	 Total Energy= -3353.79187064	 Total Energy= -3353.80108268	 Total Energy= -3353.79930747	 Total Energy= -3353.81538107
$CH_2ClI:NO_3$	 Total Energy= -1077.24267702		 Total Energy= -1077.26200274	 Total Energy= -1077.24332387
$CH_2BrI:NO_3$	 Total Energy= -3191.22915686		 Total Energy= -3191.23768244	 Total Energy= -3191.23891213

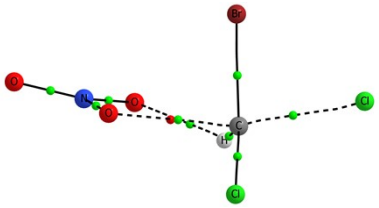
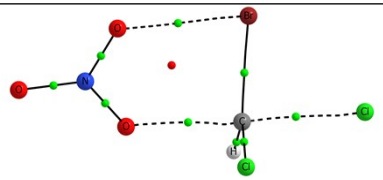
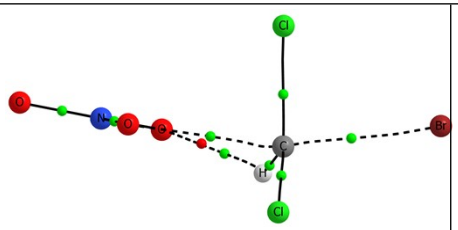
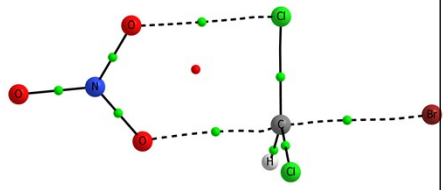
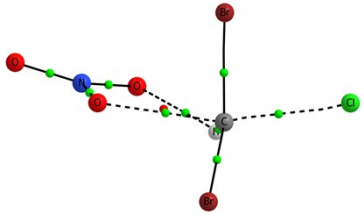
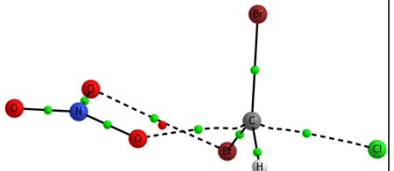
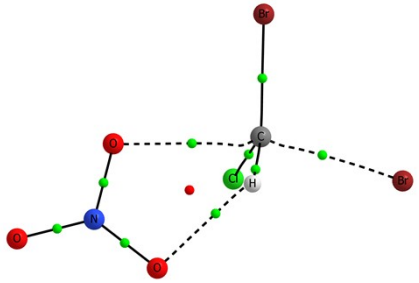
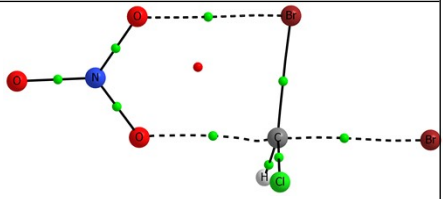
$CHCl_2Br{:}NO_3$	 Total Energy= -3813.37248510	 Total Energy= -3813.37507026	 Total Energy= -3813.38050102	 Total Energy= -3813.38349166
$CHClBr_2{:}NO_3$	 Total Energy= -5927.34733359	 Total Energy= -5927.34990387	 Total Energy= -5927.35537658	 Total Energy= -5927.36504301

Table S9. Molecular graph and energetics of the most stable conformation minima found for the S_N2 post-reaction complexes.

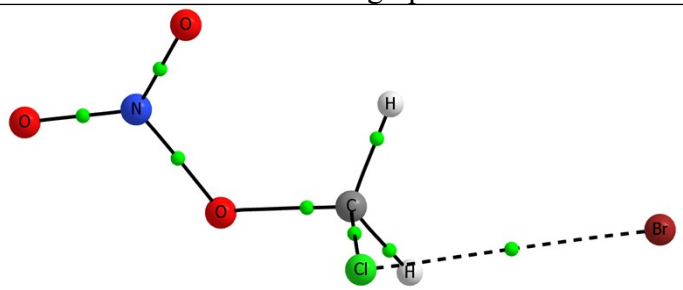
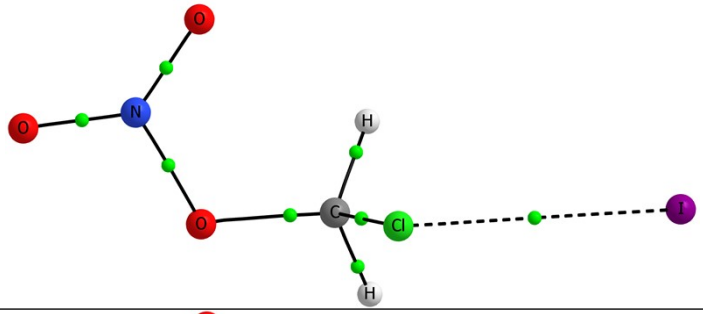
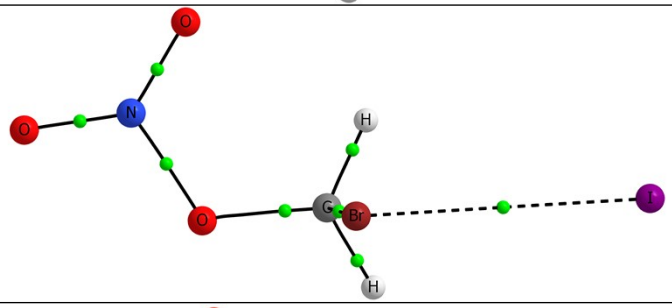
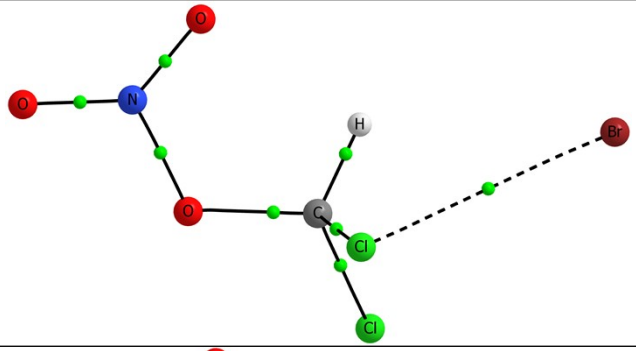
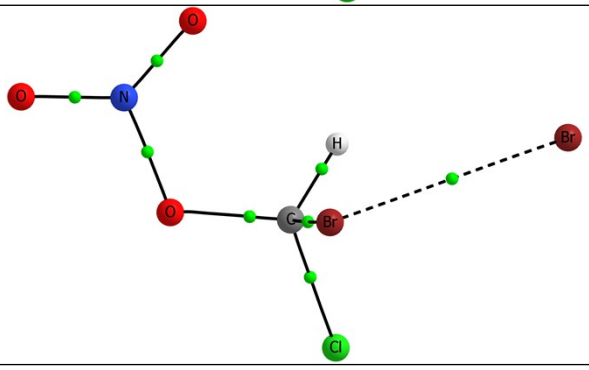
	Molecular graph	Erel (kJ mol^{-1})
NO_3:CH_2ClBr		-101.1
NO_3:CH_2ClI		-165.4
NO_3:CH_2BrI		-168.8
NO_3:$CHCl_2Br$		-100.1
NO_3:$CHClBr_2$		-107.0

Table 10. Rotational constant, vibrational frequencies (cm^{-1}), Dipole Moment (Debye) and polarizability of the stationary points in the NO_3 + CH_2BrI reaction.

***** NO_3 *******

Frequencies: 520.3829 544.3115 770.7803 805.0185 1162.3100 1705.7550

Rotational constants : .5233073608542879 .4273363007684468 .2352387397284023

Dipole Moment: 0.0599

Approx polarizability: 49.811 0.027 39.357 0.000 0.000 15.057

***** ch2bri *******

Frequencies: 146.6120 543.8876 654.5431 779.7997 1106.9191 1178.5048 1423.0635 3140.7669 3233.6536

Rotational constants : .8171409702374833 .0296375034224510 .0287592291597942

Dipole Moment: 1.3776

Approx polarizability: 100.617 -12.163 84.306 0.000 0.000 68.276

***** A_pre *******

Frequencies: 37.8883 68.3914 82.9406 103.9767 150.0334 162.8969 196.2313 520.5939 624.6842 661.7656 707.1676 782.8782 831.9952 1011.0886 1112.3181 1179.6971 1355.2282 1400.9269 1656.5464 3134.1608 3236.3368

Rotational constants : .0325792051780035 .0268225560230737 .0162639181536714

Dipole Moment: 5.0713

Approx polarizability: 160.639 27.528 134.612 -8.802 -17.166 112.936

***** A_TS *******

Frequencies: -365.3790 26.6046 36.2275 71.5572 123.7840 139.9131 192.4310 495.2876 574.1859 698.9790 700.4801 819.0216 828.4684 953.3348 1097.0311 1126.2908 1225.2971 1370.2214 1648.0203 1706.1485 3163.8776

Rotational constants : .0376250292460659 .0158212785993435 .0115646671805199

Dipole Moment: 3.1689

Approx polarizability: 210.136 16.290 146.312 9.828 13.712 100.777

Approx polarizability: 210.577 16.714 146.059 9.982 13.662 100.610

***** A_post *******

Frequencies: 18.7563 30.8821 45.0517 79.8804 95.2946 145.6292 162.2361 481.7783 553.9651 598.0262 633.7080 712.4844 776.1036 832.1481 1002.9934 1159.5682 1389.6853 1417.4080 1797.2048 3219.0695 3684.0774

Rotational constants : .0430894762536020 .0136914718515033 .0109532441940217

Dipole Moment: 3.1909

Approx polarizability: 136.683 -17.225 111.574 2.463 2.440 102.743

***** B_pre *******

Frequencies: 31.2944 60.0625 70.9323 77.7729 102.7915 144.9198 162.4738 455.0733 543.2734 646.7023 682.5578 781.8888 814.7943 916.5839 1112.7179 1182.2470 1365.6869 1410.2300 1681.0555 3141.0295 3237.4466

Rotational constants : .0308893694717296 .0243218260013732 .0149176534654517

Dipole Moment: 2.0648

Approx polarizability: 116.169 5.125 151.835 7.863 7.201 115.974

***** B_post_def2tzvp.log *******

Frequencies: 22.3328 35.1209 49.4174 80.7176 97.8316 146.0104 164.9093 487.4780 562.4135 600.8103 633.9575 713.3903 781.6757 831.3547 1003.5901 1156.0395 1392.0925 1417.4851 1795.9648 3212.3082 3684.1000

Rotational constants : .0323553836701255 .0171902256460367 .0118858894041957

Dipole Moment: 2.7158

Approx polarizability: 126.869 17.386 123.063 -3.465 0.392 101.646

***** C_pre *******

Frequencies: 14.1964 52.9150 58.3097 65.8904 89.5880 119.8842 149.3281 317.6640 536.7928 655.4271 677.7580 785.3129 811.9271 891.0922 1109.1415 1180.3388 1391.4336 1416.2284 1678.3101 3140.5072 3235.0830

Rotational constants : .0289960596673849 .0259696326316521 .0149927053868713

Dipole Moment: 1.4113

Approx polarizability: 130.389 23.422 106.815 5.247 -7.797 119.421

***** C_TS *******

Frequencies: -467.6745 27.3136 47.6936 75.5720 107.1368 150.4070 239.6753 526.9346 586.7838 695.1394 704.6596 829.9923 864.3786 936.6161 1094.8180 1159.8147 1299.1252 1353.7729 1437.5490 1671.0016 3158.4782

Rotational constants : .0300177664909768 .0221900178689618 .0138455784634848

Dipole Moment: 3.5236

Approx polarizability: 195.708 13.179 145.545 -17.122 -2.580 114.712

Approx polarizability: 198.056 12.586 143.790 -17.208 -2.204 114.726

***** C_post *******

Frequencies: 19.9012 41.5839 60.0088 73.2949 91.0194 143.1322 160.9917 492.3953 563.7651 594.5763 635.7793 712.4707 774.4419 832.4923 999.8722 1162.2349 1395.6911 1415.2808 1796.7032 3211.4849 3675.0570

Rotational constants : .0276094337236462 .0220102268216500 .0132665111942209

Dipole Moment: 3.5337

Approx polarizability: 110.345 -0.638 136.126 -5.327 -0.520 107.054

***** CHBrI *******

Frequencies: 158.6077 378.7523 578.5267 773.5827 1157.8470 3233.7658

Rotational constants : 1.1951845032739280 .0297896086498613 .0290787835629940

Dipole Moment: 0.7211

Approx polarizability: 112.352 -1.458 74.462 0.219 -0.738 63.597

***** NO3H *******

Frequencies: 492.3753 620.5749 706.3995 829.7299 989.6173 1367.5572 1417.7733 1808.6695 3826.1223

Rotational constants : .4454815204190359 .4167699909248550 .2153239625527870

Dipole Moment: 2.5409

Approx polarizability: 42.286 -3.673 30.674 -0.000 -0.000 17.005

Fig. S1. Relationship between the C-H and the O-H distances (Å) in the hydrogen transfer TS structures.

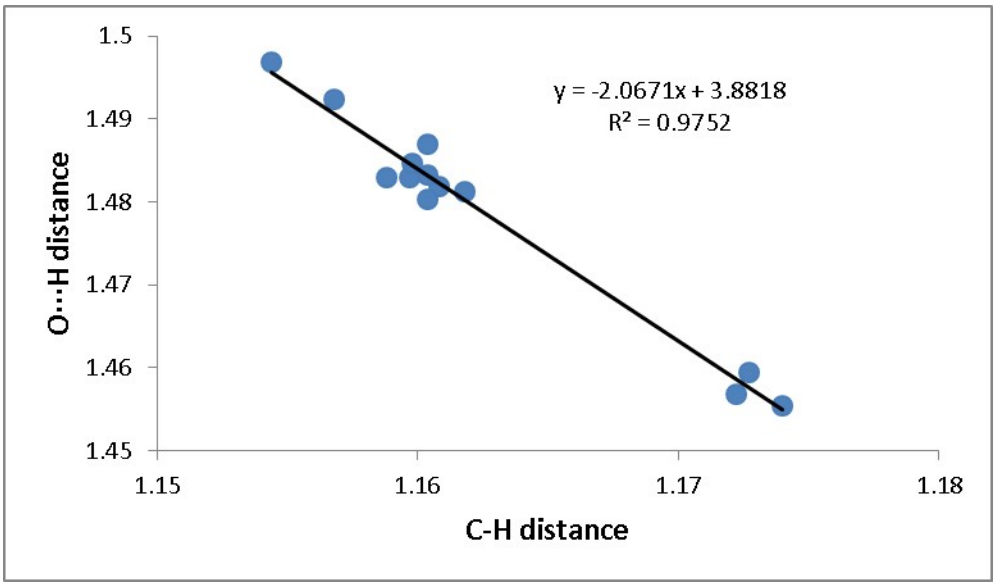


Fig. S2. Molecular electrostatic potential on the 0.001 au electron density isosurface of the hydrogen transfer products. The values (au) of the minima and maxima on the surface are indicated by cyan and black dots, respectively.