Semi-empirical supported, Ab Initio derived Thermodynamic properties for ClO₂ and its sub and extended species, applied in water treatment cycles

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Supplementary Information

Table S 1: Force Field Atom types defined for the PCFF+ force field parameterisation for chlorine oxide species

Symbols	Descriptors
c	- generic sp3 carbon
o	- generic sp3 oxygen in alcohol, ether, or acid group
h	- generic hydrogen
oh	- oxygen bonded to hydrogen
ho	- hydrogen bonded to oxygen
h*	- hydrogen bonded to fluorine, nitrogen, oxygen
cl	– chlorine atom
cl4	– chlorine in ClO_4^- anion
o_1r	– oxygen in ClO_4^- anion
p	– general phosphorous atom
s2	– sulphur in SO_2
o1	– oxygen in NO_2

Table S 2: Equivalence parameters

Type	NonB	Bond	Angle	Torsion	OOP	Force field reference
cl4	cl4	cl4	cl4	cl4	cl4	cvff file
o_1r	o_1r	o_1r	o_1r	o_1r	o_1r	*cvff* file
oh	oh	oh	oh	oh	oh	This work
ho	ho	ho	ho	Ho	ho	This work
h*	h*	h*	h*	h*	h*	This work

S1. Bond Increments parameters

Bond increments describe the charge formed during the bonding of two atoms. The assignment of the atomic charges of a molecule into bond increments, creates a set of general rules, based on the type of atoms in the bond [1]. I and J are the atom types of the bonded atoms. Delta IJ and Delta JI (presented as partial atomic charges measured in elementary charge unit e) refers to the change in atomic charges depending on the direction of the charge i.e., I to J or from J to I. Bond increments parameters are presented in Table S3.

Table S 3: Bond Increment parameters

I	J	Delta-IJ	Delta-JI	force field Reference
cl4	o_1r	0.3864	-0.6364	pcff file
cl	o	0.3864	-0.6364	This work
h*	o	0.4100	-0.4100	*pcff* file
cl	o_1r	0.3864	-0.6364	This work

Entries for bond increments: **cl [o]** and **cl [o_1r]** parameters were borrowed from **CVFF** for: **cl4 [o_1r]**. No other parameters have been published to support this study. Bond lengths for **cl [o]** = 1.7 Å, **cl4 [o_1r]** = 1.4 Å and **cl [o_1r]** = 1.6 Å were taken from the reference [2].

S2. Quartic bond parameters

The quartic bond-stretching potential is presented by:

$$E = K2 * (R - R0)^2 + K3 * (R - R0)^3 + K4 * (R - R0)^4$$

where:

- R is the current bond length and R0 the reference bond length in angstroms.

- K2, K3 and K4 are the coefficients for the quadratic, cubic and quartic terms in units of kcal/mol Å^{-2}, kcal/mol Å^{-3} and kcal/mol Å^{-4} respectively.

Table S4 presents the Quartic bond parameters used, and in the table I and J are the atom types of the bonded atoms.

Table S 4: Quartic bond parameters

I	J	R 0	K2	K3	K4	force field Reference
cl	o	1.6500	307.0632	0.0	0.0	cvff file
h	o	0.9600	493.8480	0.0	0.0	*cvff* file
cl4	o_1r	1,4523	419.3650	-838.7299	978.5182	cvff file
cl	o_1r	1.679	419.3650	-838.7299	978.5182	This work
cl4	oh	1.641	419.3650	-838.7299	978.5182	This work
o	o	1.2080	833.6868	0,.00	0.00	*cvff* file
o	o_1r	1.3603	833.6868	0,.00	0.00	This work
o_1r	o_1r	1.3227	833.6868	0,.00	0.00	This work

The entries for the **cl [o_1r]** and **cl4 [oh]** parameters were extracted from the **cl4 [o_1r]** entry in PCFF+. The relevant bond lengths (R0) were obtained from literature [2]. The entries for the **o [o_1r]** and **o_1r [o_1r]** parameters were extracted from the **o - o** entry in PCFF+. The relevant bond lengths (R0) were obtained from literature [3].

S3. Quartic angle parameters

The quartic angle is defined as follows in PCFF+:

$$\triangle = \theta - \theta_0$$

$$E = K2 * \triangle^2 + K3 * \triangle^4$$

$$\triangle^3 + K4 * \triangle^4$$

where:

- $\triangle$ represents Delta which is the change in angle value
- θ_0 is the equilibrium value of the angle.
- Theta (θ) is the current bond angle, Theta0 (θ_0) is the reference bond angle in degrees.
- The usual half factor is included in K [6].

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- K₂, K₃ *and* K₄ are quadratic force constants in units of: kcal/mol rad^{-2}.
- i, j, k are the atom types involved in the angle.

Table S5 presents the quartic angle parameters used in this study.

Table S 5: Quartic angle parameters

I	J	K	Theta0	K2	K3	K4	force field Reference
o1=	s2=	o1=	119.300	115.2627	-35.6278	-26.1261	*cvff* file
o	cl	o	115.400	115.2627	-35.6278	-26.1261	This work
*	p	*	109.5000	45.0000	0.0	0.0	pcff file
o	cl	oh	109.5000	45.0000	0.0	0.0	This work
*	o	*	109.5	60.000	0.0	0.0	*pcff* file
cl	o_1r	cl4	111,9	60.000	0.0	0.0	This work
cl4	o_1r	o_1r	110,3	60.000	0.0	0.0	This work
cl4	o_1r	o	110.4700	60.000	0.0	0.0	This work
cl	o	o_1r	111,74	60.000	0.0	0.0	This work
cl4	o_1r	cl4	119,11	60.000	0.0	0.0	This work
cl4	oh	ho	105	60.000	0.0	0.0	This work
o_1r	cl4	o_1r	112.2363	108.1226	-24.1496	-23.3346	*pcff* file
o_1r	cl4	oh	104,2	108.1226	-24.1496	-23.3346	This work
o	cl	o_1r	104,6	108.1226	-24.1496	-23.3346	This work

Parameters from the SO₂ (*cvff* file) entry were borrowed for the **o-cl-o** quartic angle. The actual quartic angle from literature [2] was substituted for Theta0. Parameters and Theta0 from the * [p] * entry were borrowed for the **o – cl - oh** quartic angle. The cl was substituted for 'p'. 'o' and 'oh' were substituted for *.

Parameters from the * [o] * entry were borrowed for the following quartic angle entries:

- cl [o_1r] cl4   o_1r was substituted for 'o'. cl and cl4 were substituted for *
- cl4 [o_1r] cl4   o_1r was substituted for 'o'. cl4 and cl4 were substituted for *
- cl4 [o_1r] o_1r   o_1r was substituted for 'o'. cl4 and o_1r were substituted for *
- cl4 [o_1r] o   o_1r was substituted for 'o'. cl4 and o were substituted for *
- cl [o] o-1r   cl and o_1r were substituted for *
- cl [oh] ho   oh was substituted for 'o'.   cl was substituted for *
- cl [o_1r] cl4:   The quartic angle for cl - o – cl bond was extracted from literature [2] and was substituted for theta0

- cl4 [o_1r] o_1r: The quartic angle for cl - o – o bond was extracted from literature [4] and was substituted for theta0

- cl4 [o_1r] o: The quartic angle for cl - o – o bond was extracted from literature [3] and was substituted for θ_0

- cl [o] o-1r: The quartic angle for cl - o – o bond was extracted from literature [3] and was substituted for θ_0

- cl [oh] ho: The quartic angle for cl -o – h bond was extracted from literature [2] and was substituted for θ_0

Parameters from the o_1r [cl4] o_1r entry were borrowed for the following Quartic angles:

a) o [1r – cl4] oh   ! oh was substituted for 'o_1r'

b) o [cl] o_1r   ! o was substituted for 'o_1r'

c) o_1r [cl4] oh   ! Quartic angle was extracted from literature [2] and was substituted for θ_0

d) o [cl – o] 1r   ! Quartic angle was extracted from literature [3] was substituted for θ_0

S4. Wilson out of plane parameters

The Wilson out-of-plane potential is defined according to the angle between one bond from the central atom and the plane defined by the other two bonds. The format of the out-of-plane potential (Wilson definition) section is:

$$E = K * (Chi – Chi0)^2$$

where I, J, K and L are the atom types of the four atoms involved in the out-of-plane term, j being the central atom: Chi ($\chi 0$) is the reference angle in degrees.

Table S 6: Wilson out of plane parameters

I	J	K	L	K-Chi	Chi0	force field Reference
*	p	*	*	0.000	0.000	*cvff* file
o	cl	o	o	0.000	0.000	*This work*
o	cl	o	oh	0.000	0.000	*This work*
o	cl	o	h	0.000	0.000	*This work*
o	cl	o	cl	0.000	0.000	*This work*
cl4	o_1r	o_1r	cl4	0.000	0.000	*This work*
o_1r	cl4	o_1r	cl4	0.000	0.000	*This work*
cl	o	o_1r	cl4	0.000	0.000	*This work*

Parameters from entry * -p- * - *   were used for all Wilson out of plane entries, cl was substituted for p. The relevant atoms were substituted for *.

S5. Torsion parameters

The three-term cosine expansion of the torsion potential is:

$$E = \sum(n=1,3) \{V(n) * [1 - \cos(n*Phi - Phi0(n))]\}$$

where V1, V2 and V3 are the barrier heights in kcal/mol and Phi (ϕ) is the current torsion angle.

$\phi01$, $\phi02$ and $\phi03$ are the reference torsion angles in degrees. The reference angles are usually 0° or 180°.

The atoms are bonded to each other in the order I-J-K-L.

Table S 7:   Torsion parameters

I	J	K	L	V(1)	Phi1(0)	V(2)	Phi2(0)	V(3)	Phi3(0)	force field Reference
*	c	o	*	0	0	0	0	0,13	0	*cvff* file
o	cl	o	o	0	0	0	0	0,13	0	*This work*
o	cl	o	h	0	0	0	0	0,13	0	*This work*
o	cl	oh	ho	0	0	0	0	0,13	0	*This work*
o_1r	cl4	o_1r	cl	0	0	0	0	0,13	0	*This work*
o_1r	cl4	o_1r	cl4	0	0	0	0	0,13	0	*This work*
o_1r	cl4	o_1r	o	0	0	0	0	0,13	0	*This work*
o_1r	cl4	oh	ho	0	0	0	0	0,13	0	*This work*
o	cl	o_1r	cl4	0	0	0	0	0,13	0	*This work*
o	cl	o	oh	0	0	0	0	0,13	0	*This work*
o	cl	oh	o	0	0	0	0	0,13	0	*This work*
o	cl	o	cl	0	0	0	0	0,13	0	*This work*
o	cl	o	o_1r	0	0	0	0	0,13	0	*This work*
o_1r	cl4	o_1r	o_1r	0	0	0	0	0,13	0	*This work*
*	o	o	*	0	0	0	0	1	0	*cvff* file
cl4	o_1r	o_1r	cl4	0	0	0	0	1	0	*This work*
cl	o	o_1r	cl4	0	0	0	0	1	0	*This work*

S6. DFT and Ab Initio structure refinement

Computational conditions applied for Gaussian-16 analyses, are presented in Table S8

Table S 8: Parameters applied for Gaussian analysis

Gaussian execution conditions	Selection
Optimization Conditions:	OPT selected plus FREQUENCY
Temperature:	298.15K
Pressure:	1 Atm
Spin polarization: Restricted Open Shell HF	ROHF: Charged and Radical Species
Spin polarization: Unrestricted Hartree Fock	UHF: Open shell, Radical, Charged species
Spin polarization: Restricted Hartree Fock	RHF: Neutral Species
Theory:	CCSD
Theory:	Hartree Fock
basis set:	cc-pv5z
Charge:	To specify for charged species
Theory:	DFT
Functional:	B3LYP, CCSD
basis set:	cc-pv5z
Spin:	Selected

The steps used (equations S1 – S5) to extract Energies of Formation, derived from Gaussian-16 applying B3LYP theory were adapted from the reference [5], and the results are presented in Table S 10 – S 11.

The initial step involved calculating the enthalpy of formation ($\Delta_f H$ (M, 0 K) for each molecule using the following equations [5]:

$$\Delta_f H(M, 0K) = \sum_{atoms} x\Delta_f \boldsymbol{H}(X, 0K) - \sum D_0(M) \qquad \text{Equation S1}$$

$$\Delta_f H(M, 0K) = \sum_{atoms} x\Delta_f \boldsymbol{H}(X, 0K) - \left[\sum x\varepsilon_0(X) - \varepsilon_0(M) - \varepsilon_{ZPE}(M)\right] \qquad \text{Equation S2}$$

$$= \sum_{atoms} x\Delta_f \boldsymbol{H}(X, 0K) - \left[627.51\sum x\varepsilon_0(X) - \varepsilon_0(M) - \varepsilon_{ZPE}(M)\right]$$

Where the equation parameters are defined as follows:

M = Molecule
X = Elements which make up M
χ = Number of atoms of X in M
$\sum D_0(M)$ = Atomization energy of the molecule
$\varepsilon_{ZPE}(M)$ = Zero Point energy of the species
$\varepsilon_0(M)$ = Total energy of the species
H_corr = Thermal correction to Enthalpy
E_tot = Total electronic energy
G_corr = Correction to the Gibbs Free Energy
Multiply by 627.51 = Conversion (Hartree to kcal)

To calculate the enthalpy of formation at 298 K ($\Delta_f H$ (M, 298 K) for each molecule, the following equation from the reference [5] were used:

$$\Delta_f H(M, 298K) = \Delta_f H(M, 0K) + [H_M^0(298K) - H_M^0(0K)] - \sum_{atoms} x[H_x^0(298K) - H_x^0(0K)] \qquad \text{Equation S3}$$

The Gibbs free energy of formations was determined using the following [5]:

$$\Delta_f G(M, 298K) = \Delta_f H(298K) - 298.15 \left[\sum S_{(X,298K)} - S_{(M,298K)}\right] \qquad \text{Equation S4}$$

$$= \Delta_f H(298K) - 298.15 \left[\sum S_{(X,298K)} - 627.51(\text{H\_corrM} - \text{G\_corrM})/298.15\right] \qquad \text{Equation S5}$$

The elemental entropy values used with equation S4 are provided in Table S9.

Table S 9: Elemental Entropu values used with equation S4.

Element	S_{298K} (Kcal/mol · K)
Cl	39.481
H	27.418
O	38.494
C	37.787

Table S 10: Gaussian Electronic energies from a B3LYP calculation

B3LYP	OClO	O	Cl	H	Units
ε_0	-610.583	-75.1005	-460.181573	-0.50243	hartree
ε_{ZPE}	0.005783	0.00	0.00	0.00	hartree
E_tot	0.00894	0.0014	0.0014	0.0014	hartree
H_corr	0.009884	0.0024	0.00236	0.00236	hartree
G_corr	-0.01926	-0.0135	-0.013508	-0.01065	hartree

Table S 11: Gaussian DFT/B3LYP/cc-pv5z/6311G output energies (Hartree) and associated Heats of Formation (kcal/mol)

Species	ε_0	ε_{ZPE}	E_tot	H_corr	G_corr	ΔH (OK)	ΔH (298K)	ΔG (298K)
O # (Singlet)	-75.1005	0	0.001416	0.00236	-0.01495	58.99	60.03	
Cl # (Doubet)	-460.182	0	0.001416	0.00236	-0.01568	28.59	52.64	
H # (Doublet)	-0.50243	0	0.001416	0.00236	-0.01065	51.63	29.69	
C # (Singlet)	-37.1984	0	0.001416	0.00236	-0.01455	169.98	170.23	
O ##	-74.9899	0	0.001416	0.00236	-0.01392			
Cl ##	-460.168	0	0.001416	0.00236	-0.01568			
H ##	-0.50226	0	0.001416	0.00236	-0.01065			
C ##	-37.7925	0	0.001416	0.00236	-0.01351			
ClO	-535.377	0.002787	0.005163	0.006107	-0.01876	29.772	29.72	22.07
[ClO]⁻	-535.461	0.001987	0.004407	0.005351	-0.01909	-23.431	-23.46	-31.37
[ClO]⁺	-534.98	0.001753	0.004201	0.005145	-0.02037	278.19	278.18	270.94
ClOO	-610.586	0.004618	0.008553	0.009497	-0.02252	21.62	21.50	6.87
[ClOO]⁻	-610.707	0.004176	0.007997	0.008941	-0.02321	-54.57	-54.76	-69.30
[ClOO]⁺	-610.142	0.003875	0.00745	0.008394	-0.0227	300.13	299.79	284.57
ClOCl	-995.618	0.003612	0.007145	0.00809	-0.02235	21.46	21.03	5.11
[ClOCl]⁻	-995.706	0.001233	0.005028	0.005973	-0.02604	-34.99	-35.26	-50.19
[ClOCl]⁺	-995.223	0.003982	0.007396	0.00834	-0.02244	269.53	269.03	253.32
Cl₂O	-995.597	0.00385	0.007412	0.008357	-0.02282	35.05	34.64	19.19
[Cl₂O]⁻ *	-995.645	0.002096	0.005615	0.006559	-0.02461	-53.42	-54.10	-69.56
[Cl₂O]⁺	-995.212	0.002828	0.006574	0.007518	-0.0246	276.12	275.83	260.96
ClClO₂	-1070.79	0.009595	0.013771	0.014715	-0.01835	37.86	36.80	11.044
ClOOO	-685.709	0.007877	0.012692	0.013636	-0.02123	68.41	67.80	43.48
[ClOOO]⁻	-685.851	0.007116	0.0108	0.011744	-0.02128	-20.62	-21.95	-47.90
Cl(O)O₂	-685.707	0.00776	0.01308	0.014024	-0.02311	69.75	69.46	46.56
[Cl(O)O₂]⁻	-685.851	0.007469	0.011147	0.012091	-0.02004	-20.63	-21.95	-47.99
ClO₃	-685.743	0.010472	0.014074	0.015018	-0.01666	49.16	47.80	21.47
[ClO₃]⁻	-685.875	0.009585	0.013418	0.014362	-0.01711	-34.08	-35.31	-61.76
[ClO₃]⁺	-685.292	0.00839	0.012558	0.013502	-0.01801	330.74	329.73	303.30
ClO₄*	-760.893	0.01041	0.014433	0.015377	-0.01675	76.79	74.64	37.12
[ClO₄]⁻	-761.083	0.014186	0.018493	0.019438	-0.01244	-40.15	-42.11	-79.79
ClOClO	-1070.76	0.00723	0.01139	0.012334	-0.02099	56.06	54.99	29.40
ClOOCl	-1070.79	0.006504	0.011388	0.012332	-0.02238	39.29	38.67	13.96
ClOClO₂	-1145.97	0.010652	0.015435	0.01638	-0.01879	50.56	48.83	12.93
ClOClO₃	-1221.14	0.016573	0.022351	0.023295	-0.0144	67.92	65.77	19.98
ClO₂ClO₂	-1221.13	0.0143	0.018233	0.019177	-0.01505	73.08	69.78	21.80
ClO₂-O-ClO₂	-1296.31	0.018927	0.024792	0.025736	-0.01268	84.34	81.21	24.39
ClO₂-O-ClO₃	-1371.51	0.027295	0.032621	0.033565	-0.00339	89.75	85.25	16.03

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Species	ε_0	ε_{ZPE}	E_tot	H_corr	G_corr	ΔH (0K)	ΔH (298K)	ΔG (298K)
ClOOClO$_3$	-1296.33	0.01996	0.026008	0.026952	-0.01163	75.18	72.17	15.45
ClO$_3$-O-ClO$_3$	-1446.7	0.030374	0.038703	0.039647	-0.00473	93.30	89.64	13.61
ClO$_2$-O-O-ClO$_2$	-1371.47	0.023365	0.031038	0.031982	-0.00977	107.20	104.17	37.96
ClO$_3$-O-O-ClO$_3$	-1521.85	0.037317	0.044028	0.044972	0.004479	124.17	118.45	28.50
[ClO$_3$-ClO$_3$]$^{-2}$	-1371.47	0.028141	0.033538	0.034483	-0.00186	110.20	105.74	36.14
OClO	-610.583	0.005783	0.00894	0.009884	-0.01926	24.50	23.89	7.45
[OClO]$^-$	-610.645	0.003267	0.006849	0.007793	-0.02175	-15.96	-16.30	-32.49
[OClO]$^+$	-610.178	0.006108	0.009185	0.010129	-0.01822	278.90	278.24	261.30
OClOO	-685.733	0.004705	0.010421	0.011365	-0.02806	51.673	51.63	30.17
[OClOO]$^-$	-685.829	0.00475	0.008655	0.009599	-0.02582	-8.70	-9.88	-33.85
OClClO$_2$	-1145.81	0.005881	0.012201	0.013145	-0.02631	147.45	146.67	113.48
[ClOH$_2$]$^+$	-536.291	0.025091	0.028046	0.028991	0.002482	204.10	202.38	179.42
HOCl	-536.045	0.013162	0.016105	0.017049	-0.00978	-15.73	-16.44	-31.03
[HOCl]$^-$	-535.926	0.006934	0.010224	0.011168	-0.01455	54.74	54.25	38.96
[HOCl]$^+$	-535.637	0.012962	0.01592	0.016864	-0.01055	239.76	239.06	224.84
HOClO	-611.193	0.015261	0.018722	0.019666	-0.01037	14.44	13.01	-11.04
[HOClO]$^-$ *	-611.066	0.011127	0.014348	0.015292	-0.01570	-55.76	-57.33	-80.78
[HOClO]$^+$	-610.834	0.015946	0.019318	0.020262	-0.01012	240.42	238.94	215.10
HOClO$_2$	-686.393	0.019286	0.023362	0.024307	-0.00765	13.26	11.18	-23.15
HOClO$_3$	-761.593	0.027229	0.031957	0.032902	-0.00083	14.84	12.13	-32.56
[HOClO$_3$]$^+$	-761.084	0.016512	0.022501	0.023446	-0.01494	327.65	325.73	283.97
HOOCl*	-611.212	0.017467	0.020866	0.02181	-0.00805	4.06	2.60	-21.57
[HOOCl]$^-$	-611.228	0.011698	0.016318	0.017262	-0.0168	-9.90	-10.60	-32.12
[HOOCl]$^+$	-610.812	0.016787	0.020038	0.020982	-0.00924	254.85	253.29	229.36
HOOClO	-686.369	0.020306	0.024864	0.025809	-0.00746	29.56	27.78	-5.719
HOOClO$_2$	-761.551	0.024822	0.029341	0.030285	-0.00357	40.10	37.26	-7.35
HOOOCl	-686.37	0.021388	0.025538	0.026482	-0.00608	29.47	27.44	-6.5
HOOOOCl	-761.564	0.022424	0.028236	0.02918	-0.00723	30.21	28.18	-14.83
HClO	-535.961	0.009811	0.012762	0.013706	-0.01325	34.60	33.90	19.39
HClO$_2$	-611.137	0.015657	0.018874	0.019818	-0.00952	49.88	48.31	23.82
HClO$_3$	-686.341	0.022859	0.026355	0.027299	-0.00356	48.51	46.07	11.05

\#   basis set: B3LYP (cc-pv5z)
\#\#   basis set: B3LYP (6-311++G/(3d2f,3p2d))
Basis sets applied:
        DFT/B3LYP (cc-pv5z)   (Predominantly applied)
        DFT/B3LYP (6-311++G/(3d2f,3p2d)   *
        DFT/B3LYP (aug-cc-pv5z)   **

S7 MOPAC-2016 – (Semi-empirical Ab Initio structure refinement and Heats of Formation)

In this study, the Heats of Formation of the selected single species and ensembles of the various chlorine species was computed using MOPAC-2016 (Version: 20.302W). Computational steps are presented in Table S 12.

Table S 12: MOPAC conditions applied for analysis

MOPAC execution conditions	
Hamiltonians applied:	AM1/MNDO/MNDOD
	PM3/PM6/RM1/PM7
SCF convergence:	0.01 kcal/mol
Structure Optimize:	Normal
Wave function:	Automatic
Periodic Cell:	Optimize
Starting Hessian:	Automatic
Convergence:	Normal
Iterations:	10 000
Initial Temp:	50K
Final Temp:	300K

Energies of Formation (ΔH_f) of single species selected for this study derived with Gaussian, MOPAC and VASP are presented in Table S 13.

Table S 13: Energies of Formation (ΔH_f) of single species derived with Gaussian, MOPAC and VASP are listed. Models exposed to VASP calculations were confined to periodic cell environments with a Space Group symmetry constraint of P1(1). (Energies displaying severe deviation from Reference entries appear in bold). Thermodynamic S and Cp entries have been derived from the MOPAC ensemble energies

Species	Literature Reference ΔH_f (298K)	*Gaussian-16* (DFT B3LYP, cc-pV5Z) ΔH_f (298K)	MOPAC-2016 (derived) ΔH_f (298K)	MOPAC-2016 (derived) S (kJ/mol)	MOPAC-2016 (derived) Cp (kJ/mol)
ClO	24.31 [6]	29.71	25.47	215.09	30.78
[ClO]⁻	-28.26 [6]	-23.46	-24	215.64	31.01
[ClO]⁺	274.84 [6]	278.18	276.94	213.25	21.66
ClOO	24.56 [6]	21.5	23.28	256.64	40.54
[ClOO]⁻	-59.28 [6]	-54.75 #	-53.36	265.18	46.01
[ClOO]⁺	286.71 [6]	299.79	293.61	258.75	35.69
ClOCl	18.62 [6]	21.03	19.45	264.16	43.33
[ClOCl]⁻	-35.28 [6]	-35.26	-36.72	279.21	48.37
[ClOCl]⁺	269.14 [6]	269.03	261.74	262.36	42.76
ClClO	31.81 [6]	34.64	37.8	272.67	45.19
[ClClO]⁻	-44.11 [6]	-54.10 #	-43.69	293.01	49.86
[ClClO]⁺	270.09 [6]	275.83	271.85	275.27	47.94
[ClClO₂]	29.16 [6]	36.79	28.96	296.4	61.96
ClOOO	53.29 [6]	67.8	45.51	297.01	52.81
[ClOOO]⁻	-25.00 [6]	-21.93	-25.06	286.06	56.29
[Cl(O)O₂]	63.37 [6]	69.46	63.47	323.26	63.22
[Cl(O)O₂]⁻	-25.22 [6]	-21.95	-35.34	300.27	62.35
ClO₃	44.46 [6]	47.79	39.31	280.33	62.65
[ClO₃]⁻	-50.83 [6]]	**-35.31**	-55.19	264.82	56.18
[ClO₃]⁺	297.67 [6]	**329.73**	300.82	273.42	35.56
[ClO₄]	57.60 [6]	**74.64**	46.14	308.9	79.68
[ClO₄]⁻	-64.98 [6]	**-42.11**	-72.83	265.7	63.11
ClOClO	41.80 [6]	54.98	38.19	302.4	62.52
ClOOCl	31.37 [7]	38.67	33.69	289.38	57.09
ClOClO₂	37.80 [8]	48.86 **	38.45	308.11	69.63
ClOClO₃	37.40 [9]	65.77	49.52	335.93	86.6
ClO₂ClO₂	N/R	69.78	50.72	340.46	96.51
ClO₂-O-ClO₂	N/R	81.21	41.27	332.84	99.84
ClOOClO₃	69 [9]	72.17	73.94	359.09	102.89
ClO₂-O-ClO₃	72.4 [9]	85.24 *	**47.01**	367.43	111.22
ClO₃-O-ClO₃	86.2 [9]	89.64 *	76.7	369.09	126.94
ClO₂-O-O-ClO₂	N/R	104.17 **	79.42	403.86	129.85
ClO₃-O-O-ClO₃	111.40 [3]$	118.45	108.37	471.17	164.93

Table S 13 continued…

Species	Literature Reference ΔH_f(298K)	*Gaussian-16* (DFT B3LYP, cc-pV5Z) ΔH_f(298K)	MOPAC-2016 (derived) ΔH_f(298K)	MOPAC-2016 (derived) S (kJ/mol)	MOPAC-2016 (derived) Cp (kJ/mol)
$[ClO_3\text{-}ClO_3]^{-2}$	N/R	105.74	106.06	403.99	126.56
$OClO$	24.36 [6]	23.89	25.47	250.18	38.97
$[OClO]^-$	-25.74 [6]	-16.29	-23.14	253.39	42.54
$[OClO]^+$	262.13 [6]	278.24	266.34	272.24	32.61
$OClOO$	54.31 [6]	51.63	44.72	368.09	67.23
$[OClOO]^-$	-8.19 [6]	-9.89	-12.15	302.31	65.09
$OClClO_2$	46.2 [26]	**146.67 #**	50.13	340.18	77.86
$[ClOH_2]^+$	194.66 [6]	202.38	197.1	246.18	27.56
$HOCl$	-18.36 [6]	-16.43 *	-17.81	236.16	36.05
$[HOCl]^-$	47.38 [6]	54.25	**-9.02 ****	240.37	40.12
$[HOCl]^+$	237.86 [6]	239.06	244.01	235.35	35.61
$HOClO$	4.94 [6]	13.01	6.77	263.6	47.48
$[HOClO]^-$	-37.31 [6]	-57.33 #	-34.19	283.68	57.8
$[HOClO]^+$	236.82 [6]	238.93	233.62	271.55	52.3
$HOClO_2$	10.90 [30]	11.18 **	-3.27	288.18	62.57
$HOClO_3$	0.43 [6]	12.13 **	3.71	307.07	74.37
$[HOClO_3]^+$	282.36 [6]	325.73 #	273.23	312.33	80.74
$HOOCl$	-0.32 [6]	2.60 *	-0.68	263.45	49.09
$[HOOCl]^-$	-8.12 [6]	-10.6	**-39.22**	270.3	52.15
$[HOOCl]^+$	244.70 [6]	253.27 #	244.23	266.73	51.32
$HOOClO$	27.30 [10]	27.78 *	23.08	293.57	65.99
$HOOClO_2$	16.55 [6]	**37.26 ****	19.25	322.75	82.36
$HOOOCl$	14.00 [10]	**27.44 ***	11.88	286.64	58.79
$HOOOOCl$	22.70 [11]	28.18	24.78	329.09	84.55
$HClO$	33.24 [6]	33.89 *	30.45	237.13	38.579
$HClO_2$	45.65 [6]	48.31 *	49.06	253.22	47.44
$HClO_3$	57.1 [10]	46.07 *	45.7	264.06	50.98

N/R - not reported
* Restricted: DFT/B3LYP/cc-pv5z
**Restricted open shell. DFT/B3LYP/cc-pv5z
Unrestricted: DFT/B3LYP/6-311++G(3d2f,3p2d)
$ Indicates that the ΔHf (298K) of ClO3-O-O-ClO3 is
calculated from Energies published by Beltran et al.,1999 [5].

Ensemble models were processed in periodic space, extracted from the GIBBS GCMC simulations, and the heats of formation calculated using MOPAC are presented in Table S 14, and compared to literature values.

Table S 14: Heats of Formation of ENSEMBLE models (GEMC derived) calculated with MOPAC

| Ensemble Models | ΔH_f (calculated) | | ΔH_f kJ/mol) | Literature Reference ΔH_f (kJ/mol) |
	MODEL Space	MOPAC Hamiltonian		
	Single	PM6	106.56	
ClO	Ensemble	MNDOD	**91.50**	101.71 [6]
	Single	MNDOD	97.40	
ClOO	Ensemble	MNDO	**101.17**	102.76 [6]
	Single	AM1	81.38	
ClOCl	Ensemble	AM1	**82.55**	77.91 [6]
	Single	MNDOD	119.83	
ClClO	Ensemble	RM1	**143.97**	31.84 [6]
	Single	PM6	121.17	
ClClO$_2$	Ensemble	MNDOD	**93.47**	122.00 [6]
	Single	MNDO	190.54	
ClOOO	Ensemble	MNDOD	**209.20**	222.97 [6]
	Single	MNDOD	263.59	
Cl(O)O$_2$	Ensemble	MNDOD	**276.73**	265.14 [6]
	Single	PM6	164.47	
ClO$_3$	Ensemble	RM1	**173.72**	185.35 [6]
	Single	PM3	211.46	
ClO$_4$	Ensemble	PM7	**204.68**	241.00 [6]
	Single	PM6	159.79	
ClOClO	Ensemble	AM1	**161.00**	174.90 [6]
	Single	AM1	140.96	
ClOOCl	Ensemble	AM1	**127.53**	131.25 [12]
	Single	MNDOD	160.87	
ClOClO$_2$	Ensemble	MNDOD	**164.22**	158.15 [9]
	Single	PM7	207.19	
ClOClO$_3$	Ensemble	PM6	**163.18**	156.49 [9]
	Single	MNDOD	431.62	
ClO$_2$ClO$_2$	Ensemble	AM1	**278.45**	Not reported
	Single	RM1	211.50	
ClO$_2$-O-ClO$_2$	Ensemble	RM1	**210.96**	Not reported
	Single	PM7	289.66	
ClOOClO$_3$	Ensemble	PM7	**275.47**	288.69 [9]
	Single	MNDOD	196.52	
ClO$_2$-O-ClO$_3$	Ensemble	PM6	**281.50**	302.92 [9]

| Ensemble Models | ΔH_f (calculated) | | ΔH_f (kJ/mol) | Literature Reference ΔH_f (kJ/mol) |
	MODEL Space	MOPAC Hamiltonian		
	Single	PM6	324.93	
$C\ell O_3\text{-O-}C\ell O_3$	Ensemble	PM6	**330.28**	345.59 [9]
	Single	PM6	332.29	
$C\ell O_2\text{-O-O-}C\ell O_2$	Ensemble	AM1	**439.19**	Not reported
	Single	PM6	453.42	
$C\ell O_3\text{-O-O-}C\ell O_3$	Ensemble	PM6	**449.57**	466.09 [3] $^{\$}$
	Single	MNDOD	106.57	
$OC\ell O$	Ensemble	MNDOD	**84.22**	101.92 [6]
	Single	PM6	111.67	
$OC\ell OO$	Ensemble	MNDOD	**224.81**	227.19 [6]
	Single	RM1	209.74	
$OC\ell C\ell O_2$	Ensemble	RM1	**207.99**	193.30 [6]
	Single	PM6	-74.52	
$HOC\ell$	Ensemble	PM6	**-77.66**	-76.81 [6]
	Single	PM7	0.92	
$HOC\ell O$	Ensemble	PM7	**27.15**	20.66 [6]
	Single	MNDOD	-13.31	
$HOC\ell O_2$	Ensemble	MNDOD	**-11.80**	-4.6 [6]
	Single	MNDOD	15.52	
$HOC\ell O_3$	Ensemble	MNDOD	**13.26**	1.79 [6]
	Single	RM1	-2.85	
$HOOC\ell$	Ensemble	AM1	**-3.68**	-1.34 [6]
	Single	RM1	92.26	
$HOOC\ell O$	Ensemble	MNDOD	**94.98**	90.12 [6]
	Single	PM6	80.63	
$HOOC\ell O_2$	Ensemble	MNDOD	**80.88**	69.24 [6]
	Single	MNDOD	49.71	
$HOOOC\ell$	Ensemble	AM1	**44.69**	42.30 [10]
	Single	PM6	103.68	
$HOOOOC\ell$	Ensemble	PM6	90.29	94.98 [10]

$\$$ Indicates that the ΔHf (298K) of $C\ell O3$-O-O-$C\ell O3$ is calculated from Energies published by Beltran et al. [3]

Table S 15: Calculated Gibbs Free Energies of Formation, obtained with Gaussian-16, applying DFT B3LYP/cc-pv5z

Species	ΔH_f (0K) (kJ/mol)	ΔH_f (298K) (kJ/mol)	ΔG_f (298K) (kJ/mol)	Species	ΔH_f (0K) (kJ/mol)	ΔH_f (298K) (kJ/mol)	ΔG_f (298K) (kJ/mol)
ClO	124.64	124.41	92.40	OClO	102.58	100.02	31.19
[ClO]$^-$	-98.10	-98.22	-131.34	[OClO]$^-$	-66.82	-68.24	-135.99
[ClO]$^+$	1164.73	1164.68	1134.37	[OClO]$^+$	1167.70	1164.93	1094.05
ClOO	90.52	90.02	28.76	OClOO	216.33	216.16	126.32
[ClOO]$^-$	-228.47	-229.23	-290.15	[OClOO]$^-$	-36.43	-41.32	-141.72
[ClOO]$^+$	1256.58	1255.16	1191.44	OClClO$_2$	617.34	614.08	475.08
ClOCl	89.85	88.05	21.39	[ClOH$_2$]$^+$	854.48	847.32	751.20
[ClOCl]$^-$	-146.50	-147.63	-210.14	HOCl	-65.86	-68.83	-129.87
[ClOCl]$^+$	1128.47	1126.37	1060.60	[HOCl]$^-$	229.19	227.13	163.12
ClClO	146.75	145.03	80.30	[HOCl]$^+$	1003.83	1000.90	941.36
[ClClO]$^-$	-223.66	-226.51	-291.23	HOClO	60.46	54.47	-46.22
[ClClO]$^+$	1156.06	1154.84	1092.59	[HOClO]$^-$	-233.46	-240.03	-338.21
ClClO$_2$	158.51	154.03	46.22	[HOClO]$^+$	1006.59	1000.35	900.58
ClOOO	286.42	283.86	182.04	HOClO$_2$	55.52	46.77	-96.92
[ClOOO]$^-$	-86.33	-91.86	-200.92	HOClO$_3$	62.13	50.79	-136.32
Cl(O)O$_2$	292.03	290.81	194.94	[HOClO$_3$]$^+$	1371.80	1363.77	1188.93
[Cl(O)O$_2$]$^-$	-86.33	-91.86	-200.92	HOOCl	17.00	10.89	-90.31
ClO$_3$	205.82	200.09	89.89	[HOOCl]$^-$	-41.45	-44.38	-134.48
[ClO$_3$]$^-$	-142.69	-147.84	-258.58	[HOOCl]$^+$	1067.01	1060.47	960.28
[ClO$_3$]$^+$	1384.74	1380.51	1269.86	HOOClO	123.76	116.31	-23.95
ClO$_4$	321.46	312.50	155.41	HOOClO$_2$	167.89	156.00	-30.77
[ClO$_4$]$^-$	-168.10	-176.31	-334.06	HOOOCl	123.38	114.89	-27.21
ClOClO	234.71	230.19	123.09	HOOOOCl	126.48	117.98	-62.09
ClOOCl	164.50	161.90	58.45	HClO	144.86	141.89	81.18
ClOClO$_2$	211.68	204.44	54.14	HClO$_2$	208.84	202.22	99.73
ClOClO$_3$	284.37	275.37	83.65	HClO$_3$	203.10	192.89	46.26
ClO$_2$ClO$_2$	305.97	292.15	91.27	H$_2$O	-208.34	-211.18	-271.43
ClO$_2$-O-ClO$_2$	353.11	340.01	102.12	CO$_2$	-1717.30	-1716.67	-1786,8
ClOOClO$_3$	314.76	302.16	64.69	C$_2$H$_6$	102.58	100.02	356.67
ClO$_2$-O-ClO$_3$	375.77	356.92	67.11	OH$^-$(g)			-138.79 [33]
ClO$_2$-O-O-ClO$_2$	448.82	436.14	158.93	HCl			292.66 [43]
ClO$_3$-O-O-ClO$_3$	519.87	495.93	119.32	[HOO]$^-$			1547.02 [43]
[ClO$_3$ClO$_3$]$^{-2}$	461.39	442.71	151.31	Cl$^-$			-549.31 [33]

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