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Supporting information

Solid- vs. Liquid-state Thermal Decomposition: Thermolysis of Halogenated Benzene Derivatives with 2-Nitrodiazene-1-*N*-oxide Moiety

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Contents

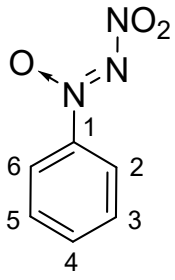
1. Synthesis and characterization of (nitro-NNO-azoxy)benzene derivatives

General Remarks: Silica gel "Silpearl UV 254" was used for preparative column chromatography. Analytical thin-layer chromatography (TLC) was carried out on "Silufol" TLC silica gel UV-254 aluminum sheets. All reagents were purchased from Acros and Sigma-Aldrich. The solvents were purified before use in accordance with to standard procedures.

Experimental Procedure for Two-step Synthesis (nitro-*NNO*-azoxy)benzenes from nitrosobenzenes

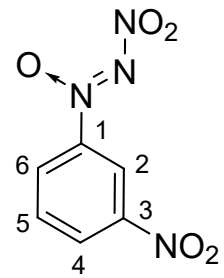
To a stirred solution of *N*,*N*-dibromoacetamide (5 mmol) in CH_2Cl_2 (10 ml) was added a solution of the corresponding nitroso compound (5 mmol) in CH_2Cl_2 (10 ml). The resulting solution was vigorously stirred at 25 °C for 2 h. Then the reaction mixture was concentrated under reduced pressure at 25 °C to give the crude corresponding (acetyl-*NNO*-azoxy)benzenes. The residue was dissolved in dry MeCN (5 ml) and $(NO_2)_2SiF_6$ (2.5 mmol) was added portionwise at –20 °C. The reaction mixture was warmed to 25 °C and vigorously stirred at this temperature for 1 h. Then the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, 10:1 or 40:1).

1-(nitro-*NNO*-azoxy)benzene (1): White crystals, m.p. 26–27 °C (lit. m.p. 26–27 °C).[1] 75% yield.



R_f (petroleum ether/ethyl acetate, 10:1) = 0.51. ^{1}H NMR (500.13 MHz, $CDCl_3$)δ: 7.57 (t, 2H, H(3), H(5), $^3J_{HH}$ = 8.2 Hz), 7.21 (t, 1H, H(4), $^3J_{HH}$ = 7.5 Hz), 8.10 (dd, 2H, H(2), H(6), $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 1.1 Hz) ppm. ^{13}C NMR (125.76 MHz, $CDCl_3$)δ: 122.2 (s, C(2), C(6)), 129.8 (s, C(3), C(5)), 134.7 (s, C(4)), 142.8 (br. s, C(1)) ppm. The ^{1}H–^{13}C HSQC and HMBC experiments were used to assign the signals. ^{14}N NMR (36.14 MHz, $CDCl_3$)δ: –32 (N(O)=N–$\underline{N}O_2$, $\Delta\nu_{1/2}$ = 20 Hz), –43 ($\underline{N}$(O)=N–NO_2, $\Delta\nu_{1/2}$ = 130 Hz) ppm. IR (KBr): ν = 2955 (w), 2884 (w), 1635 (s), 1505 (w), 1328 (w), 1282 (s) cm^{-1}. Elemental analysis calcd (%) for $C_6H_5N_3O_3$: C 43.12, H 3.02, N 25.14; found: C 43.15, H 3.03, N 25.01.

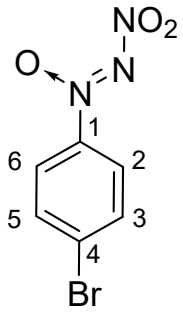
3-Nitro-1-(nitro-*NNO*-azoxy)benzene (2): Pale yellow crystals, m.p. 53–54 °C (lit. m.p. 53–54 °C).[1] 46% yield.



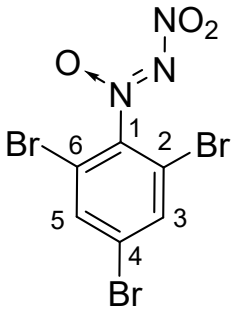
R_f (petroleum ether/ethyl acetate, 10:1) = 0.61.^{1}H NMR (600.13 MHz, $CDCl_3$)δ: 7.92 (t, 1H, H(5), $^3J_{HH}$ = 8.3 Hz), 8.56 (d, 1H, H(4) or H(6), $^3J_{HH}$ = 8.3 Hz), 8.64 (d, 1H, H(6) or H(4), $^3J_{HH}$ = 8.3 Hz), 9.02 (s, 1H, H(2) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$)δ: 118.0 (s, C(2)), 127.8 (s,

C(4) or C(6)), 129.0 (s, C(4) or C(6)), 131.3 (s, C(5)), 143.3 (br. s, C(1)), 148.5 (br. s, C(3)) ppm. The ^{1}H–^{13}C HSQC and HMBC experiments were used to assign the signals. ^{14}N NMR (43.37 MHz, $CDCl_3$)δ: –18 (NO_2, $\Delta\nu_{½}$ = 150 Hz), –38 (N(O)=N–$\underline{N}O_2$, $\Delta\nu_{½}$ = 30 Hz), –51 (*N*(O)=N–NO_2, $\Delta\nu_{½}$ = 130 Hz) ppm. IR (KBr): ν = 2923 (w), 2877 (w), 2854 (w), 1625 (s), 1535 (s), 1493 (s), 1485 (m), 1434 (w), 1351 (s), 1322 (m), 1286 (m), 1265 (s), 1165 (w), 1148 (w) cm^{-1}. Elemental analysis calcd (%) for $C_6H_4N_4O_5$: C 33.97, H 1.90, N 26.41; found: C 34.01, H 1.92, N 26.21.

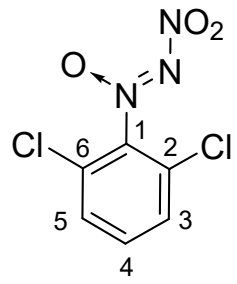
4-Bromo-1-(nitro-*NNO*-azoxy)benzene (3): Yellowish crystals, m.p. 74–75 °C (lit. m.p. 74–76 °C).[1] 50% yield. R_f (petroleum ether/ethyl acetate, 40:1) = 0.42. An analytical sample was obtained by three-fold recrystallization from mixture hexane/CH_2Cl_2 (10:1) at –20 °C. ^{1}H NMR (600.13 MHz, $CDCl_3$) δ = 7.73 (d, 2H, H(3), H(5), $^{3}J_{H,H}$ = 8.9 Hz), 8.01 (d, 2H, H(2), H(6), $^{3}J_{H,H}$ = 8.9 Hz) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$) δ = 123.7 (s, C(2), C(6)), 129.8 (br. s, C(4)), 133.0 (s, C(3), C(5)), 141.7 (br. s, C(1)) ppm. The ^{1}H–^{13}C HSQC and HMBC experiments were used to assign the signals. ^{14}N NMR (43.37 MHz, $CDCl_3$) δ = –36 (N(O)=N–$\underline{N}O_2$, $\Delta\nu_{½}$ = 20 Hz), –48 ($\underline{N}$(O)=N–NO_2, 75 Hz) ppm. IR (KBr): ν = 2921 (w), 2870 (w), 1606 (s), 1576 (m), 1519 (w), 1473 (s), 1396 (w), 1310 (w), 1280 (m), 1175 (w), 1108 (w) cm^{-1}. Elemental analysis calcd (%) for $C_6H_4BrN_3O_3$: C 29.29, H 1.64, N 17.08; found: C 29.31, H 1.65, N 16.91.



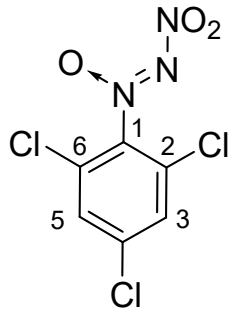
2,4,6-Tribromo-1-(nitro-*NNO*-azoxy)benzene (NDO3): Beige crystals, m.p. 113–114 °C.[2] 53% yield. R_f (petroleum ether/ethyl acetate, 40:1) = 0.46. ^{1}H NMR (500.13 MHz, $CDCl_3$) δ = 7.87 (s, 2H, H(3), H(5)) ppm. ^{13}C NMR (125.76 MHz, $CDCl_3$) δ = 117.4 (s, C(2), C(6)), 126.1 (s, C(4)), 134.8 (s, C(3), C(5)), 141.6 (s, C(4)) ppm. The ^{1}H–^{13}C HSQC and HMBC experiments were used to assign the signals. ^{14}N NMR (43.37 MHz, $CDCl_3$) δ = –38 (N(O)=N–$\underline{N}O_2$, $\Delta\nu_{½}$ = 25 Hz), –50 ($\underline{N}$(O)=N–NO_2, $\Delta\nu_{½}$ = 115 Hz) ppm. IR (KBr): ν = 2891 (w), 2814 (w), 1620 (s), 1551 (m), 1493 (m), 1430 (w), 1415 (w), 1370 (w), 1350 (w), 1329 (w), 1282 (m), 1248 (w), 1198 (w), 1161 (w), 1131 (w), 1112 (w) cm^{-1}. Elemental analysis calcd (%) for $C_6H_2Br_3N_3O_3$: C 17.85, H 0.50, N 10.41; found: C 17.87, H 0.52 N 10.20.



2,6-Dichloro-1-(nitro-*NNO*-azoxy)benzene (4): Brown crystals, m.p. 53–54 °C (lit. m.p. 54–56 °C).[1] 64% yield. R_f (petroleum ether/ethyl acetate, 10:1) = 0.57. ^{1}H NMR (500.13 MHz, $CDCl_3$) δ = 7.80–7.93 (m, 3H, H(3), H(4), H(5)) ppm. ^{13}C NMR (125.76 MHz, $CDCl_3$) δ = 128.4 (s, C(2), C(6)), 130.6 (s, C(3), C(5)), 135.1 (s, C(4)), 140.0 (br.s, C(1)) ppm. The ^{1}H–^{13}C HSQC and HMBC experiments were used to assign the signals. ^{14}N NMR (36.14 MHz, $CDCl_3$) δ = –37 (N(O)=N–$\underline{N}O_2$, $\Delta\nu_{½}$ = 25 Hz), –53 ($\underline{N}$(O)=N–NO_2, $\Delta\nu_{½}$ = 85 Hz) ppm. IR (KBr): ν = 2917 (w), 2892 (w), 1624 (s), 1578 (m), 1556 (m), 1492 (s), 1448 (m), 1388 (w), 1370 (w), 1330 (m), 1304 (s), 1277 (s), 1206 (m), 1168 (m) cm^{-1}. Elemental analysis calcd (%) for $C_6H_3Cl_2N_3O_3$: C 30.54, H 1.28, N 17.80; found: C 30.60, H 1.35, N 17.53.



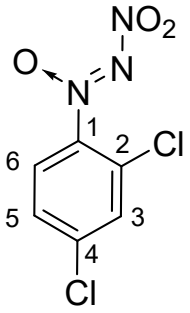
2,4,6-Trichloro-1-(nitro-*NNO*-azoxy)benzene (NDO2): Beige crystals, m.p. 80–81 °C (lit. m.p. 80–81 °C).[3] 80% yield. R_f (petroleum ether/ethyl acetate, 40:1) = 0.70. ^{1}H NMR (500.13 MHz, $CDCl_3$) δ = 7.84 (s, 2H, H(3), H(5)) ppm. ^{13}C NMR (125.76 MHz, $CDCl_3$) δ = 129.5 (br. s, C(4)), 130.8 (s, C(3), C(5)), 135.1 (s, C(2), C(6)), 140.3 (br.s, C(1)) ppm. The ^{1}H–^{13}C HSQC and HMBC experiments were used to assign the signals. ^{14}N NMR (36.14 MHz, $CDCl_3$) δ = –36 (N(O)=N–$\underline{N}O_2$, $\Delta\nu_{½}$ = 30 Hz), –52 ($\underline{N}$(O)=N–NO_2, $\Delta\nu_{½}$ = 90 Hz) ppm. IR (KBr): ν = 2952 (w), 2926 (w), 2901 (w), 2855 (w), 1624 (s), 1566 (s), 1494 (s), 1451 (m), 1430 (m), 1390 (m), 1371 (m), 1330 (w), 1286 (s), 1196 (w), 1128 (m) cm^{-1}. Elemental analysis calcd (%) for $C_6H_2Cl_3N_3O_3$: C 26.65, H 0.75, N 15.54; found: C 26.76, H 0.77, N 15.32.

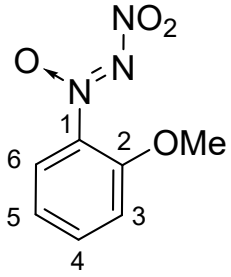


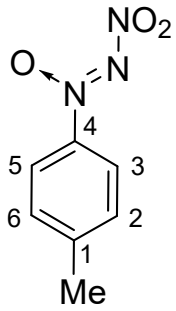
Experimental Procedure for Electrochemical Synthesis of (nitro-*NNO*-azoxy)benzenes NDO1 and 5

An undivided 20 mL jacketed electrochemical cell was equipped with a carbon felt anode (30 × 15 mm^2) and a platinum wire cathode, and connected to a DC regulated power supply. Electrodes were completely immersed in the solution given S = 4.5 cm^2 of working anode surface. A mixture of nitrosobenzene or corresponding nitroso compounds **NDO1**,**5–11** (1.0 mmol, 107–329 mg), and ADN (4.0 equiv., 4.0 mmol, 496 mg) in MeCN (20 mL) was electrolyzed using constant current conditions (I = 60 mA, j_{anode} = 13.3 mA·cm^{-2}) at 23–25 °C under magnetic stirring. After passing 2.0 F·mol^{-1} of electricity (reaction time 54 min), electrodes were washed with CH_2Cl_2 (3 × 20 mL). The combined organic phase was washed with H_2O (20 mL) and brine (20

mL), dried over Na_2SO_4 and concentrated under reduced pressure. Products **NDO1** and **5–11** were purified by column chromatography on silica gel (petroleum ether/ethyl acetate, 40:1 (for compounds **6**–**8**), 10:1 (for compounds **NDO1**, **5**, **10**, **11**), 6:1 (for compound **9**).

2,4-Dichloro-1-(nitro-*NNO*-azoxy)benzene (NDO1): Brown crystals, m.p. 45–46 °C.[2] 53% yield.  R_f (petroleum ether/ethyl acetate, 10:1) = 0.50. An analytical sample was obtained by recrystallization from hexane at –20 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$) δ = 7.47 (d, 1H, H(5), $^3J_{H,H}$ = 8.6 Hz), 7.62 (s, 1H, H(3)), 7.71 (d, 1H, H(6), $^3J_{H,H}$ = 8.6 Hz) ppm. ^{13}C NMR (125.76 MHz, $CDCl_3$) δ = 126.5 (s, C(6)), 128.4 (s, C(5)), 131.7 (s, C(3)), 139.5 (s, C(2)), 140.0 (br.s, C(1)) ppm. The ^{1}H–^{13}C HSQC and HMBC experiments were used to assign the signals. ^{14}N NMR (36.14 MHz, $CDCl_3$) δ = –36 (N(O)=N–$\underline{N}O_2$, $\Delta\nu_{½}$ = 25 Hz), –49 ($\underline{N}$(O)=N–NO_2, $\Delta\nu_{½}$ = 100 Hz) ppm. IR (KBr): ν = 2940 (w), 2875 (w), 1619 (s), 1582 (s), 1566 (s), 1482 (s), 1464 (s), 1393 (w), 1376 (m), 1342 (w), 1317 (m), 1274 (s), 1145 (m), 1107 (m) cm^{-1}. Elemental analysis calcd (%) for $C_6H_3Cl_2N_3O_3$: C 30.54, H 1.28, N 17.80; found: C 30.55, H 1.31, N 17.63.

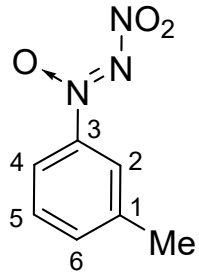
1-Methoxy-2-(nitro-*NNO*-azoxy)benzene (5): Yellow oil.[2] 51% yield.  R_f (petroleum ether/ethyl acetate, 10:1) = 0.71. ^{1}H NMR (300.13 MHz, $CDCl_3$)δ: 3.89 (s, 3H, OMe), 7.24 (dd, 1H, H(6), $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 2.5 Hz), 7.46 (t, 1H, H(5), $^3J_{HH}$ = 8.3 Hz), 7.60 (t, 1H, H(4), $^3J_{HH}$ = 2.3 Hz), 7.69 (dd, 1H, H(3), $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 2.2 Hz) ppm. ^{13}C NMR (75.49 MHz, $CDCl_3$)δ: 55.9 (s, OMe), 107.2 (s, C(4)), 114.3 (s, C(3)), 121.0 (s, C(6)), 130.4 (s, C(5)), 143.8 (br. s, C(2)), 160.4 (s, C(1)) ppm. The ^{1}H–^{13}C HSQC and HMBC experiments were used to assign the signals. ^{14}N NMR (43.4 MHz, $CDCl_3$)δ: –34 (N(O)=N–$\underline{N}O_2$, $\Delta\nu_{½}$ = 20 Hz), –45 ($\underline{N}$(O)=N–NO_2, $\Delta\nu_{½}$ = 115 Hz) ppm. IR (KBr): ν = 2969 (w), 2941 (w), 2841 (w), 1612 (s), 1503 (s), 1472 (m), 1447 (m), 1384 (w), 1335 (m), 1319 (m), 1290 (m), 1271 (s), 1250 (s), 1185 (w), 1106 (w) cm^{-1}. Elemental analysis calcd (%) for $C_7H_7N_3O_4$: C 42.65, H 3.58, N 21.31; found: C 42.66, H 3.58, N 21.21.



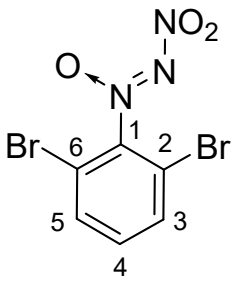
1-Methyl-4-(nitro-*NNO*-azoxy)benzene (6): Orange oil.[2] 80% yield. R_f (petroleum ether/ethyl acetate, 40:1) = 0.25. ^{1}H NMR (500.13 MHz, $CDCl_3$) δ:

2.48 (s, 3H, Me), 7.35 (d, 2H, H(2), H(6), $^3J_{HH}$ = 8.2 Hz), 7.99 (d, 2H, H(3), H(5), $^3J_{HH}$ = 8.2 Hz) ppm. ^{13}C NMR (125.76 MHz, $CDCl_3$) δ: 21.1 (s, Me), 121.5 (s, C(3), C(5)), 129.7 (s, C(2), C(6), 139.9 (br. s, C(4)), 145.6 (s, C(1)) ppm. The ^{1}H–^{13}C HSQC and HMBC experiments were used to assign the signals. ^{14}N NMR (36.14 MHz, $CDCl_3$) δ: –33 (N(O)=N–$\underline{N}O_2$, $\Delta\nu_{½}$ = 20 Hz), –45 ($\underline{N}$(O)=N–NO_2, $\Delta\nu_{½}$ = 130 Hz) ppm. IR (KBr): ν = 2952 (w), 2889 (w), 1611 (s), 1519 (w), 1478 (s), 1383 (w), 1345 (w), 1318 (w), 1268 (s), 1181 (m), 1116 (w) cm^{-1}. Elemental analysis calcd (%) for $C_7H_7N_3O_3$: C 46.41, H 3.90, N 23.20; found: C 46.45, H 3.93, N 23.01.

1-Methyl-3-(nitro-*NNO*-azoxy)benzene (7): Orange oil.[2] 74% yield. R_f (petroleum ether/ethyl acetate, 40:1) = 0.50. ^{1}H NMR (500.13 MHz, $CDCl_3$) δ: 2.47 (s, 3H, Me), 7.45 (t, 1H, H(5), $^3J_{HH}$ = 7.8 Hz), 7.52 (m, 1H, H(6)), 7.90–7.92 (m, 2H, H(2), H(4)) ppm. ^{13}C NMR (125.76 MHz, $CDCl_3$) δ: 21.3 (s, Me), 119.3 (s, C(4)), 122.5 (s, C(2)), 129.4 (s, C(5)), 135.3 (s, C(6)), 140.3 (s, C(1)), 142.7 (br. s, C(3)) ppm. The ^{1}H–^{13}C HSQC and HMBC experiments were used to assign the signals. ^{14}N NMR (43.4 MHz, $CDCl_3$) δ: –35 (N(O)=N–$\underline{N}O_2$, $\Delta\nu_{½}$ = 15 Hz), –46 ($\underline{N}$(O)=N–NO_2, $\Delta\nu_{½}$ = 100 Hz) ppm. IR (KBr): ν = 2924 (w), 2871 (w), 1610 (s), 1502 (s), 1470 (m), 1427 (w), 1383 (w), 1316 (w), 1295 (w), 1270 (s), 1220 (w), 1169 (w) cm^{-1}. Elemental analysis calcd (%) for $C_7H_7N_3O_3$: C 46.41, H 3.90, N 23.20; found: C 46.46, H 3.91, N 23.05.

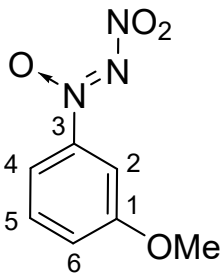


2,4-Dibromo-1-(nitro-*NNO*-azoxy)benzene (8): Orange crystals, m.p. 71–72 °C.[2] 34% yield. R_f (petroleum ether/ethyl acetate, 40:1) = 0.54. ^{1}H NMR (600.13 MHz, $CDCl_3$) δ = 7.60 (d, 1H, H(6), $^3J_{H,H}$ = 8.5 Hz), 7.67 (d, 1H, H(5), $^3J_{H,H}$ = 8.4 Hz), 7.96 (s, 1H, H(3)) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$) δ = 117.4 (s, C(4) or C(2)), 127.3 (s, C(6)), 128.1 (s, C(2) or C(4)), 132.6 (s, C(5)), 138.2 (s, C(3)), 143.0 (br. s, C(1)) ppm. The ^{1}H–^{13}C HSQC and HMBC experiments were used to assign the signals. ^{14}N NMR (43.37 MHz, $CDCl_3$) δ = –37 (N(O)=N–$\underline{N}O_2$, $\Delta\nu_{½}$ = 35 Гц), –47 ($\underline{N}$(O)=N–NO_2, $\Delta\nu_{½}$ = 80 Гц) ppm. IR (KBr): ν = 2931 (w), 2881 (w), 2811 (w), 1606 (s), 1568 (s), 1535 (s), 1479 (s), 1459 (s), 1387 (w), 1371 (m), 1331 (m), 1288 (s), 1245 (s), 1149 (m), 1109 (w) cm^{-1}. Elemental analysis calcd (%) for $C_6H_3Br_2N_3O_3$: C 22.18, H 0.93, N 12.93; found: C 22.18, H 0.94, N 12.71.



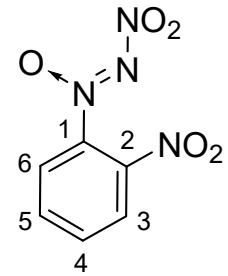
2,6-Dibromo-1-(nitro-*NNO*-azoxy)benzene (9): Beige crystals, m.p. 97–98 °C.[2] 53% yield. R_f (petroleum ether/ethyl acetate, 6:1) = 0.49. ^{1}H NMR

(600.13 MHz, $CDCl_3$) δ = 7.35 (t, $^3J_{H,H}$ = 8.1 Hz, 1H, H(4)), 7.70 (d, $^3J_{H,H}$ = 8.2 Hz, 2H, H(3), H(5)) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$) δ = 118.1 (s, C(2), C(6)), 133.8 (s, C(3), C(5)), 134.0 (s, C(4)), 143.7 (br. s, C(1)) ppm. The ^1H–^{13}C HSQC and HMBC experiments were used to assign the signals. ^{14}N NMR (43.37 MHz, $CDCl_3$) δ = –37 (N(O)=N–$\underline{N}O_2$, $\Delta\nu_{½}$ = 25 Hz), –48 ($\underline{N}$(O)=N–NO_2, $\Delta\nu_{½}$ = 125 Hz) ppm. IR (KBr): ν = 2917 (w), 2889 (w), 2849 (w), 1633 (s), 1567 (m), 1535 (s), 1490 (s), 1441 (m), 1422 (w), 1370 (w), 1327 (w), 1295 (m), 1274 (s), 1288 (s), 1201 (m), 1161 (w) cm^{-1}. Elemental analysis calcd (%) for $C_6H_3Br_2N_3O_3$: C 22.18, H 0.93, N 12.93; found: C 22.18, H 0.94, N 12.71.



1-Methoxy-3-(nitro-*NNO*-azoxy)benzene (10): Yellow oil.[2] 79% yield. R_f (petroleum ether/ethyl acetate, 10:1) = 0.57. ^1H NMR (600.13 MHz, $CDCl_3$) δ: 3.88 (s, 3H, OMe), 7.24 (dd, 1H, H(6), $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 2.3 Hz), 7.46 (t, 1H, H(5), J_{HH} = 8.3 Hz), 7.57 (s, 1H, H(2)), 7.69 (dd, 1H, H(4), $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.8 Hz) ppm. ^{13}C NMR (150.9 MHz, $CDCl_3$) δ: 55.9 (s, OMe), 107.1 (s, C(2)), 114.2 (s, C(4)), 121.0 (s, C(6)), 130.4 (s, C(5)), 143.5 (br. s, C(3)), 160.2 (s, C(1)) ppm. The ^1H–^{13}C HSQC and HMBC experiments were used to assign the signals. ^{14}N NMR (43.4 MHz, $CDCl_3$) δ: –34 (N(O)=N–$\underline{N}O_2$, $\Delta\nu_{½}$ = 30 Hz), –46 ($\underline{N}$(O)=N–NO_2, $\Delta\nu_{½}$ = 215 Hz) ppm. IR (KBr): ν = 2970 (w), 2942 (w), 2841 (w), 1612 (s), 1585 (m), 1530 (m), 1502 (s), 1472 (m), 1447 (m), 1384 (w), 1335 (m), 1319 (m), 1290 (m), 1271 (s), 1250 (s), 1185 (w), 1106 (w) cm^{-1}. Elemental analysis calcd (%) for $C_7H_7N_3O_4$: C 42.65, H 3.58, N 21.31; found: C 42.72, H 3.59, N 21.05.

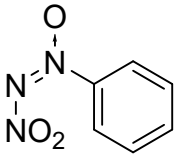
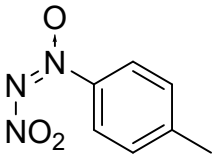
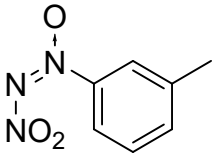
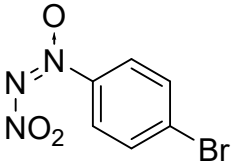
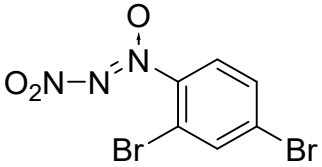
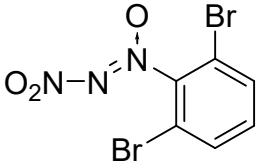
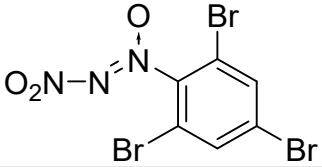
2-Nitro-1-(nitro-*NNO*-azoxy)benzene (11): Pale yellow crystals, m.p. 38–39 °C. 70% yield. R_f (petroleum ether/ethyl acetate, 10:1) = 0.55. ^1H NMR (600.13 MHz, $CDCl_3$) δ: 7.88–7.92 (m, 3H, H(4), H(5), H(6)), 8.22 (d, 1H, H(3), $^3J_{HH}$ = 7.3 Hz) ppm. ^{13}C NMR (150.90 MHz, $CDCl_3$) δ: 126.0 (s, C(6)), 126.3 (s, C(3)), 133.8 (s, C(4)), 134.7 (br. s, C(5)), 137.1 (br. s, C(1)), 142.4 (br. s, C(2)) ppm. The ^1H–^{13}C HSQC and HMBC experiments were used to assign the signals. ^{14}N NMR (43.37 MHz, $CDCl_3$) δ: –20 (NO_2, $\Delta\nu_{½}$ = 55 Hz), –39 (N(O)=N–$\underline{N}O_2$, $\Delta\nu_{½}$ = 15 Hz), –51 ($\underline{N}$(O)=N–NO_2, $\Delta\nu_{½}$ = 50 Hz) ppm. IR (KBr): ν = 2918 (w), 2887 (w), 1621 (s), 1542 (s), 1494 (s), 1449 (w), 1437 (w), 1406 (w), 1351 (s), 1313 (w), 1280 (s), 1265 (s), 1169 (w), 1147



(w) cm^{-1}. Elemental analysis calcd (%) for $C_6H_4N_4O_5$: C 33.97, H 1.90, N 26.41; found: C 34.00, H 1.94, N 26.25.

2. Thermal behavior and kinetic analysis of the thermolysis of nitrodiazene-*N*-oxides

Table S1. Structures of nitrodiazenoxides and their characteristic temperatures obtained by DSC at 5 K min^{-1} heating rate: melting point (the extrapolated onset of endotherm), "decomposition onset" (the onset temperature of the exothermic event under specified conditions), and temperature corresponding to the exothermic peak.

id	Structure	Melting point, °C	Onset temperature, °C	Peak temperature, °C
1		26	113	140
6		<RT	113	143
7		<RT	108	141
3		69	107	140
8		72	99	130
9		95	95	133
NDO3		114	114	132

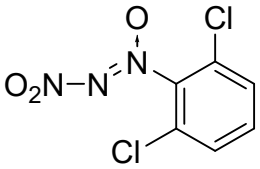
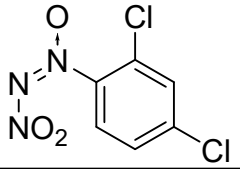
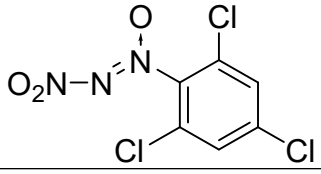
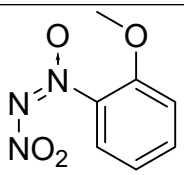
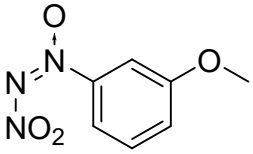
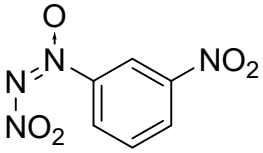
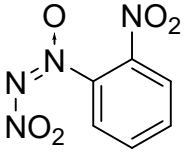
4		54	100	131
NDO1		45	99	130
NDO2		78	78	130
5		<RT	106	145
10		<RT	108	143
2		53	106	144
11		40	104	136

Table S2. Additional kinetic models optimized for **NDO1** (see the main part in Table 1 in the article).

Model	1G	1H	1I	1K	1L
Dataset	TGA, noniso and iso	TGA, noniso and iso	int-DSC and TGA, noniso and iso	int-DSC and TGA, noniso and iso	DSC and TGA, noniso and iso
Reaction scheme	Eq.(1)	Eq.(2)	Eq.(1)	Eq.(2)	Eq.(1)

$\ln(A_1, s^{-1})$	33.17(4)	36.0(1)	35.44(3)	38.81(4)	38.04(5)
E_{a1}, kJ mol^{-1}	128.3(1)	137.5(2)	133.9(1)	146.1(1)	143.1(1)
n_1	1.01(1)		1.13(1)		1*
m_1	-0.01(1)		0.25(1)		0*
q_1	0.999*		0.999*		
$\ln(A_2, s^{-1})$		1.0(8)		1.0(4)	
E_{a2}, kJ mol^{-1}		35.3(2.4)		34.3(1.1)	
BIC	-31395	-33818	-32860	-37644	-20794

Note: The standard errors are shown in brackets. The values kept fixed in the course of optimization are marked with an asterisk.

Table S3. Optimized formal kinetic models for thermal decomposition of **NDO2**.

Model	2A	2B	2C	2D
Dataset	DSC, 0.5-10K/min	DSC, 0.5-10K/min	DSC, 0.5-10K/min	TGA, 0.5-10K/min
Reaction scheme	Eq.(1)	Eq.(2)	Eq.(2)	Eq.(1)
$\ln(A_1, s^{-1})$	36.04(2)	39.35(7)	39.15(6)	37.64(5)
E_{a1}, kJ mol^{-1}	135.9(1)	147.9(2)	147.2(2)	142.5(1)
n_1	1.12(1)			1.51(1)
m_1	0.20(1)			-0.03(1)
q_1	0.999*			0.999*
$\ln(A_2, s^{-1})$		7.3(5)	5.4(5)	
E_{a2}, kJ mol^{-1}		47.7(1.7)	41.8(1.7)	
t_{trig}, °C	-	-	81.8	
BIC	-28568	-22741	-23235	-28864

Note: The standard errors are shown in brackets. The values kept fixed in the course of optimization are marked with an asterisk.

Table S4. Additional kinetic models optimized for **NDO2**.

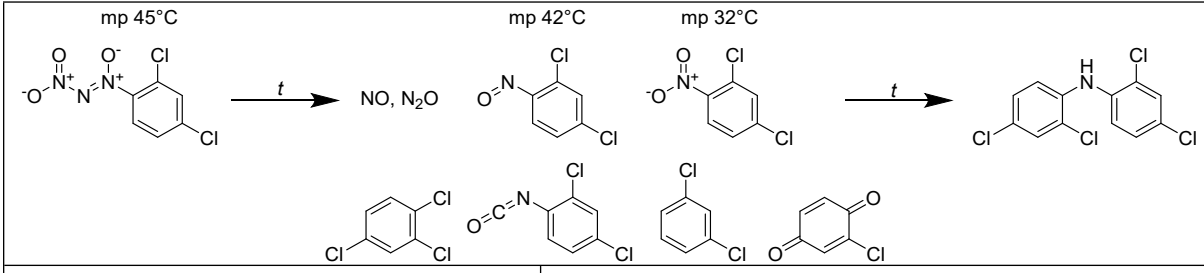
Model	2E	2F	2G	2H	2I	2K
Dataset	TGA,	int-DSC	int-DSC	DSC and	DSC and	DSC and

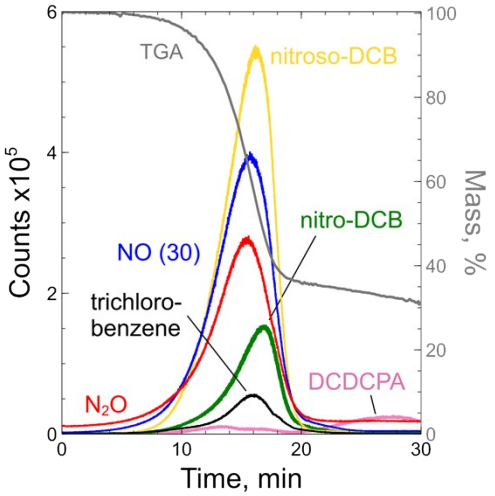
	noniso and iso	and TGA, noniso and iso	and TGA, noniso and iso	DTG, noniso and iso	DTG, noniso and iso	DTG, noniso and iso
Reaction scheme	Eq.(1)	Eq.(1)	Eq.(2)	Eq.(1)	Eq.(1)	Eq.(2)
$\ln(A_1, s^{-1})$	32.24(4)	36.84(3)	38.47(5)	38.08(4)	38.71(4)	38.28(7)
E_{a1}, kJ mol^{-1}	125.8(1)	138.9(1)	145.0(2)	143.0(1)	145.4(1)	144.2(2)
n_1	1.03(1)	1.07(1)		1.05(1)	1*	
m_1	-0.03(1)	0.14(1)		0.08(1)	0*	
q_1	0.999*	0.999*		0.999*		
$\ln(A_2, s^{-1})$			1			31.57(9)
E_{a2}, kJ mol^{-1}			35.1(3.8)			128.4(2.7)
T_{trig}, °C						
BIC	-33482	-39989	-39558	-29262	-28030	-28746

Note: The standard errors are shown in brackets. The values kept fixed in the course of optimization are marked with an asterisk.

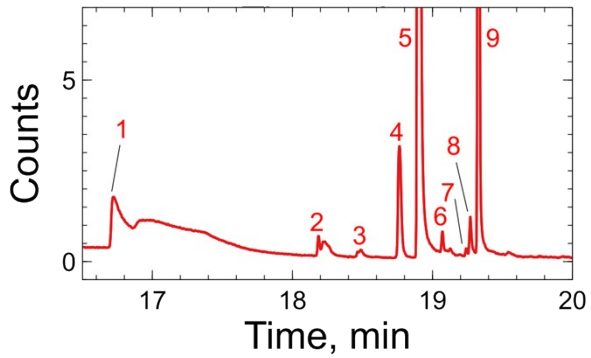
3. Evolved gases analysis

NDO1:

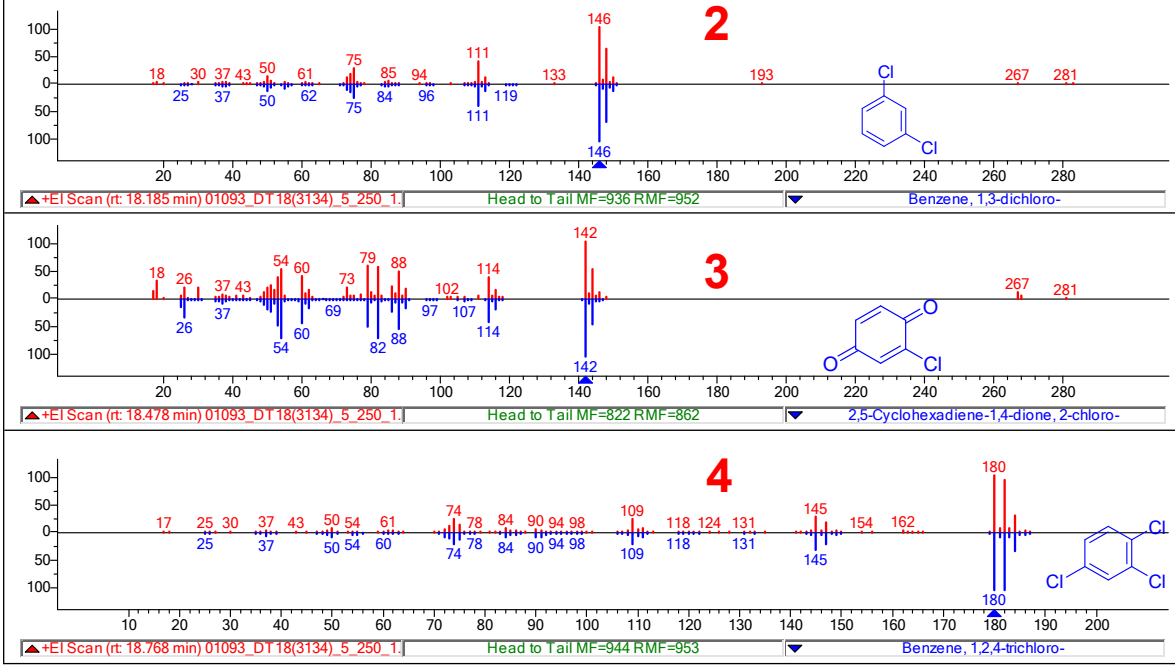


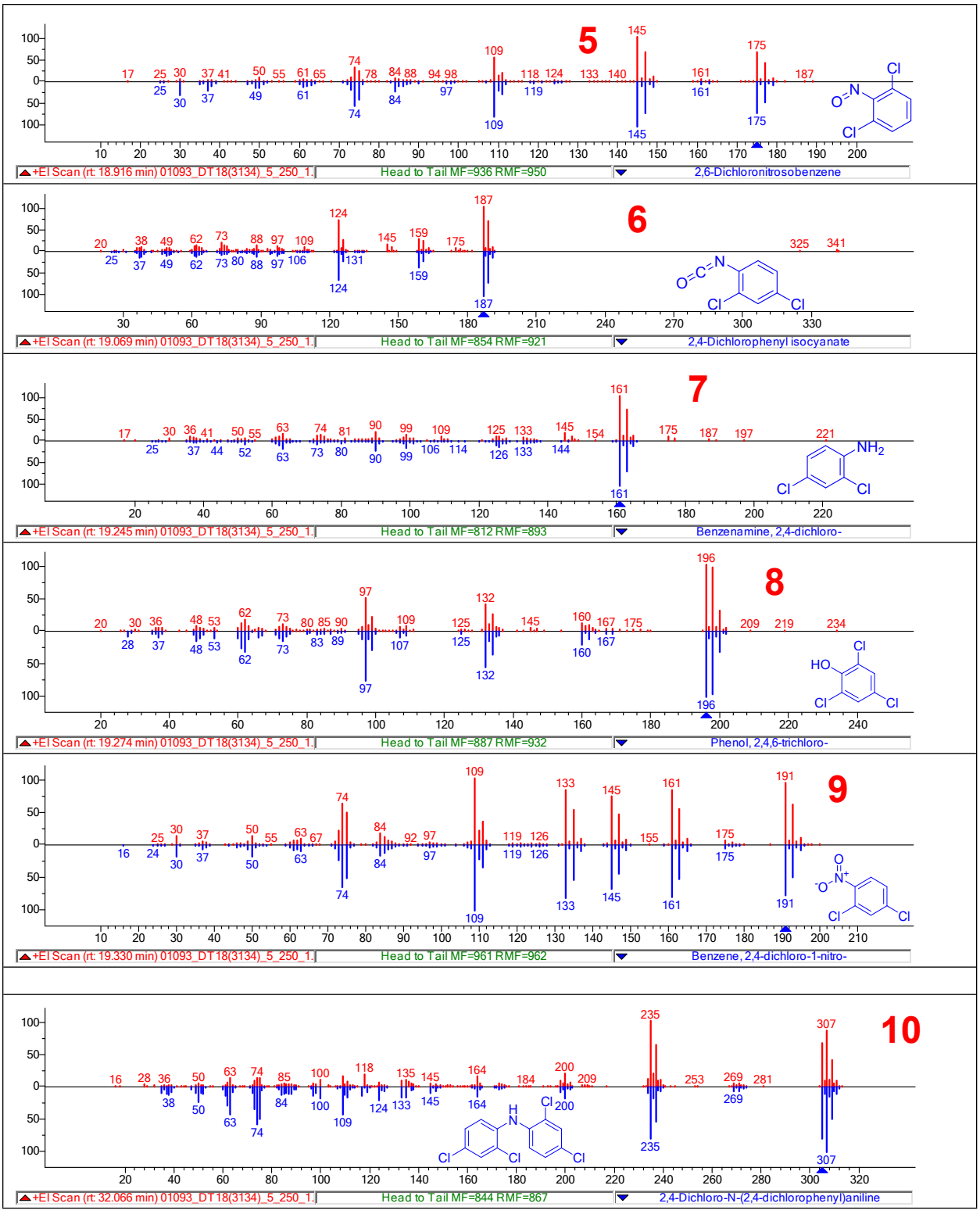


Direct mode – mass spectrometry of evolved gases along with the corresponding TGA signal under linear heating conditions.



GC/MS mode – at the point of maximal weight loss rate the gases are extracted and passed through CG and MS. The mass spectra of the separated gases are shown below (red bars) along with their assignments in the NIST mass spectra database.




5
+EI Scan (rt: 18.916 min) 01093_DT18(3134)_5_250_1.
Head to Tail MF=936 RMF=950
2,6-Dichloronitrosobenzene
6
+EI Scan (rt: 19.069 min) 01093_DT18(3134)_5_250_1.
Head to Tail MF=854 RMF=921
2,4-Dichlorophenyl isocyanate
7
+EI Scan (rt: 19.245 min) 01093_DT18(3134)_5_250_1.
Head to Tail MF=812 RMF=893
Benzenamine, 2,4-dichloro-
8
+EI Scan (rt: 19.274 min) 01093_DT18(3134)_5_250_1.
Head to Tail MF=887 RMF=932
Phenol, 2,4,6-trichloro-
9
+EI Scan (rt: 19.330 min) 01093_DT18(3134)_5_250_1.
Head to Tail MF=961 RMF=962
Benzene, 2,4-dichloro-1-nitro-
10
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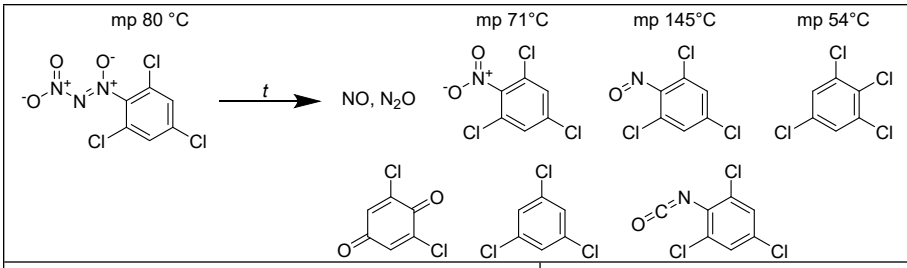
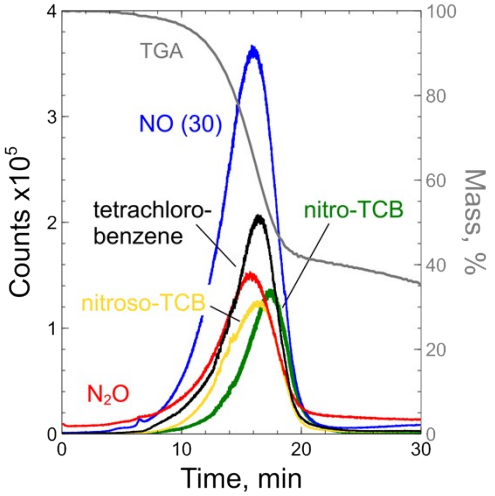
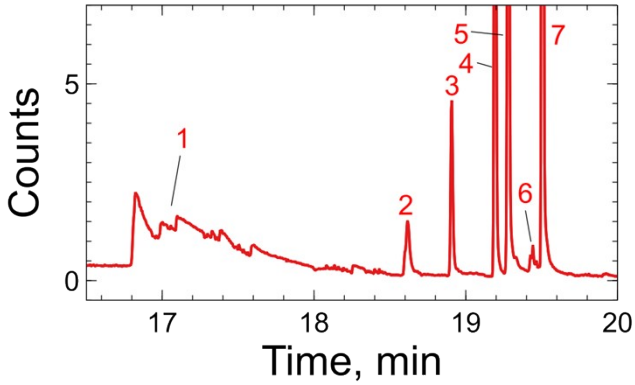
Head to Tail MF=844 RMF=867
2,4-Dichloro-N-(2,4-dichlorophenyl)aniline

NDO2:

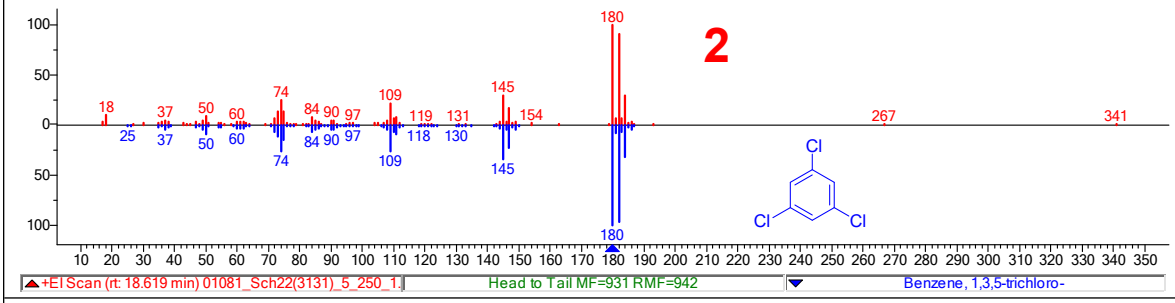


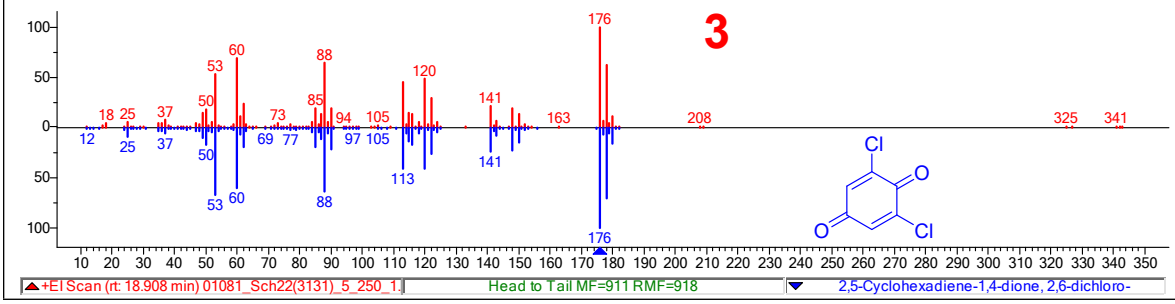


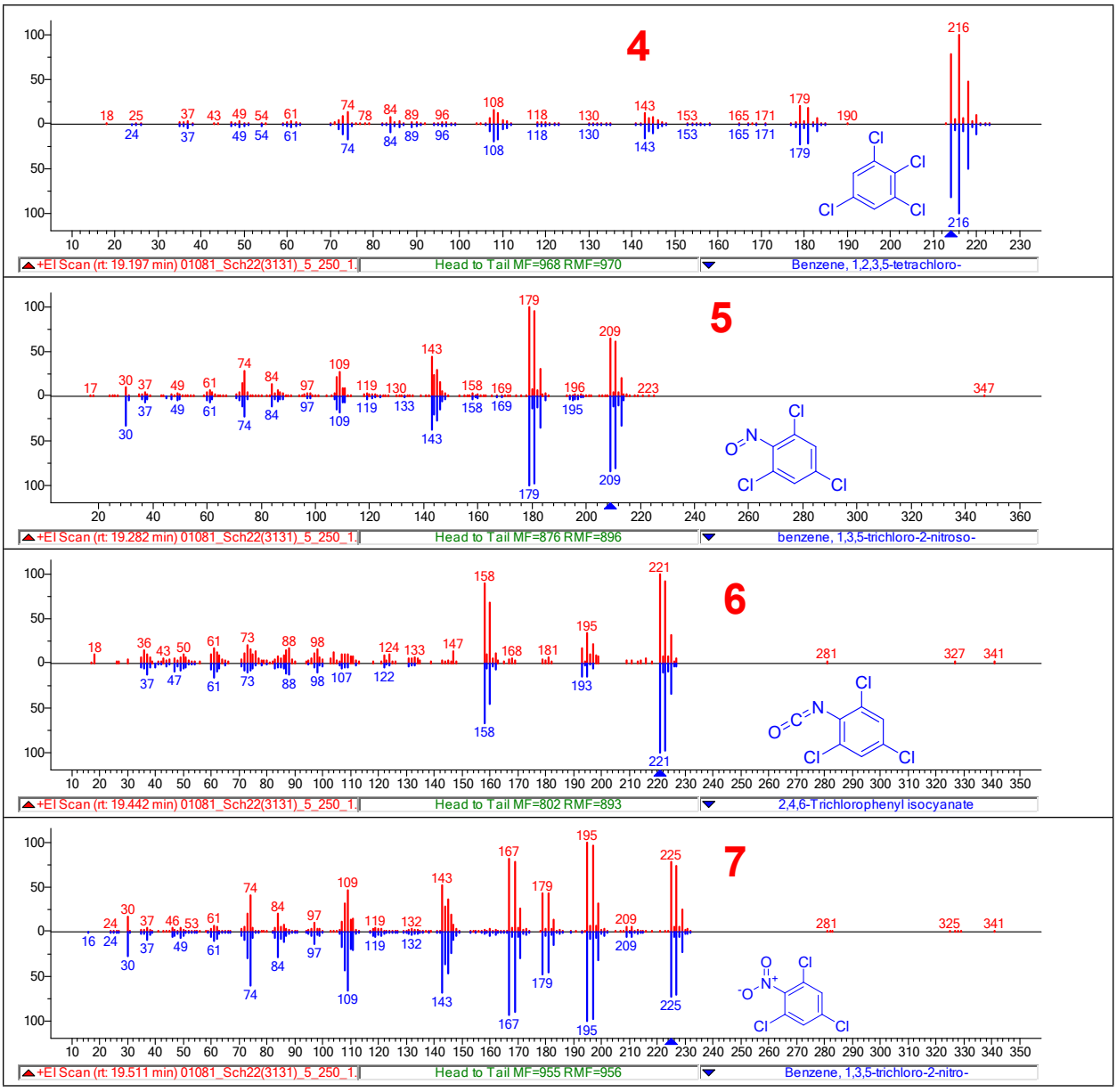
Direct mode – mass spectrometry of evolved gases along with the corresponding TGA signal under linear heating conditions.



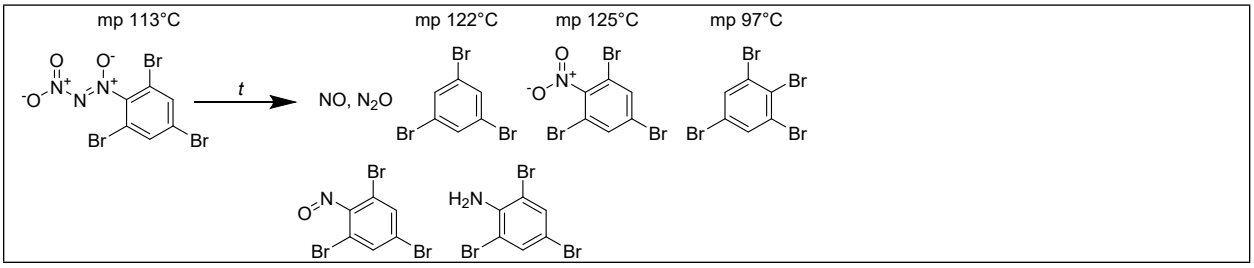
GC/MS mode – at the point of maximal weight loss rate the gases are extracted and passed through CG and MS. The mass spectra of the separated gases are shown below (red bars) along with their assignments in the NIST mass spectra database.

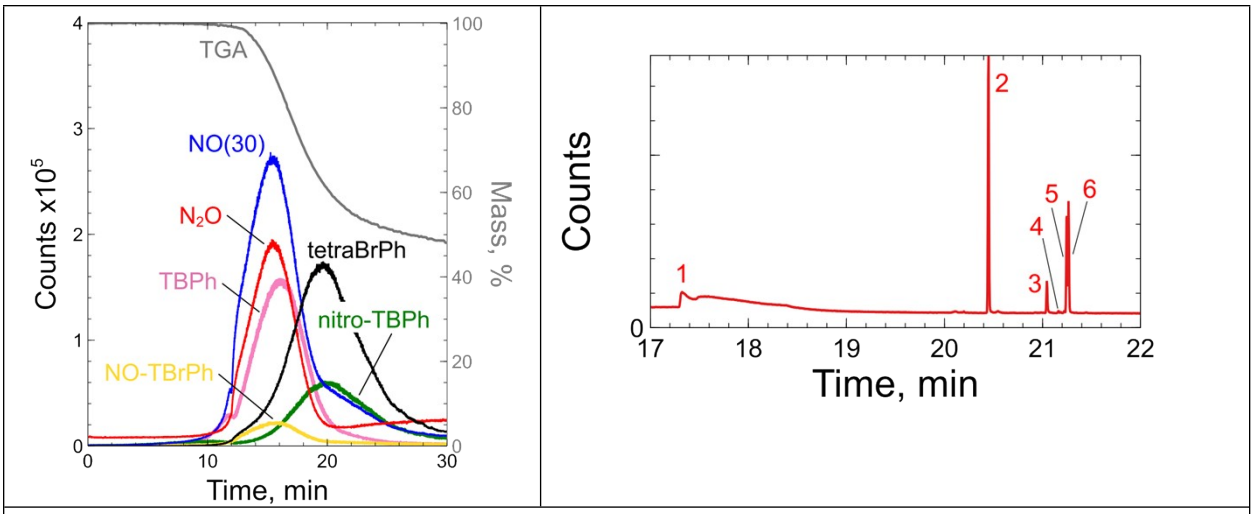


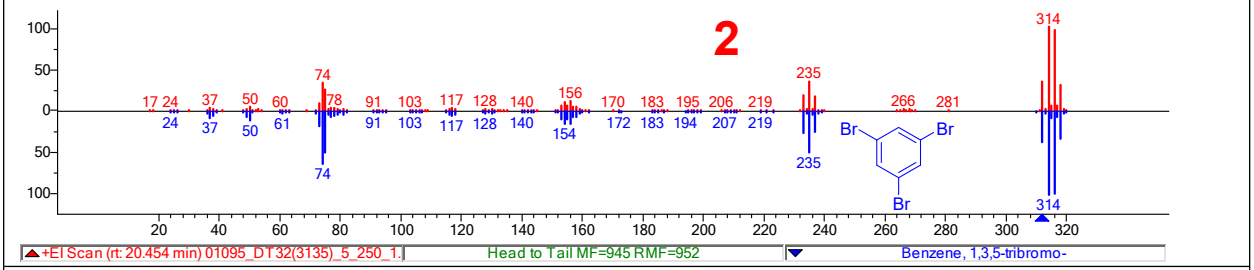



4
+EI Scan (rt: 19.197 min) 01081_Sch22(3131)_5_250_1
Head to Tail MF=968 RMF=970
Benzene, 1,2,3,5-tetrachloro-
5
+EI Scan (rt: 19.282 min) 01081_Sch22(3131)_5_250_1
Head to Tail MF=876 RMF=896
benzene, 1,3,5-trichloro-2-nitroso-
6
+EI Scan (rt: 19.442 min) 01081_Sch22(3131)_5_250_1
Head to Tail MF=802 RMF=893
2,4,6-Trichlorophenyl isocyanate
7
+EI Scan (rt: 19.511 min) 01081_Sch22(3131)_5_250_1
Head to Tail MF=955 RMF=956
Benzene, 1,3,5-trichloro-2-nitro-

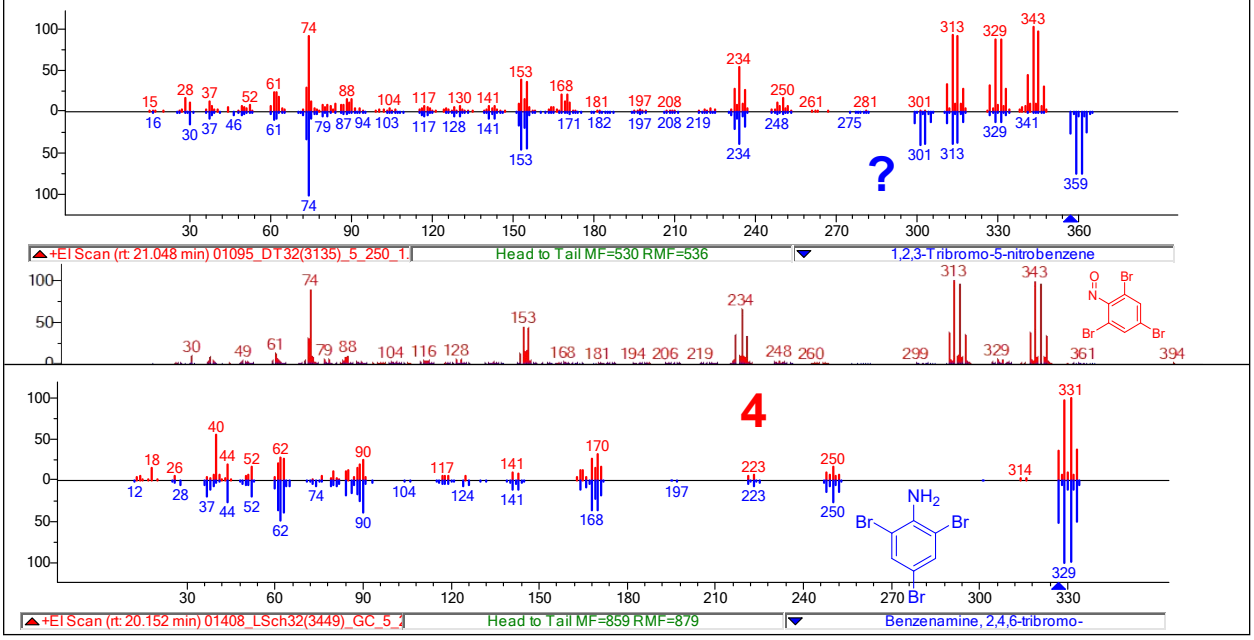
NDO3:

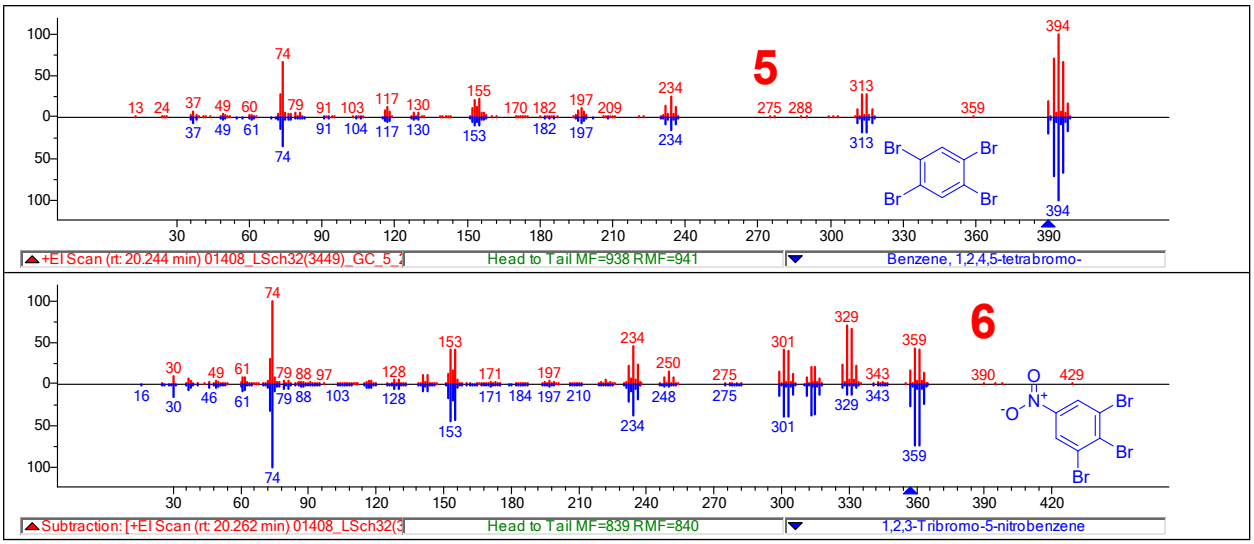

mp 113°C
t
NO, N2O
mp 122°C
mp 125°C
mp 97°C





Gas product #3 does not match any species from NIST database (best fit shown by blue bars). By structural analogy with previous compounds, we assighn this to a nitroso derivative. In order to justify this, we heated up 1-nitroso-2,4,6-tribromobenzene separately. Its mass spectrum coincides with the unidentified product (the experimental spectrum for a nitroso product is given below)




5
+EI Scan (rt: 20.244 min) 01408_LSch32(3449)_GC_5_2
Head to Tail MF=938 RMF=941
Benzene, 1,2,4,5-tetrabromo-
6
Subtraction: [+EI Scan (rt: 20.262 min) 01408_LSch32(3
Head to Tail MF=839 RMF=840
1,2,3-Tribromo-5-nitrobenzene

4. PCM estimations of the solvation free energies for various decomposition channels of NDO1

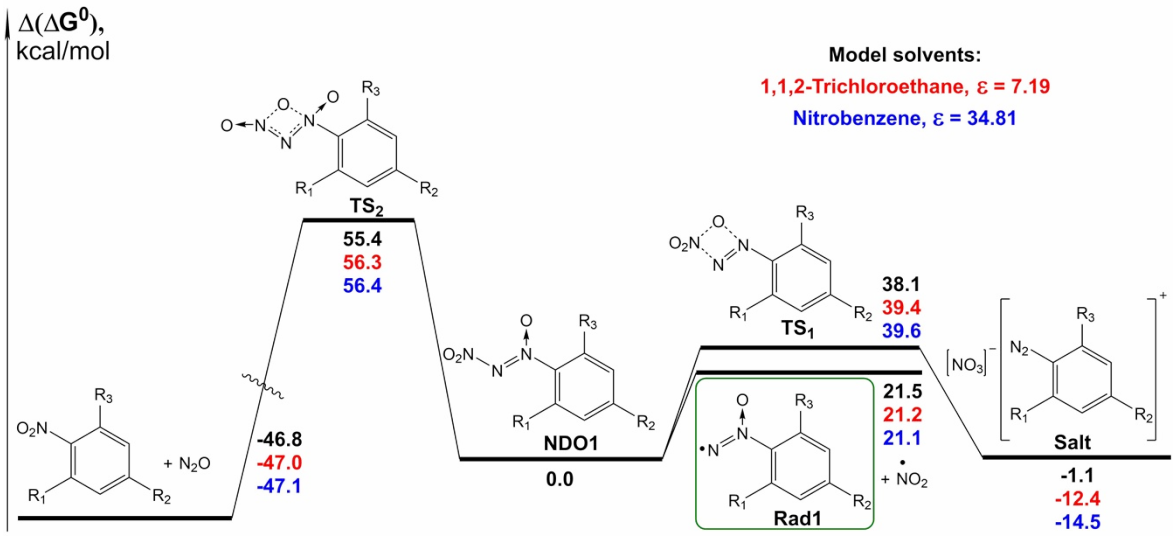


Figure S1. The stationary points on the PES for the decomposition channels of **NDO1** at 298 K in two model solvents with the dielectric constants of ε = 7.2 and 34.8 (cf. Figure 7 in the manuscript). All solvation Gibbs free energy values are calculated at the M06-2X/6-311++G(2df,p) level of theory and are given in kcal mol^{-1}.

5. Raw computational data: optimized geometries, electronic energies, and thermal corrections to thermodynamic potentials of all compounds under study

M06-2X/6-311++G(2df,p) geometries, zero-point vibrational energies (unscaled) and thermal corrections to thermodynamic potentials, M06-2X/6-311++G(2df,p) and CCSD(T)-F12/vdz-f12 electronic energies. All values are in Hartrees.

NDO1

Zero-point correction= 0.099338 (Hartree/Particle)
Thermal correction to Energy= 0.111226
Thermal correction to Enthalpy= 0.112170
Thermal correction to Gibbs Free Energy= 0.058861
Electronic energy:
M06-2X = -1540.5154519
CCSD(T)-F12 = -1538.84020983

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.549680	-1.476181	0.124597
2	6	0	1.923808	-1.608338	0.048931
3	6	0	2.703276	-0.464179	-0.035696
4	6	0	2.136865	0.800424	-0.051187
5	6	0	0.759901	0.933081	0.032693
6	6	0	-0.015797	-0.214609	0.125936
7	1	0	-0.094109	-2.343777	0.187202
8	1	0	2.388595	-2.584198	0.055582
9	1	0	2.757192	1.682330	-0.134476
10	7	0	-1.465314	-0.108460	0.264994
11	7	0	-2.106542	-0.779037	-0.595366
12	8	0	-1.920183	0.569464	1.173556
13	7	0	-3.529859	-0.664412	-0.298567
14	8	0	-4.105910	0.199628	-0.886069
15	8	0	-3.960607	-1.495836	0.444446
16	17	0	4.420694	-0.612208	-0.133168
17	17	0	0.062102	2.500548	-0.045235

TS1 (NDO1)

Zero-point correction= 0.096705 (Hartree/Particle)
Thermal correction to Energy= 0.108408
Thermal correction to Enthalpy= 0.109352
Thermal correction to Gibbs Free Energy= 0.056824

Electronic energy:
M06-2X = -1540.4456737
CCSD(T)-F12 = -1538.77740294

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.761486	-1.582917	-0.138930
2	6	0	-2.142680	-1.555775	-0.064607
3	6	0	-2.786411	-0.330643	0.026708
4	6	0	-2.080463	0.861191	0.040419
5	6	0	-0.696525	0.828593	-0.028438
6	6	0	-0.053827	-0.396916	-0.110833
7	1	0	-0.223028	-2.518366	-0.220916
8	1	0	-2.717743	-2.471143	-0.079506
9	1	0	-2.597030	1.809257	0.099325
10	7	0	1.400482	-0.458913	-0.212142
11	7	0	2.022169	-0.824959	-1.163496
12	8	0	2.011306	-0.074791	0.912332
13	7	0	3.620116	-0.370857	0.125360
14	8	0	4.038788	-1.385503	0.517864
15	8	0	4.047937	0.650968	-0.235076
16	17	0	0.193974	2.299349	-0.054771
17	17	0	-4.512649	-0.281891	0.116311

Salt (NDO1)

Zero-point correction= 0.096902 (Hartree/Particle)
Thermal correction to Energy= 0.109996
Thermal correction to Enthalpy= 0.110940
Thermal correction to Gibbs Free Energy= 0.053503
Electronic energy:
M06-2X = -1540.5191809
CCSD(T)-F12 = -1538.83394961

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.070521	1.138051	-0.053685
2	6	0	2.325938	0.586956	-0.218159
3	6	0	2.510029	-0.764845	0.043244
4	6	0	1.466944	-1.582118	0.464114
5	6	0	0.204702	-1.050057	0.620366
6	6	0	0.026191	0.303649	0.359874
7	1	0	3.150174	1.206112	-0.544080
8	1	0	1.644566	-2.631546	0.652617

9	1	0	-0.651469	-1.648342	0.898928
10	7	0	-1.219220	0.901247	0.546589
11	7	0	-2.088809	1.541827	0.724351
12	8	0	-2.304831	-1.141359	-0.287705
13	7	0	-3.559611	-0.946604	-0.276795
14	8	0	-3.968834	0.145357	0.164872
15	8	0	-4.315904	-1.800771	-0.682623
16	17	0	0.807119	2.803611	-0.354892
17	17	0	4.076458	-1.439915	-0.163776

TS2 (NDO1)

Zero-point correction= 0.096604 (Hartree/Particle)
Thermal correction to Energy= 0.107996
Thermal correction to Enthalpy= 0.108940
Thermal correction to Gibbs Free Energy= 0.057587
Electronic energy:
M06-2X = -1540.4184257
CCSD(T)-F12 = -1538.75063772

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.513548	0.982346	0.000263
2	6	0	-1.867020	0.802727	0.229974
3	6	0	-2.437693	-0.442020	0.009886
4	6	0	-1.682347	-1.518255	-0.426446
5	6	0	-0.326454	-1.343969	-0.646577
6	6	0	0.238830	-0.100295	-0.440318
7	1	0	-2.467411	1.631160	0.580275
8	1	0	-2.148339	-2.480322	-0.588233
9	1	0	0.295695	-2.160891	-0.984004
10	7	0	1.662755	0.083218	-0.739296
11	7	0	2.334563	0.221912	0.981799
12	8	0	1.994404	0.923117	-1.519915
13	7	0	2.829524	-0.849586	0.757708
14	8	0	3.483276	-1.707942	1.237014
15	8	0	2.396273	-1.121967	-0.773748
16	17	0	-4.128811	-0.647860	0.293093
17	17	0	0.191749	2.517999	0.300024

TS2_Prod (NDO1)

Zero-point correction= 0.084772 (Hartree/Particle)
Thermal correction to Energy= 0.093920
Thermal correction to Enthalpy= 0.094864

Thermal correction to Gibbs Free Energy= 0.048715
Electronic energy:
M06-2X = -1355.9128749
CCSD(T)-F12 = -1355.9128749

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.320928	0.742887	-0.026820
2	6	0	1.057344	0.910080	-0.031114
3	6	0	1.886078	-0.197125	0.020308
4	6	0	1.371343	-1.485034	0.054509
5	6	0	0.000898	-1.651479	0.040350
6	6	0	-0.836621	-0.548159	0.017494
7	1	0	1.473141	1.906818	-0.082274
8	1	0	2.035734	-2.337134	0.087418
9	17	0	3.597342	0.037670	0.030337
10	1	0	-0.443446	-2.637543	0.051510
11	17	0	-1.297075	2.153222	-0.147293
12	7	0	-2.282575	-0.822146	0.049937
13	8	0	-2.658183	-1.812812	-0.536745
14	8	0	-2.984395	-0.068352	0.678456

Product N_2O

Zero-point correction= 0.011603 (Hartree/Particle)
Thermal correction to Energy= 0.014235
Thermal correction to Enthalpy= 0.015180
Thermal correction to Gibbs Free Energy= -0.009662
Electronic energy:
M06-2X = -184.6581411
CCSD(T)-F12 = -184.45477081

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.000000	0.000000	-1.186130
2	7	0	0.000000	0.000000	-0.075540
3	8	0	0.000000	0.000000	1.103961

Rad1 (NDO1)

Zero-point correction= 0.083339 (Hartree/Particle)
Thermal correction to Energy= 0.092705

Thermal correction to Enthalpy= 0.093650
Thermal correction to Gibbs Free Energy= 0.046528
Electronic energy:
M06-2X = -1335.387392
CCSD(T)-F12 = -1333.92346867

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.023169	1.683326	0.016427
2	6	0	1.391288	1.474102	0.032085
3	6	0	1.870182	0.172968	0.014251
4	6	0	1.014745	-0.917916	-0.023705
5	6	0	-0.353837	-0.704926	-0.036515
6	6	0	-0.831392	0.597621	-0.007936
7	1	0	-0.389494	2.683844	0.030175
8	1	0	2.080399	2.306522	0.058332
9	1	0	1.405222	-1.925939	-0.049120
10	7	0	-2.275707	0.840574	0.021405
11	7	0	-2.731025	1.361494	-1.005951
12	8	0	-2.906802	0.525401	1.041671
13	17	0	3.575921	-0.105171	0.033177
14	17	0	-1.427657	-2.042662	-0.118387

Radical NO_2

Zero-point correction= 0.009193 (Hartree/Particle)
Thermal correction to Energy= 0.012115
Thermal correction to Enthalpy= 0.013059
Thermal correction to Gibbs Free Energy= -0.014770
Electronic energy:
M06-2X = -205.0652725
CCSD(T)-F12 = -204.85534431

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.000014	0.313930	0.000006
2	8	0	-1.090096	-0.137347	0.000020
3	8	0	1.090108	-0.137342	-0.000025

TS_Rad1–N_2O (NDO1)

Zero-point correction= 0.080251 (Hartree/Particle)
Thermal correction to Energy= 0.089880

Thermal correction to Enthalpy= 0.090824
Thermal correction to Gibbs Free Energy= 0.042681
Electronic energy:
M06-2X = -1335.3536194
CCSD(T)-F12 = -1333.89074590

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.258987	0.811742	0.025766
2	6	0	-1.129465	0.915080	0.033209
3	6	0	-1.898322	-0.236158	-0.018591
4	6	0	-1.323593	-1.497474	-0.066117
5	6	0	0.061697	-1.607258	-0.062734
6	6	0	0.793963	-0.452381	-0.018938
7	1	0	-1.595626	1.890180	0.083840
8	1	0	-1.948551	-2.379868	-0.098577
9	7	0	2.696313	-0.856335	-0.049474
10	7	0	3.200028	0.079615	-0.498295
11	8	0	2.787413	-1.983241	0.386431
12	17	0	-3.623615	-0.089316	-0.015193
13	1	0	0.556026	-2.570291	-0.077284
14	17	0	1.202136	2.251767	0.102216

Rad2 (NDO1)

Zero-point correction= 0.069015 (Hartree/Particle)
Thermal correction to Energy= 0.075613
Thermal correction to Enthalpy= 0.076557
Thermal correction to Gibbs Free Energy= 0.036370
Electronic energy:
M06-2X = -1150.7326011
CCSD(T)-F12 = -1149.47051157

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.227156	0.037128	0.000276
2	6	0	-0.045681	-0.695717	0.000203
3	6	0	1.158887	-0.007736	0.000111
4	6	0	1.216507	1.378699	-0.000099
5	6	0	0.028510	2.106460	0.000007
6	6	0	-1.144016	1.401755	0.000084
7	1	0	-0.067328	-1.777603	0.000047
8	1	0	2.175466	1.879513	-0.000273
9	17	0	2.637721	-0.915258	-0.000054

10	1	0	0.043550	3.189135	-0.000309
11	17	0	-2.759720	-0.767953	-0.000120

NDO2

Zero-point correction= 0.089357 (Hartree/Particle)
Thermal correction to Energy= 0.102730
Thermal correction to Enthalpy= 0.103674
Thermal correction to Gibbs Free Energy= 0.046202
Electronic energy:
M06-2X = -2000.1130467
CCSD(T)-F12 = -1997.98542929

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.024264	0.721794	1.207515
2	6	0	0.359254	2.065112	1.212367
3	6	0	0.522690	2.716834	0.000000
4	6	0	0.359254	2.065112	-1.212367
5	6	0	0.024264	0.721794	-1.207515
6	6	0	-0.136655	0.062537	0.000000
7	1	0	0.490479	2.589403	2.148397
8	1	0	0.490479	2.589403	-2.148397
9	7	0	-0.524690	-1.344723	0.000000
10	7	0	0.460263	-2.130639	0.000000
11	8	0	-1.715623	-1.615521	0.000000
12	7	0	-0.045965	-3.503938	0.000000
13	8	0	-0.188922	-3.989814	-1.080445
14	8	0	-0.188922	-3.989814	1.080445
15	17	0	0.943790	4.390062	0.000000
16	17	0	-0.188922	-0.126843	-2.685407
17	17	0	-0.188922	-0.126843	2.685407

TS1 (NDO2)

Zero-point correction= 0.086866 (Hartree/Particle)
Thermal correction to Energy= 0.099922
Thermal correction to Enthalpy= 0.100866
Thermal correction to Gibbs Free Energy= 0.044740
Electronic energy:
M06-2X = -2000.0448249
CCSD(T)-F12 = -1997.92365527

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	0.743696	1.204615	-0.056625
2	6	0	2.126331	1.211257	0.015598
3	6	0	2.797767	-0.000071	0.049714
4	6	0	2.126212	-1.211342	0.015512
5	6	0	0.743581	-1.204560	-0.056681
6	6	0	0.060027	0.000071	-0.095695
7	1	0	2.666392	2.147038	0.045058
8	1	0	2.666198	-2.147166	0.044950
9	7	0	-1.391373	0.000141	-0.206048
10	7	0	-2.014729	0.000330	-1.222467
11	8	0	-1.983415	-0.000133	0.988838
12	7	0	-3.612007	-0.000044	0.158355
13	8	0	-4.029863	1.085924	0.177898
14	8	0	-4.029714	-1.086078	0.177422
15	17	0	-0.127641	2.686067	-0.103217
16	17	0	-0.127893	-2.685936	-0.103208
17	17	0	4.523324	-0.000154	0.136831

Salt (NDO2)

Zero-point correction= 0.087106 (Hartree/Particle)
Thermal correction to Energy= 0.101452
Thermal correction to Enthalpy= 0.102396
Thermal correction to Gibbs Free Energy= 0.042399
Electronic energy:
M06-2X = -2000.1158664
CCSD(T)-F12 = -1997.97903225

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.058050	1.351083	-0.064894
2	6	0	-2.266687	0.793974	0.298475
3	6	0	-2.449489	-0.573827	0.138679
4	6	0	-1.458680	-1.403385	-0.371820
5	6	0	-0.243174	-0.859026	-0.730398
6	6	0	-0.065907	0.519687	-0.580786
7	1	0	-3.051080	1.415304	0.706290
8	1	0	-1.623780	-2.466693	-0.472078
9	7	0	1.158996	1.069900	-0.909673
10	7	0	2.130113	1.475601	-1.204547
11	8	0	1.708490	-0.112929	1.206911
12	7	0	2.911746	-0.485329	1.077955
13	8	0	3.550293	-0.058507	0.091293
14	8	0	3.412472	-1.242696	1.882578
15	17	0	-3.955175	-1.264663	0.591530

16	17	0	1.020250	-1.820737	-1.337578
17	17	0	-0.762090	3.024942	0.124747

TS2 (NDO2)

Zero-point correction= 0.086596 (Hartree/Particle)
Thermal correction to Energy= 0.099275
Thermal correction to Enthalpy= 0.100219
Thermal correction to Gibbs Free Energy= 0.045708
Electronic energy:
M06-2X = -2000.0070142
CCSD(T)-F12 = -1997.88663623

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.540581	1.217878	-0.200734
2	6	0	-1.889628	1.161501	0.097030
3	6	0	-2.501353	-0.074409	0.219088
4	6	0	-1.799508	-1.246230	0.015680
5	6	0	-0.444619	-1.194688	-0.283390
6	6	0	0.194923	0.040246	-0.347551
7	1	0	-2.450176	2.076738	0.225095
8	1	0	-2.295376	-2.205113	0.068898
9	7	0	1.631411	0.160624	-0.653926
10	7	0	2.188842	1.021273	0.927003
11	8	0	1.948171	0.656515	-1.691408
12	7	0	2.776947	-0.005181	1.132914
13	8	0	3.470034	-0.556271	1.913708
14	8	0	2.456789	-0.872448	-0.185283
15	17	0	-4.180842	-0.150988	0.603339
16	17	0	0.323154	-2.692338	-0.640786
17	17	0	0.178264	2.763515	-0.399777

TS2_Prod (NDO2)

Zero-point correction= 0.075005 (Hartree/Particle)
Thermal correction to Energy= 0.085625
Thermal correction to Enthalpy= 0.086569
Thermal correction to Gibbs Free Energy= 0.036305
Electronic energy:
M06-2X = -1815.509303
CCSD(T)-F12 = -1813.58423775

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	0.047457	-1.204768	-0.006199
2	6	0	-1.337396	-1.211147	-0.008074
3	6	0	-2.009765	-0.000014	0.000033
4	6	0	-1.337389	1.211137	0.008119
5	6	0	0.047444	1.204778	0.006301
6	6	0	0.728642	-0.000003	0.000027
7	1	0	-1.878425	-2.146792	-0.016872
8	1	0	-1.878448	2.146766	0.016864
9	17	0	-3.737509	0.000006	-0.000016
10	17	0	0.918526	-2.687474	-0.024709
11	17	0	0.918528	2.687470	0.024653
12	7	0	2.200785	0.000006	0.000042
13	8	0	2.739108	-0.148373	1.068052
14	8	0	2.739037	0.148379	-1.068091

Product N_2O

Zero-point correction= 0.011603 (Hartree/Particle)
Thermal correction to Energy= 0.014235
Thermal correction to Enthalpy= 0.015180
Thermal correction to Gibbs Free Energy= -0.009662
Electronic energy:
M06-2X = -184.6581411
CCSD(T)-F12 = -184.45477081

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.000000	0.000000	-1.186130
2	7	0	0.000000	0.000000	-0.075540
3	8	0	0.000000	0.000000	1.103961

Rad1 (NDO2)

Zero-point correction= 0.073612 (Hartree/Particle)
Thermal correction to Energy= 0.084327
Thermal correction to Enthalpy= 0.085272
Thermal correction to Gibbs Free Energy= 0.034523
Electronic energy:
M06-2X = -1794.9857992
CCSD(T)-F12 = -1793.06873207

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	-0.022418	-0.073339	1.206832
2	6	0	-0.014145	1.311031	1.212128
3	6	0	-0.010565	1.982306	0.000000
4	6	0	-0.014145	1.311031	-1.212128
5	6	0	-0.022418	-0.073339	-1.206832
6	6	0	-0.025800	-0.757341	0.000000
7	1	0	-0.009591	1.853348	2.146990
8	1	0	-0.009591	1.853348	-2.146990
9	7	0	0.016731	-2.220167	0.000000
10	7	0	-1.096483	-2.758752	0.000000
11	8	0	1.126997	-2.770686	0.000000
12	17	0	-0.001139	3.708975	0.000000
13	17	0	-0.022418	-0.939513	-2.690476
14	17	0	-0.022418	-0.939513	2.690476

Radical NO_2

Zero-point correction= 0.009193 (Hartree/Particle)
Thermal correction to Energy= 0.012115
Thermal correction to Enthalpy= 0.013059
Thermal correction to Gibbs Free Energy= -0.014770
Electronic energy:
M06-2X = -205.0652725
CCSD(T)-F12 = -204.85534431

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.000014	0.313930	0.000006
2	8	0	-1.090096	-0.137347	0.000020
3	8	0	1.090108	-0.137342	-0.000025

TS_Rad1–N_2O (NDO2)

Zero-point correction= 0.070422 (Hartree/Particle)
Thermal correction to Energy= 0.081573
Thermal correction to Enthalpy= 0.082517
Thermal correction to Gibbs Free Energy= 0.029923
Electronic energy:
M06-2X = -1794.9528311
CCSD(T)-F12 = -1793.03676172

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.028133	1.209910	0.049186

2	6	0	1.360489	1.214872	0.004964
3	6	0	2.029081	-0.000019	-0.016310
4	6	0	1.360453	-1.214890	0.005030
5	6	0	-0.028168	-1.209888	0.049247
6	6	0	-0.671847	0.000021	0.054232
7	1	0	1.905049	2.149189	-0.011613
8	1	0	1.904986	-2.149224	-0.011500
9	7	0	-2.575383	0.000019	-0.047498
10	7	0	-2.865981	0.000426	1.070488
11	8	0	-2.860100	-0.000395	-1.217816
12	17	0	3.758305	-0.000046	-0.066581
13	17	0	-0.907672	2.691680	0.084008
14	17	0	-0.907748	-2.691631	0.084139

Rad2 (NDO2)

Zero-point correction= 0.059683 (Hartree/Particle)
Thermal correction to Energy= 0.067509
Thermal correction to Enthalpy= 0.068453
Thermal correction to Gibbs Free Energy= 0.024795
Electronic energy:
M06-2X = -1610.3333369
CCSD(T)-F12 = -1608.61723712

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.209267	-0.703340	0.000075
2	6	0	-1.212491	0.687071	-0.000053
3	6	0	0.006706	1.348536	-0.000103
4	6	0	1.219534	0.674451	-0.000057
5	6	0	1.201963	-0.715540	-0.000295
6	6	0	-0.007032	-1.352263	-0.000143
7	1	0	-2.143798	1.237137	0.000117
8	1	0	2.156323	1.215056	-0.000018
9	17	0	0.015768	3.081230	0.000056
10	17	0	-2.693288	-1.588502	0.000038
11	17	0	2.676990	-1.615415	0.000104

NDO3

Zero-point correction= 0.087916 (Hartree/Particle)
Thermal correction to Energy= 0.101954
Thermal correction to Enthalpy= 0.102898
Thermal correction to Gibbs Free Energy= 0.042197
Electronic energy:

M06-2X = -8342.0141806
CCSD(T)-F12 = -1865.85354413

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.105637	-0.307524	1.207990
2	6	0	0.110611	-1.692695	1.212721
3	6	0	0.113005	-2.363835	0.000000
4	6	0	0.110611	-1.692695	-1.212721
5	6	0	0.105637	-0.307524	-1.207990
6	6	0	0.099267	0.370042	0.000000
7	1	0	0.113400	-2.234378	2.147846
8	1	0	0.113400	-2.234378	-2.147846
9	7	0	0.131978	1.830482	0.000000
10	7	0	-1.014257	2.352875	0.000000
11	8	0	1.220745	2.383513	0.000000
12	7	0	-0.854127	3.807139	0.000000
13	8	0	-0.831852	4.313082	-1.080667
14	8	0	-0.831852	4.313082	1.080667
15	35	0	0.105637	0.643985	-2.824650
16	35	0	0.105637	0.643985	2.824650
17	35	0	0.120243	-4.247305	0.000000

TS1 (NDO3)

Zero-point correction= 0.085251 (Hartree/Particle)
Thermal correction to Energy= 0.099010
Thermal correction to Enthalpy= 0.099954
Thermal correction to Gibbs Free Energy= 0.040670
Electronic energy:
M06-2X = -8341.9456766
CCSD(T)-F12 = -1865.79177494

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.333153	1.204979	-0.055701
2	6	0	1.717075	1.211793	0.000088
3	6	0	2.388765	0.000180	0.025941
4	6	0	1.717040	-1.211418	0.001225
5	6	0	0.333098	-1.204875	-0.055789
6	6	0	-0.350510	0.000052	-0.087762
7	1	0	2.257364	2.147492	0.024507
8	1	0	2.257376	-2.147071	0.026469
9	7	0	-1.804533	0.001073	-0.181589
10	7	0	-2.438139	0.003866	-1.191376

11	8	0	-2.383578	-0.001436	1.019423
12	7	0	-4.019683	-0.000673	0.207518
13	8	0	-4.438073	1.084921	0.234426
14	8	0	-4.435797	-1.087304	0.227832
15	35	0	-0.614319	2.825380	-0.088261
16	35	0	-0.613484	-2.825730	-0.088295
17	35	0	4.272077	0.000236	0.099005

Salt (NDO3)

Zero-point correction= 0.085108 (Hartree/Particle)
Thermal correction to Energy= 0.100298
Thermal correction to Enthalpy= 0.101242
Thermal correction to Gibbs Free Energy= 0.037548
Electronic energy:
M06-2X = -8342.0161313
CCSD(T)-F12 = -1865.84759377

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.124039	0.943529	-0.579016
2	6	0	-1.148061	1.393241	-0.286691
3	6	0	-2.134911	0.473072	0.042466
4	6	0	-1.893404	-0.894017	0.080244
5	6	0	-0.628913	-1.358103	-0.222126
6	6	0	0.359447	-0.433637	-0.553006
7	1	0	-1.359878	2.452981	-0.296532
8	1	0	-2.677223	-1.588231	0.347233
9	7	0	1.636057	-0.896368	-0.829875
10	7	0	2.641699	-1.237620	-1.087387
11	8	0	1.943067	-0.009911	1.464172
12	7	0	3.141535	0.395370	1.510246
13	8	0	3.899433	0.079458	0.567914
14	8	0	3.525020	1.081359	2.434817
15	35	0	-3.853718	1.095226	0.461439
16	35	0	-0.244238	-3.185644	-0.168419
17	35	0	1.500605	2.129098	-0.973821

TS2 (NDO3)

Zero-point correction= 0.084942 (Hartree/Particle)
Thermal correction to Energy= 0.098363
Thermal correction to Enthalpy= 0.099308
Thermal correction to Gibbs Free Energy= 0.041485
Electronic energy:

M06-2X = -8341.9063836
CCSD(T)-F12 = -1865.75387536

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.149576	1.222198	-0.203338
2	6	0	-1.517118	1.184872	0.002423
3	6	0	-2.148745	-0.041572	0.118555
4	6	0	-1.448856	-1.225015	-0.011679
5	6	0	-0.075166	-1.192865	-0.217766
6	6	0	0.580358	0.033834	-0.259453
7	1	0	-2.077313	2.106841	0.064971
8	1	0	-1.959349	-2.176699	0.028450
9	7	0	2.042548	0.124214	-0.444370
10	7	0	2.474460	1.040094	1.148403
11	8	0	2.457604	0.572912	-1.468021
12	7	0	3.028627	0.015630	1.440595
13	8	0	3.644888	-0.512855	2.297884
14	8	0	2.807245	-0.898372	0.136222
15	35	0	0.748200	-2.853716	-0.543311
16	35	0	0.642435	2.908832	-0.432529
17	35	0	-4.005093	-0.094313	0.421355

TS2_Prod (NDO3)

Zero-point correction= 0.073314 (Hartree/Particle)
Thermal correction to Energy= 0.084662
Thermal correction to Enthalpy= 0.085606
Thermal correction to Gibbs Free Energy= 0.031905
Electronic energy:
M06-2X = -8157.4098732
CCSD(T)-F12 = -1681.45221062

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.254613	-1.205026	0.000004
2	6	0	-1.130843	-1.211495	-0.000003
3	6	0	-1.803117	-0.000021	-0.000005
4	6	0	-1.130856	1.211479	-0.000012
5	6	0	0.254584	1.205034	-0.000013
6	6	0	0.935138	0.000005	-0.000014
7	1	0	-1.671663	-2.147210	-0.000053
8	1	0	-1.671712	2.147173	-0.000009
9	7	0	2.408867	0.000035	0.000028

10	8	0	2.946845	-0.000028	1.078468
11	8	0	2.946851	0.000075	-1.078446
12	35	0	1.201656	2.826263	0.000001
13	35	0	-3.687502	-0.000014	0.000006
14	35	0	1.201692	-2.826262	-0.000009

Product N_2O

Zero-point correction= 0.011603 (Hartree/Particle)
Thermal correction to Energy= 0.014235
Thermal correction to Enthalpy= 0.015180
Thermal correction to Gibbs Free Energy= -0.009662
Electronic energy:
M06-2X = -184.6581411
CCSD(T)-F12 = -184.45477081

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.000000	0.000000	-1.186130
2	7	0	0.000000	0.000000	-0.075540
3	8	0	0.000000	0.000000	1.103961

Rad1 (NDO3)

Zero-point correction= 0.071914 (Hartree/Particle)
Thermal correction to Energy= 0.083335
Thermal correction to Enthalpy= 0.084279
Thermal correction to Gibbs Free Energy= 0.030192
Electronic energy:
M06-2X = -8136.8863013
CCSD(T)-F12 = -1660.93668627

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.021908	0.274984	1.206578
2	6	0	0.003985	-1.109722	1.212847
3	6	0	-0.003625	-1.780296	0.000000
4	6	0	0.003985	-1.109722	-1.212847
5	6	0	0.021908	0.274984	-1.206578
6	6	0	0.031724	0.959812	0.000000
7	1	0	-0.005182	-1.651757	2.147564
8	1	0	-0.005182	-1.651757	-2.147564
9	7	0	-0.000435	2.424172	0.000000

10	7	0	1.115805	2.955962	0.000000
11	8	0	-1.107338	2.981235	0.000000
12	35	0	-0.027182	-3.663735	0.000000
13	35	0	0.021908	1.213760	-2.831480
14	35	0	0.021908	1.213760	2.831480

Radical NO_2

Zero-point correction= 0.009193 (Hartree/Particle)
Thermal correction to Energy= 0.012115
Thermal correction to Enthalpy= 0.013059
Thermal correction to Gibbs Free Energy= -0.014770
Electronic energy:
M06-2X = -205.0652725
CCSD(T)-F12 = -204.85534431

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.000014	0.313930	0.000006
2	8	0	-1.090096	-0.137347	0.000020
3	8	0	1.090108	-0.137342	-0.000025

TS_Rad1–N_2O (NDO3)

Zero-point correction= 0.068761 (Hartree/Particle)
Thermal correction to Energy= 0.080595
Thermal correction to Enthalpy= 0.081539
Thermal correction to Gibbs Free Energy= 0.025796
Electronic energy:
M06-2X = -8136.8541842
CCSD(T)-F12 = -1660.90550415

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.240591	1.209632	-0.040743
2	6	0	-1.149151	1.215426	-0.010426
3	6	0	-1.817566	-0.000047	0.002781
4	6	0	-1.149078	-1.215482	-0.010429
5	6	0	0.240661	-1.209602	-0.040749
6	6	0	0.881369	0.000034	-0.042261
7	1	0	-1.693108	2.150040	0.002335
8	1	0	-1.692981	-2.150127	0.002331
9	7	0	2.780273	0.000020	0.083492
10	7	0	3.093127	0.000188	-1.028724

11	8	0	3.046617	-0.000167	1.259163
12	35	0	1.200612	2.827681	-0.056705
13	35	0	-3.703737	-0.000101	0.038861
14	35	0	1.200793	-2.827574	-0.056739

Rad2 (NDO3)

Zero-point correction= 0.058001 (Hartree/Particle)
Thermal correction to Energy= 0.066516
Thermal correction to Enthalpy= 0.067460
Thermal correction to Gibbs Free Energy= 0.020159
Electronic energy:
M06-2X = -7952.2350573
CCSD(T)-F12 = -1476.48633813

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.685766	-1.203796	-0.000038
2	6	0	0.704818	-1.217949	-0.000007
3	6	0	1.372241	-0.000807	-0.000004
4	6	0	0.706205	1.217078	0.000016
5	6	0	-0.684399	1.204564	0.000081
6	6	0	-1.324914	0.000751	0.000026
7	1	0	1.249275	-2.152410	-0.000026
8	1	0	1.251746	2.150912	0.000012
9	35	0	3.261356	-0.001898	-0.000033
10	35	0	-1.675633	-2.808634	-0.000020
11	35	0	-1.672298	2.810601	0.000041

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