Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Photolytic Insertion of Carbon Monoxide into Nitrosyl Chloride: Formation of Nitrosoformyl Chloride

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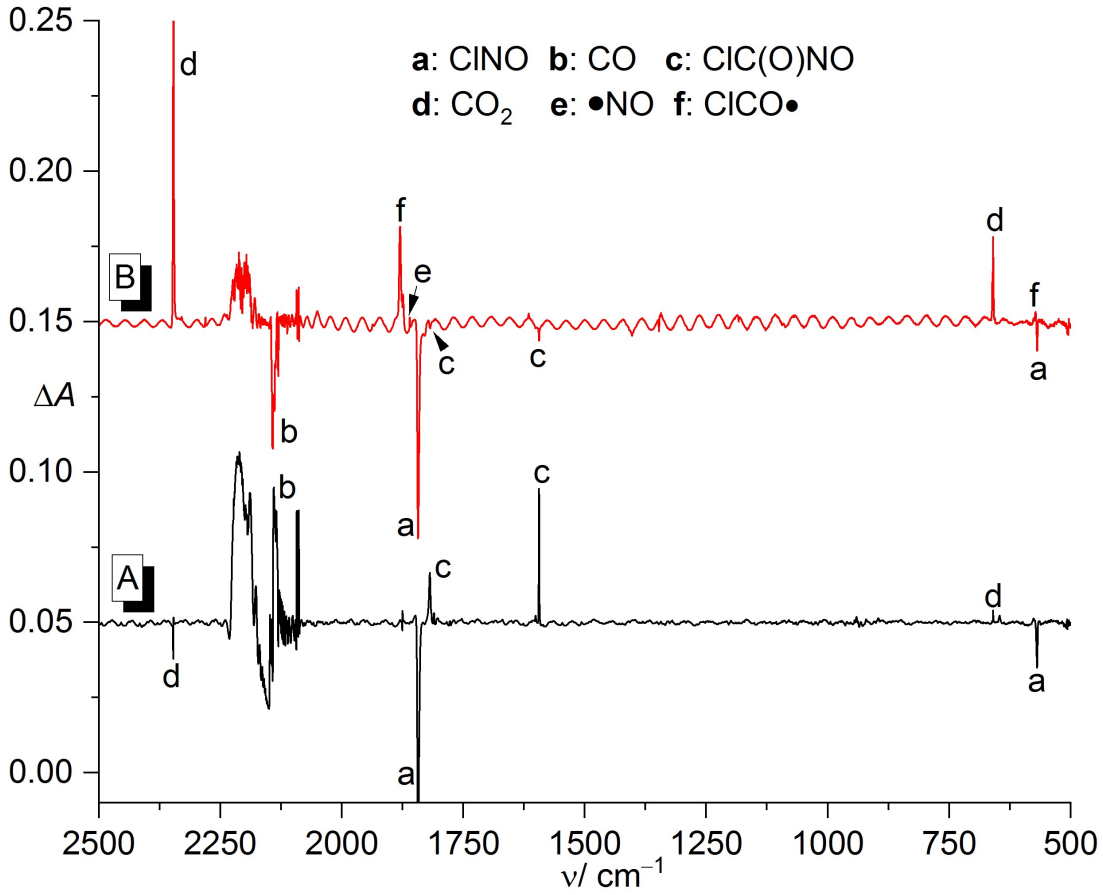

Fig. S1 (A) IR difference spectrum reflecting the changes of the ClNO/CO (1 : 1000) mixture upon irradiation upon 266 nm (5 min) at 20 K. (B) IR difference spectrum reflecting the change of the same matrix upon subsequent irradiation at 193 nm (10 min).

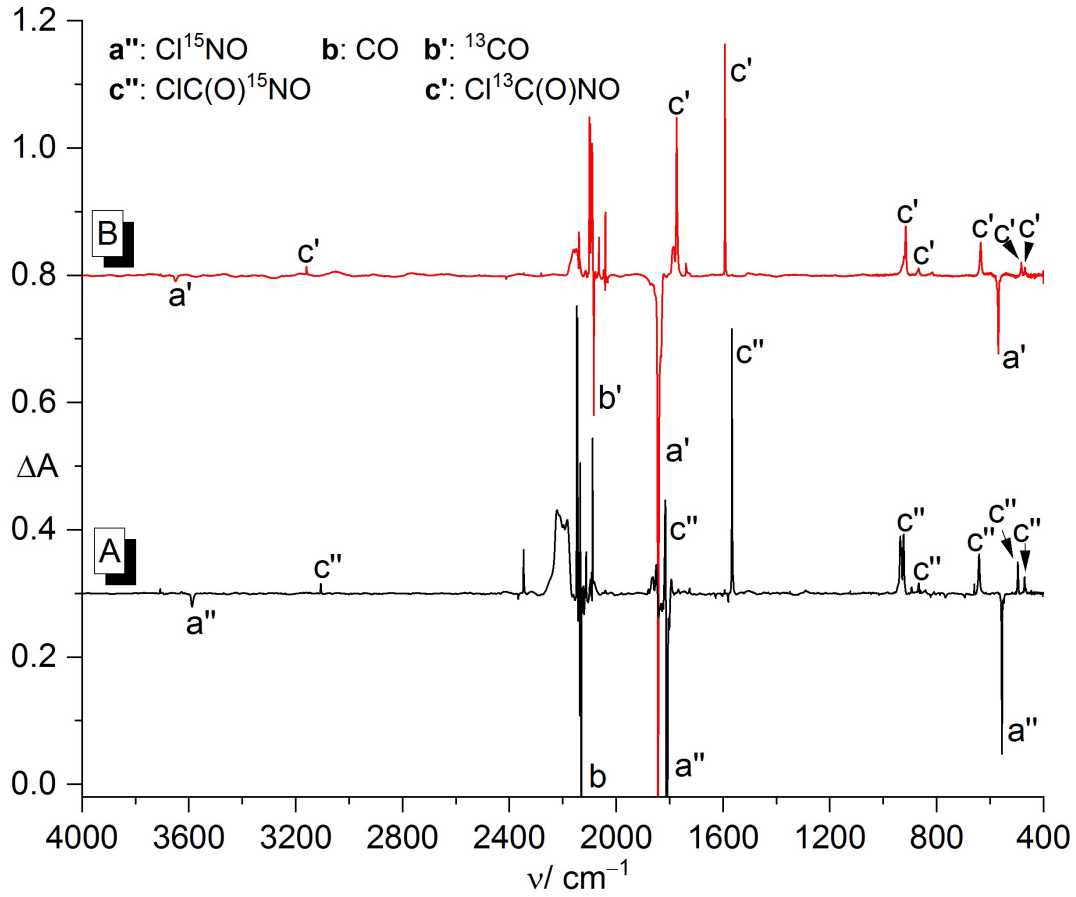

Fig. S2 (A) IR difference spectrum reflecting the changes of the $Cl^{15}NO$/CO (1 : 1000) mixture upon irradiation at 365 nm (50 min) at 20 K. (B) IR difference spectrum (4000–400 cm^{-1}) reflecting the changes of the ClNO/^{13}CO (1 : 1000) mixture upon irradiation at 365 nm (50 min) at 20 K.

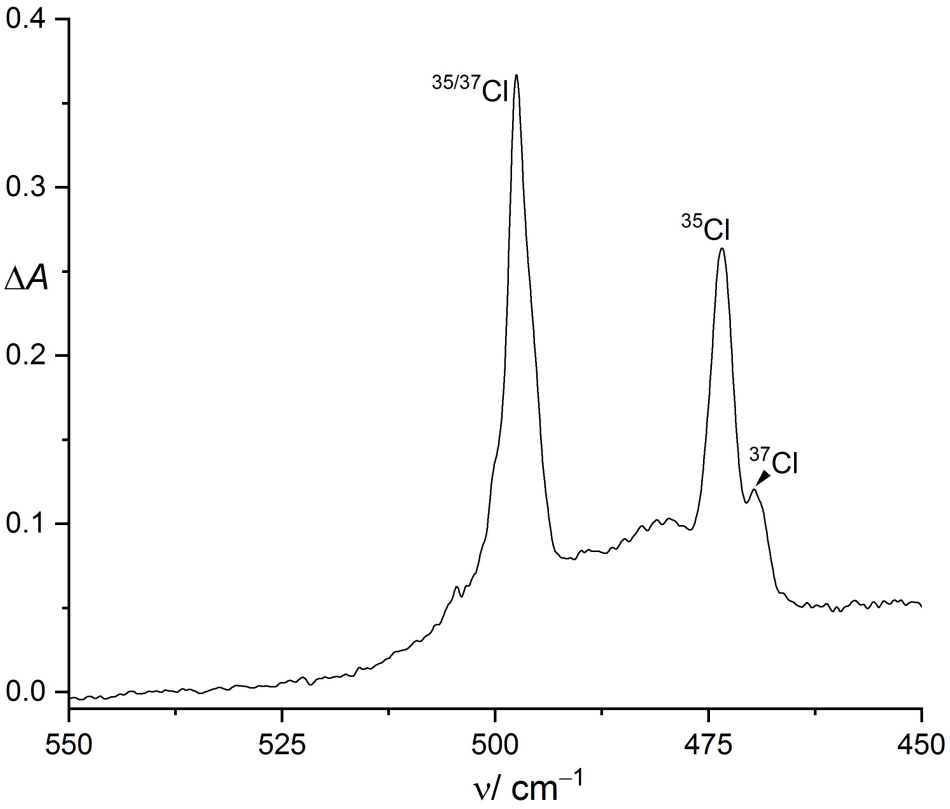

Fig. S3 Part of the IR spectrum for the two IR bands of ClC(O)NO in the range of 550–450 cm^{-1}. The most prominent bands of $^{35/37}Cl$ isotopomer is indicated.

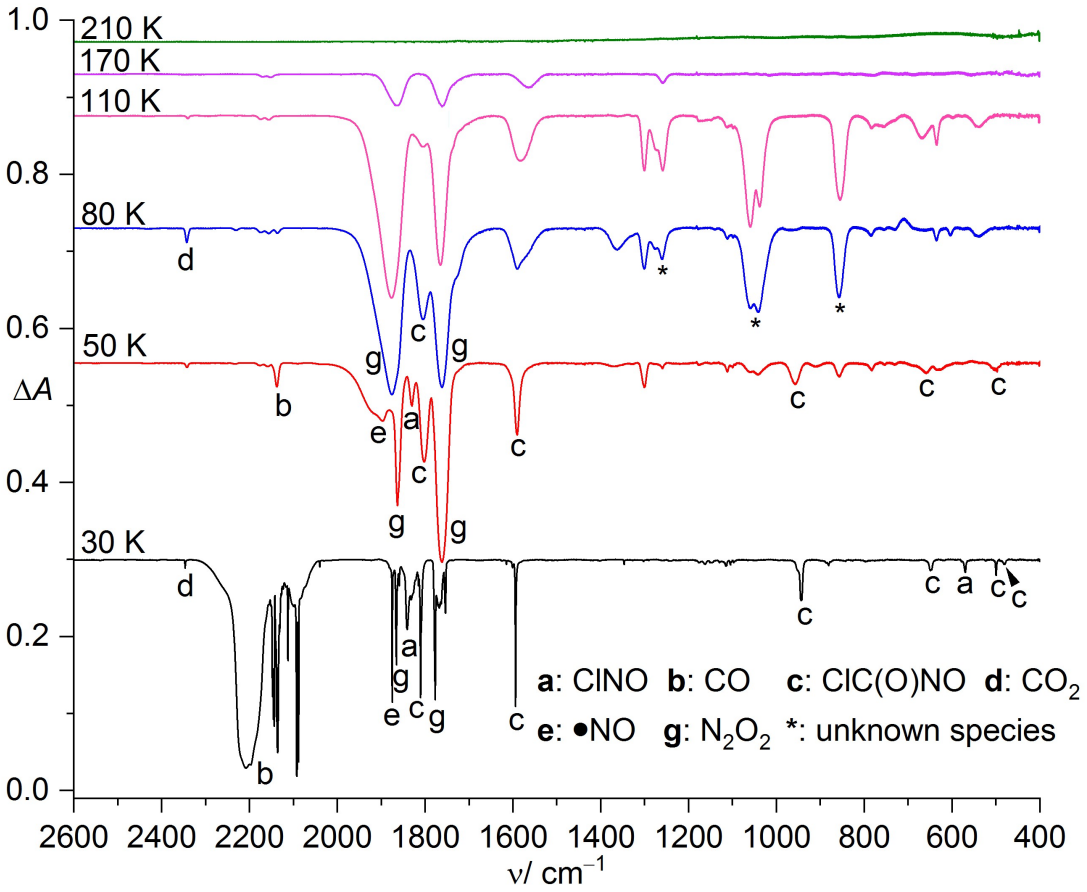

Fig. S4 IR spectra of the photolysis products of ClNO in solid CO at different temperatures.

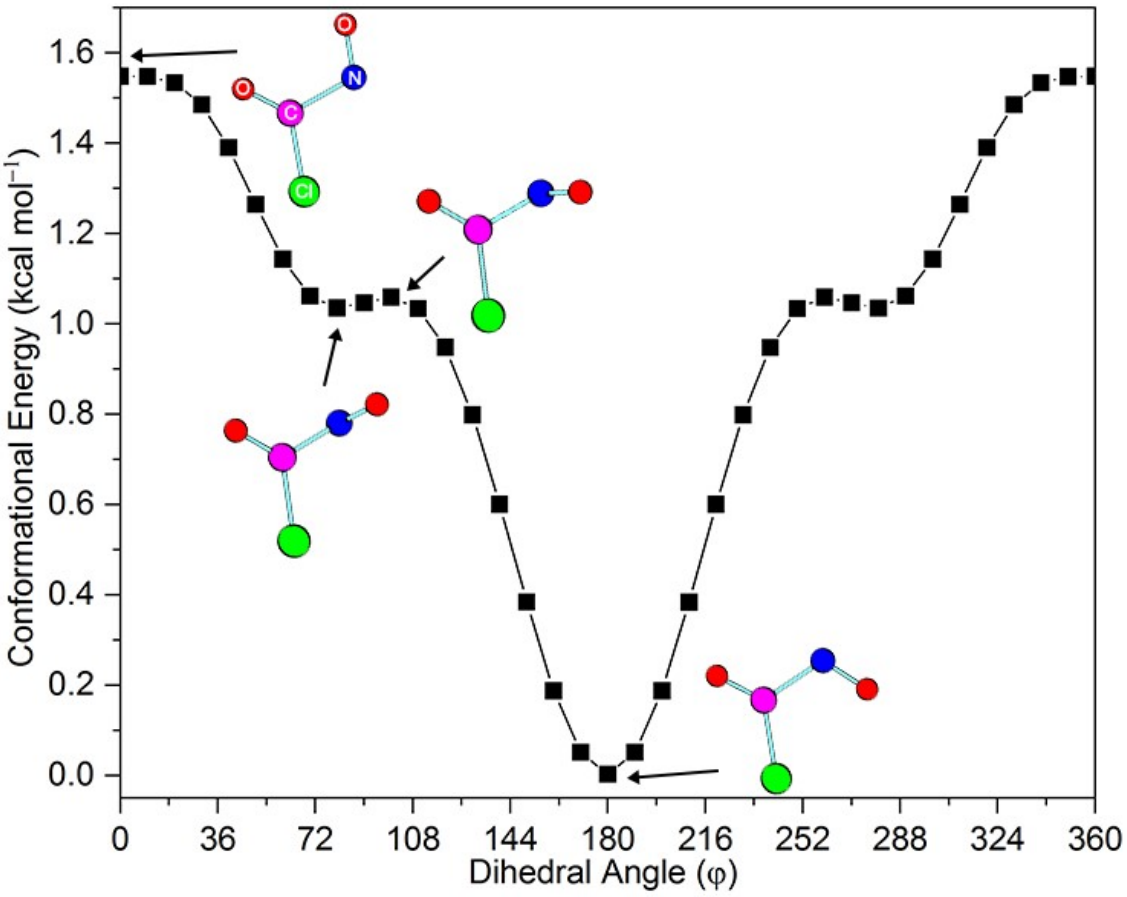

Fig. S5 Relaxed potential energy scan graph of ClC(O)NO. The calculations were fully relaxed simulations, with geometry optimisations at each fixed dihedral at a scan rate of 10 degrees in 36 steps to cover the entire 360 degrees at the B3LYP/6-311+G(3df) level.

Table S1. B3LYP/6-311+G(3df) calculated IR frequencies (> 400 cm^{-1}) and intensities (km mol^{-1}, in parentheses) of ClC(O)NO and its isomers.

trans-ClC(O)NO		*cis*-ClC(O)NO		non-planar ClC(O)NO		ClONCO	ClC(O)ON	$ClCNO_2$	ClCNOO
normal	guess=mix	normal	guess=mix	normal	guess=mix				
1890 (328)	1889 (328)	1894 (302)	1888 (299)	1874 (350)	1874 (351)	2238 (948)	1954 (611)	1589 (298)	1730 (39)
1713 (152)	1684 (152)	1718 (207)	1679 (202)	1659 (135)	1659 (135)	1310 (39)	1858 (546)	1389 (90)	1044 (90)
909 (127)	854 (127)	891 (245)	884 (609)	850 (137)	851 (135)	854 (16)	707 (396)	956 (49)	943 (17)
633 (51)	620 (51)	699 (14)	609 (9)	825 (67)	824 (64)	701 (26)	532 (< 1)	844 (52)	689 (146)
495 (17)	498 (17)	466 (17)	470 (16)	503 (65)	504 (64)	621 (32)	404 (31)	752 (65)	584 (249)
462 (34)	444 (34)	461 (16)	467 (16)	423 (5)	423 (5)	588 (17)		563 (4)	431 (81)

Table S2. Calculated $^{35/37}$Cl isotopic shifts of *trans*-ClC(O)NO.

B3LYP[a] ν_{harm}	Obs[b] matrix	$\Delta\nu(^{35/37}Cl)$ Cal[c]	Mode[d]
1890 (328)	1818.8 (vs)	0.0	A', ν_1, ν(CO)
1713 (152)	1594.0 (vs)	0.0	A', ν_2, ν(NO)
909 (127)	940.3 (s)	0.2	A', ν_3, ν(CN)
633 (51)	646.4 (m)	0.1	A', ν_4, $\delta_{i.p.}$(CNO)
495 (17)	497.5 (m)	0.1	A", ν_5, $\delta_{o.o.p.}$(ClCO)
462 (34)	473.4 (vw)	4.9	A', ν_6, ν(CCl)
399 (14)	n.o.[e]	1.7	A', ν_7, $\delta_{i.p.}$(OCN)
233 (< 1)	n.o.	2.5	A', ν_8, $\delta_{i.p.}$(ClCN)
81 (1)	n.o.	0.1	A", ν_9, τ(OCNO)

[a]B3LYP/6-311+G(3df) calculated IR frequencies and intensities (km mol^{-1}, in parentheses). [b]Observed band positions in CO-matrix and the relative intensities (vs: very strong, s: strong, m: medium, w: weak, vw: very weak). [c]Isotopic shifts calculated at the B3LYP/6-311+G(3df) level. [d]Assignment of the vibrational modes based on the calculated vibrational displacement vectors at the B3LYP/6-311+G(3df) level. [e]The abbreviation “n.o.” denotes “not observed”.

Table S3. TD B3LYP/6-311+G(3df) calculated vertical transitions of ClC(O)NO.

trans		*cis*		non-planar	
energy (nm)	oscillator strength (*f*)	energy (nm)	oscillator strength (*f*)	energy (nm)	oscillator strength (*f*)
307	0.0050	946	0.0002	307	0.0050
254	0.0125	303	0.0001	253	0.0125
243	0.0026	260	0.0001	243	0.0025
225	0.0005	259	0.0146	225	0.0005
207	0.0955	246	0.0003	207	0.0955
204	0.0016	202	0.1565	204	0.0017
180	0.0081	180	0.0224	180	0.0080
178	0.0055	172	0.0008	178	0.0053
177	0.0020	163	0.0656	177	0.0020

Calculated atomic coordinates and energies for all optimized structures

trans-ClC(O)NO
B3LYP/6-311+G(3df)

O	1.53844100	-1.09552400	0.00000000
N	1.48150100	0.07806900	0.00000000
C	0.00000000	0.64562600	0.00000000
Cl	-1.25472400	-0.59415900	0.00000000
O	-0.16846600	1.80558200	0.00000000

Zero-point correction= 0.015312
Thermal correction to Energy= 0.020556
Thermal correction to Enthalpy= 0.021500
Thermal correction to Gibbs Free Energy= -0.014539
Sum of electronic and zero-point Energies= -703.505236
Sum of electronic and thermal Energies= -703.499992
Sum of electronic and thermal Enthalpies= -703.499048
Sum of electronic and thermal Free Energies= -703.535087

cis-ClC(O)NO
B3LYP/6-311+G(3df)

O	2.17409800	-0.36023000	0.00000000
N	1.09203100	-0.81731000	0.00000000
C	0.00000000	0.37465800	0.00000000
Cl	-1.59889900	-0.33864400	0.00000000
O	0.26803500	1.51400200	0.00000000

Zero-point correction= 0.015268
Thermal correction to Energy= 0.020589
Thermal correction to Enthalpy= 0.021534
Thermal correction to Gibbs Free Energy= -0.015659
Sum of electronic and zero-point Energies= -703.504466
Sum of electronic and thermal Energies= -703.499144
Sum of electronic and thermal Enthalpies= -703.498199
Sum of electronic and thermal Free Energies= -703.535392

non-planar ClC(O)NO
B3LYP/6-311+G(3df)

O	1.90071500	-0.68795300	-0.34539800
N	1.18563600	-0.32531100	0.53246800
C	0.01389400	0.50816900	0.06019500
Cl	-1.41810300	-0.50816000	-0.03624700
O	0.06490200	1.67131300	-0.08863400

Zero-point correction=	0.015314
Thermal correction to Energy=	0.020557
Thermal correction to Enthalpy=	0.021501
Thermal correction to Gibbs Free Energy=	-0.014530
Sum of electronic and zero-point Energies=	-703.505234
Sum of electronic and thermal Energies=	-703.499991
Sum of electronic and thermal Enthalpies=	-703.499047
Sum of electronic and thermal Free Energies=	-703.535078

ClCNOO

B3LYP/6-311+G(3df)

C	-0.44132100	0.08315200	0.43744100
Cl	-2.01120800	-0.13743500	-0.07433800
N	0.53459100	0.54222100	-0.13609100
O	1.82192200	0.50048800	-0.01802600
O	2.31511900	-0.74524600	-0.03300700

Zero-point correction=	0.013655
Thermal correction to Energy=	0.018888
Thermal correction to Enthalpy=	0.019832
Thermal correction to Gibbs Free Energy=	-0.015595
Sum of electronic and zero-point Energies=	-703.316524
Sum of electronic and thermal Energies=	-703.311291
Sum of electronic and thermal Enthalpies=	-703.310346
Sum of electronic and thermal Free Energies=	-703.345773

ClONCO

B3LYP/6-311+G(3df)

N	0.59142800	-0.69605800	-0.43220000
C	1.54746200	-0.00705600	-0.04968300
O	2.53828400	0.55826900	0.13007300
O	-0.54186700	-0.80154300	0.37446500
Cl	-1.72918200	0.40358500	-0.04193000

Zero-point correction=	0.015724
Thermal correction to Energy=	0.020838
Thermal correction to Enthalpy=	0.021783
Thermal correction to Gibbs Free Energy=	-0.014007
Sum of electronic and zero-point Energies=	-703.464772
Sum of electronic and thermal Energies=	-703.459658
Sum of electronic and thermal Enthalpies=	-703.458714
Sum of electronic and thermal Free Energies=	-703.494504

$ClCNO_2$

B3LYP/6-311+G(3df)

C	0.28385400	-0.00198000	0.85666100
Cl	1.60565600	0.00029400	-0.17405900
N	-0.93029200	0.00019200	0.06821900
O	-1.40520200	1.09449400	-0.16547800
O	-1.40570200	-1.09380200	-0.16683400

Zero-point correction= 0.015291
Thermal correction to Energy= 0.020187
Thermal correction to Enthalpy= 0.021131
Thermal correction to Gibbs Free Energy= -0.013534
Sum of electronic and zero-point Energies= -703.386346
Sum of electronic and thermal Energies= -703.381451
Sum of electronic and thermal Enthalpies= -703.380507
Sum of electronic and thermal Free Energies= -703.415172

TS1
B3LYP/6-311+G(3df)

O	-1.80724800	-0.77916600	-0.33702000
N	-1.26280900	-0.15987500	0.51840200
C	-0.00265300	0.54758700	0.05266400
Cl	1.35908100	-0.56381900	-0.01132600
O	0.02614900	1.70648100	-0.13201100

Zero-point correction= 0.015207
Thermal correction to Energy= 0.019605
Thermal correction to Enthalpy= 0.020549
Thermal correction to Gibbs Free Energy= -0.013075
Sum of electronic and zero-point Energies= -703.505305
Sum of electronic and thermal Energies= -703.500907
Sum of electronic and thermal Enthalpies= -703.499963
Sum of electronic and thermal Free Energies= -703.533587

TS2
B3LYP/6-311+G(3df)

O	-2.04314300	-0.46815600	-0.31758800
N	-1.27109400	-0.32749900	0.47847600
C	0.63487800	-0.86860600	0.02845800
Cl	0.49714700	1.33325500	-0.02859500
O	1.62275400	-1.42699400	-0.06165800

Zero-point correction= 0.013575

Thermal correction to Energy=	0.018990
Thermal correction to Enthalpy=	0.019935
Thermal correction to Gibbs Free Energy=	-0.016084
Sum of electronic and zero-point Energies=	-703.478202
Sum of electronic and thermal Energies=	-703.472787
Sum of electronic and thermal Enthalpies=	-703.471843
Sum of electronic and thermal Free Energies=	-703.507861

TS3
B3LYP/6-311+G(3df)

O	1.91348800	-0.86838400	-0.10915800
N	1.01411600	-0.12657700	0.09451900
C	-0.14881100	0.22216300	0.52055200
Cl	-1.66078600	-0.21006400	-0.09198300
O	0.83993900	1.25890300	-0.16849500

Zero-point correction=	0.014609
Thermal correction to Energy=	0.018955
Thermal correction to Enthalpy=	0.019899
Thermal correction to Gibbs Free Energy=	-0.013584
Sum of electronic and zero-point Energies=	-703.368145
Sum of electronic and thermal Energies=	-703.363799
Sum of electronic and thermal Enthalpies=	-703.362855
Sum of electronic and thermal Free Energies=	-703.396337