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Thermochemistry of the higher chlorine oxides ClO_x ($x = 3, 4$) and Cl_2O_x ($x = 3-7$)[†]

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Abstract

Heats of formation for ClO_3 , ClO_4 , Cl_2O_3 , Cl_2O_4 , Cl_2O_5 , Cl_2O_6 and Cl_2O_7 molecules are determined at the B3LYP, B3PW91, mPW1PW91 and B1LYP levels of the density functional theory employing a series of extended basis sets, and using Gaussian-3 model chemistries. Modified Gaussian-3 calculations, which employ accurate B3LYP/6-311 + G(3d2f) molecular geometries and vibrational frequencies, were also performed. Heats of formation were calculated from both total atomization energies and isodesmic reaction schemes. The latter method in conjunction with Gaussian-3 models leads to the most reliable results. The best values at 298 K for ClO_3 , ClO_4 , Cl_2O_3 and Cl_2O_4 as derived from an average of G3//B3LYP and G3//B3LYP/6-311 + G(3d2f) calculations are 43.1, 54.8, 31.7 and 37.4 kcal mol⁻¹. From calculations carried out at the G3(MP2)//B3LYP and G3(MP2)//B3LYP/6-311 + G(3d2f) levels, heats of formation for Cl_2O_5 , Cl_2O_6 and Cl_2O_7 are predicted to be 53.2, 52.2 and 61.5 kcal mol⁻¹. All best values are reproduced within 1 kcal mol⁻¹ by using mPW1PW91/6-311 + G(3d2f) isodesmic energies. Enthalpy changes for relevant Cl–O bond fission reactions are reported. Comparisons with previous thermodynamics data are made.

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Keywords: Chlorine oxides; Heats of formation; Ab initio; Density functional theory

1. Introduction

It is at present largely accepted that simple chlorine oxides are key participants in the destruction of stratospheric ozone. Due to this, the photochemistry, chemical kinetics and thermochemistry of these species [1,2] have occupied center stage in the discussion of ozone loss since the discovery of the Antarctic ‘ozone hole’ [3]. However, the detection

in polar stratosphere of elevated concentrations of ClO and OClO has increased the interest for the possible formation of higher oxides such as Cl_2O_3 (ClOClO_2), Cl_2O_4 (ClOClO_3), Cl_2O_5 (ClOOCIO_3), Cl_2O_6 ($\text{O}_2\text{ClOClO}_3$) and Cl_2O_7 ($\text{O}_3\text{ClOClO}_3$), acting as temporary reservoirs of these and other species. In particular, the potential ozone-depleting catalytic cycle $\text{Cl}_2\text{O}_4 + 2\text{O}_3 \rightarrow \text{Cl}_2\text{O}_6 + 2\text{O}_2$ has been recently suggested [4]. In addition, transient species as ClO_3 and ClO_4 radicals could also play a role in stratospheric mechanisms. Laboratory kinetic studies show that Cl_2O_6 and Cl_2O_7 and small amounts of OClO, Cl_2 and O_2 are formed in the reaction between Cl atoms and Cl_2O_4 [5], while the photolysis of OClO produces

[†] Dedicated to the memory of Dr María Inés López.

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Cl_2O_4 and Cl_2O_6 and, in some experimental conditions, small amounts of Cl_2O_7 [6–10]. ClO_3 and ClO_4 radicals are probably involved in the formation of these oxides. Despite of their importance, large uncertainties in the thermochemistry of most of the mentioned higher chlorine oxides still remain [1,2].

We have focused the present theoretical work on the thermochemistry of seven species, namely, ClO_3 , ClO_4 , Cl_2O_3 , Cl_2O_4 , Cl_2O_5 , Cl_2O_6 and Cl_2O_7 . Several studies related on the heats of formation of these molecules have been recently reported. The estimated values have been derived from kinetics and equilibrium studies [11–14], from photoionization of the stable chlorine oxides [15], from proposed valence additivity schemes [16] and from a variety of quantum-chemical calculations [17–23]. However, most of the published heats of formation are controversial. The large uncertainties in the recommended values have motivated the present study. Our main goal is the determination of the heats of formation for the above listed molecules, and the energetics of their principal unimolecular dissociation pathways. For this, a variety of density functional theory (DFT) methods and the Gaussian-3 model chemistry have been employed to calculate thermodynamic properties. Taking into account the relevance of the molecules considered we will make comparisons between the present results and those reported in earlier experimental and theoretical studies.

2. Computational details

The methodology employed is similar to that used in recent publications from this laboratory [24–27]. Heats of formation were computed by both total atomization energies and by using selected isodesmic (equal bond) and isogyric reactions. In such reactions, the numbers of each type of bond as well as the spin multiplicities are conserved. As a consequence, systematic errors due to incompleteness of the basis sets and electron correlation energy cancel to a great extension, leading to heats of formation which are often more accurate than those obtained by atomization energies [28,29]. The results obtained using a variety of density functional methods which employed different exchange (B3 [30,31], B1 [32] and mPW [33]) and correlation (LYP [34] and PW91 [35,36])

functionals were compared with those derived from Gaussian-3 (G3(MP2)//B3LYP and G3//B3LYP [37]) calculations. Under certain assumptions about additivity, the final G3//B3LYP total energies (which account for spin-orbit, core and high level empirical corrections) are effectively at the QCISD(T,FULL)/G3Large level. The G3(MP2)//B3LYP uses a reduced order of perturbation theory and only valence electrons in the treatment of the correlation energy. The average absolute deviation from well-known experimental heats of formation is $0.93 \text{ kcal mol}^{-1}$ for the G3//B3LYP model and $1.13 \text{ kcal mol}^{-1}$ for the G3(MP2)//B3LYP [37].

Modified Gaussian-3 calculations which employ B3LYP/6-311 + G(3d2f) (unscaled frequencies), instead of standard B3LYP/6-31G(d) molecular geometries and vibrational frequencies (scaled by 0.96), were also carried out. These approaches are here denoted as G3(MP2)//B3LYP/6-311 + G(3d2f) and G3//B3LYP/6-311 + G(3d2f), respectively. The latter one is expected to give the more accurate heat of formation values reported here. Following the notation of the GAUSSIAN 98 suite of programs employed in the present study [38], the B3LYP, B3PW91, mPW1PW91 and B1LYP hybrid HF-DFT methods were used to compute fully optimized geometries using analytical gradient methods, harmonic vibrational frequencies via analytical second derivatives methods, and total energies. The default integration grid was used for all calculations. The 6-311 + G(3df), 6-311 + G(3d2f) Pople's basis sets [39] and the augmented correlation consistent polarized valence (aug-cc-pV) Dunning's basis sets, namely the triple-zeta (TZ) and quadruple-zeta (QZ) sets [40] were employed in all DFT calculations. Additional B3LYP computations with basis ranging from 6-31G(d) to 6-311 + G(3d) were also carried out. In this way, the specific influence of the different functionals as well as basis sets effects on calculated heats of formation were studied.

3. Results and discussion

3.1. Heats of formation determined from total atomization energies

The total atomization energy, $\sum D_0$, is the energy needed to dissociate a molecule into its separate atoms.

Due to the fact, that this process is not isogyric, an accurate determination of the energy of all the species is required, placing stringent requirements on the quantum methods employed. Heats of formation at 0 K, $\Delta H_{f,0}$, were obtained by subtracting the computed total atomization energies from the experimental heats of formation of chlorine, $28.59 \pm 0.001 \text{ kcal mol}^{-1}$, and oxygen atoms, $58.99 \pm 0.02 \text{ kcal mol}^{-1}$ [41]. $H^\circ(298.15 \text{ K}) - H^\circ(0 \text{ K})$ values for chlorine and oxygen atoms of 1.10 and 1.04 kcal mol^{-1} [42] and calculated thermal contributions were employed to transform $\Delta H_{f,0}$ to the values at 298 K, $\Delta H_{f,298}$. The resulting $\sum D_0$, and $\Delta H_{f,298}$ for ClO_3 , ClO_4 , Cl_2O_3 and Cl_2O_4 at all DFT and ab initio methods used are listed in Table 1. Due to limitations in the computational resources, no G3//B3LYP and G3//B3LYP/6-311 + G(3d2f) calculations were carried out for the more complex oxides: Cl_2O_5 , Cl_2O_6 and Cl_2O_7 .

Therefore, methods which lead to a significant saving in the disk storage as B3LYP/6-311 + G(3d2f), mPW1PW91/6-311 + G(3d2f), G3(MP2)//B3LYP and G3(MP2)//B3LYP/6-311 + G(3d2f) were employed. The results obtained for these molecules are shown in Table 2.

Heats of formation computed using the Becke's three-parameter exchange functional (B3) [30,31] in conjunction with the nonlocal functional provided by the Lee–Yang–Parr expression (LYP) [34], B3LYP, with a variety of basis sets are listed in the first part of Table 1. Large basis sets effects for all the oxides studied are apparent. In addition, large structural changes have been also observed. For instance, an stable C_{3v} structure is predicted at the B3LYP/6-311G(d) level for ClO_3 (a ClO bond distance of 1.502 Å and a OClO bond angle of 114.0°), while a C_{2v} structure is obtained with the basis 6-311G(d)

Table 1
Calculated atomization energies and heats of formation (in kcal mol^{-1}) for ClO_3 , ClO_4 , Cl_2O_3 and Cl_2O_4

Level of theory	ClO_3		ClO_4		Cl_2O_3		Cl_2O_4	
	$\sum D_0$	$\Delta H_{f,298}$	$\sum D_0$	$\Delta H_{f,298}$	$\sum D_0$	$\Delta H_{f,298}$	$\sum D_0$	$\Delta H_{f,298}$
B3LYP/6-31G(d)	116.5	87.8	146.2	116.6	158.8	74.3	187.6	103.6
B3LYP/6-311G(d)	96.5	108.1	127.9	134.9	144.6	88.5	167.9	123.4
B3LYP/6-311 + G(d)	96.2	108.4	123.2	121.5	145.3	87.8	165.0	126.3
B3LYP/6-311 + G(2d)	131.5	72.8	163.5	99.3	172.2	60.8	204.5	86.7
B3LYP/6-311 + G(3d)	142.2	62.0	179.2	83.5	182.0	51.1	220.4	70.6
B3LYP/6-311 + G(3df)	154.2	50.0	195.0	67.7	192.3	40.7	236.4	54.6
B3LYP/6-311 + G(3d2f)	154.9	49.3	196.2	66.4	192.9	40.0	237.6	53.4
B3LYP/aug-cc-pVTZ	137.1	67.1	169.7	92.9	178.1	53.9	211.0	80.0
B3LYP/aug-cc-pVQZ	147.0	57.2	180.6	82.1	185.9	47.0	225.5	65.6
B3PW91/6-311 + G(3df)	163.1	41.1	207.2	55.4	200.2	32.7	249.8	41.1
B3PW91/6-311 + G(3d2f)	163.8	40.4	208.6	54.0	200.9	32.0	251.2	39.8
B3PW91/aug-cc-pVTZ	145.3	58.9	181.3	81.3	185.1	47.9	224.7	66.3
B3PW91/aug-cc-pVQZ	155.4	48.8	192.6	70.0	193.5	39.5	237.8	53.1
mPW1PW91/6-311 + G(3df)	157.3	46.8	200.9	61.7	193.5	39.4	243.6	47.3
mPW1PW91/6-311 + G(3d2f)	158.1	46.0	202.3	60.2	194.3	38.6	245.0	46.0
mPW1PW91/aug-cc-pVTZ	139.4	64.8	174.5	88.1	178.4	54.5	217.1	73.8
mPW1PW91/aug-cc-pVQZ	149.5	54.7	188.6	74.0	186.0	46.9	231.0	59.9
B1LYP/6-311 + G(3df)	138.9	65.3	175.7	87.0	174.2	58.7	214.8	76.1
B1LYP/6-311 + G(3d2f)	139.5	64.7	176.9	85.8	178.8	58.1	216.0	75.0
B1LYP/aug-cc-pVTZ	121.8	82.4	150.2	112.5	159.9	73.0	189.7	101.3
B1LYP/aug-cc-pVQZ	131.9	72.3	164.1	98.5	168.1	64.9	204.3	86.7
G3(MP2)//B3LYP	151.8	52.5	194.7	68.2	194.3	38.8	241.4	49.9
G3(MP2)//B3LYP/6-311 + G(3d2f)	154.1	50.1	197.7	64.9	195.0	38.0	244.8	46.2
G3//B3LYP	153.5	50.9	197.7	65.2	195.3	37.8	244.4	46.9
G3//B3LYP/6-311 + G(3d2f)	156.5	47.7	201.8	60.9	196.7	36.3	249.0	42.1

Table 2

Calculated atomization energies and heats of formation (in kcal mol⁻¹) for Cl₂O₅, Cl₂O₆ and Cl₂O₇

Level of theory	Cl ₂ O ₅		Cl ₂ O ₆		Cl ₂ O ₇	
	$\sum D_0$	$\Delta H_{f,298}$	$\sum D_0$	$\Delta H_{f,298}$	$\sum D_0$	$\Delta H_{f,298}$
B3LYP/6-311 + G(3d2f)	280.2	69.7	331.5	76.8	373.4	93.1
mPW1PW91/6-311 + G(3d2f)	285.7	63.9	340.0	68.2	387.4	78.9
G3(MP2)//B3LYP	281.1	69.0	336.3	72.4	380.7	86.2
G3(MP2)//B3LYP/6-311 + G(3d2f)	268.5	63.3	340.3	68.1	387.0	79.5

(ClO bond distances of 1.473, 1.576 and 1.576 Å, and OClO bond angles of 88.6, 111.9 and 111.9°) and 6-311 + G(d) (ClO bond distances of 1.473, 1.580 and 1.580 Å, and OClO bond angles of 88.3, 112.2 and 112.2°). Larger basis sets lead to sym-ClO₃ structures. In fact, identical ClO bond lengths of 1.455 Å and identical bond angles of 114.2° are predicted at the B3LYP/6-311 + G(3d2f) level. These values agree very well with those resulting in CCSD(T)/6-311G(2df) calculations of 1.458 Å and 114.2° [20]. In average, the ClO bond distances obtained at the B3LYP/6-311 + G(3d2f) level are about 0.04 Å shorter than those estimated at the B3LYP/6-31G(d) level, the differences between the angles are less than 1° and the vibrational zero-point energies (ZPE) are about 0.8 kcal mol⁻¹ higher. The comparison between theoretical and experimental equilibrium structures and vibrational frequencies for the current molecules have been discussed in detail elsewhere [17–22,43–47]. Our results agree very well with those reported in these studies and, for the sake of clarity, no details are given here.

B3LYP results indicate the necessity of including both d and f polarization functions on the basis sets [48]. In this context, probably due to the hypervalent character of the higher oxides studied, the DFT computed energies are not fully convergent even with the large 6-311 + G(3d2f) basis set. To explore the performance of the aug-cc-pVTZ and aug-cc-pVQZ basis, single-point DFT calculations were carried out at the corresponding DFT/6-311 + G(3d2f) geometries. ZPE and thermal corrections were also estimated at this latter level of theory. The total number of basis functions in the 6-311 + G(3d2f) basis for ClO₃, ClO₄, Cl₂O₃ and Cl₂O₄ are 192, 238, 246 and 292, respectively. These numbers are smaller than those corresponding to the

aug-cc-pVQZ basis (which include, in addition to three d and two f polarization functions, a set of g functions on the chlorine and oxygen atoms) of 324, 404, 408 and 488 basis functions. However, as shown in Table 1, the latter basis set gives worse results with a major computational effort. These findings indicate that for the present cases, the convergence of the energies calculated with Dunning's basis sets [40] is slower than that obtained with Pople's basis sets [39]. Certainly, extrapolations of the total energies to the complete basis set limit should be employed in compounds with pronounced hypervalent character [49].

By contrasting $\Delta H_{f,298}$ values derived from B3LYP and B3PW91 calculations it is shown that the PW91 correlated functional predicts a higher stability for all of the compounds studied. On the other hand, the comparison of the results obtained with either B3LYP with B1LYP or B3PW91 with mPW1PW91 methods, makes evident that the B3 exchange functional in conjunction with the PW91 functional performs better than other DFT methods employed. On the other hand, the B1LYP model yields the poorest performance.

In order to improve the correlation energy treatment, Gaussian-3 calculations were carried out. As mentioned, the G3//B3LYP model provides effective QCISD(T,FULL) total energies calculated with the G3Large basis set which includes core polarization functions (3d2f polarization functions for chlorine atoms and 2df for oxygen atoms) [37]. The G3MP2Large basis set implemented in the G3(MP2)//B3LYP model does not include core correlation functions. The G3-based treatments are expected to give the more accurate results of the present paper. However, the use of a reduced Møller–Plesset order and the lack of treatment of core correlation effects, yields a slightly poorer

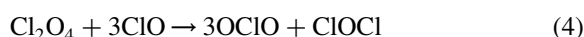
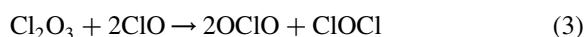
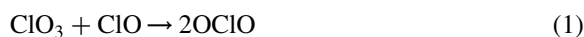
performance of the G3(MP2)//B3LYP model when compared with the G3//B3LYP ones.

Tables 1 and 2 demonstrate that the use of accurate B3LYP/6-311 + G(3d2f) molecular structures and vibrational frequencies in the Gaussian-3 treatments always leads to $\Delta H_{f,298}$ values lower than those obtained with the standard models.

3.2. Heats of formation determined from isodesmic reaction energies

As noted above, an appropriate way to deal with limitations in the treatment of the correlation energy and basis set size is to use suitable isodesmic and isogyric reaction schemes. In fact, more reliable heats of formation are often obtained by combining computed isodesmic enthalpy changes with very well-established thermochemical data for the other molecules involved in the reaction. In this study, the working reactions (1)–(4) were used to determine heats of formation for ClO_3 , ClO_4 , Cl_2O_3 and Cl_2O_4

molecules, respectively.



The computed isodesmic enthalpy changes, $\Delta H_{r,298}$, in combination with the experimental heats of formation for ClO, OCIO and ClOCl of 24.3 ± 0.02 , 22.6 ± 0.3 and 18.5 ± 0.8 kcal mol^{−1} [50,51] were employed to estimate the $\Delta H_{f,298}$ values summarized in Table 3. All calculated enthalpy changes are very different from zero. This fact indicates that Cl–O bond energies for the molecules involved in these reactions are far from being simply additive. When the oxidation state of polyvalent atoms present in an isodesmic reaction is conserved, small enthalpy changes are, sometimes, expected [52].

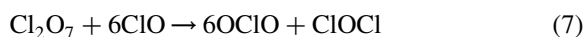
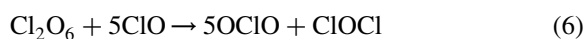
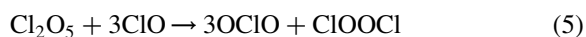
The pronounced differences found between the $\Delta H_{f,298}$ values computed from $\sum D_0$ with the four DFT

Table 3
Enthalpies of isodesmic reactions (1)–(4) and heats of formation (in kcal mol^{−1}) for ClO_3 , ClO_4 , Cl_2O_3 and Cl_2O_4

Level of theory	ClO_3		ClO_4		Cl_2O_3		Cl_2O_4	
	$\Delta H_{r,298}$	$\Delta H_{f,298}$	$\Delta H_{r,298}$	$\Delta H_{f,298}$	$\Delta H_{r,298}$	$\Delta H_{f,298}$	$\Delta H_{r,298}$	$\Delta H_{f,298}$
B3LYP/6-31G(d)	−18.5	29.4	−27.1	46.3	−7.0	22.1	−16.1	29.5
B3LYP/6-311G(d)	−23.9	44.8	−25.4	44.6	−4.3	19.4	−13.9	27.3
B3LYP/6-311 + G(d)	−27.4	48.3	−15.9	35.1	−6.0	21.1	−19.9	33.3
B3LYP/6-311 + G(2d)	−23.5	44.4	−38.7	57.9	−11.9	26.9	−26.5	39.9
B3LYP/6-311 + G(3d)	−23.8	44.7	−38.7	57.9	−14.2	29.3	−27.1	40.5
B3LYP/6-311 + G(3df)	−23.1	44.0	−38.5	57.7	−15.2	30.3	−27.0	40.4
B3LYP/6-311 + G(3d2f)	−23.0	43.9	−38.2	57.4	−15.2	30.3	−26.7	40.1
B3LYP/aug-cc-pVQZ	−22.9	43.8	−42.5	61.7	−14.4	29.5	−27.7	41.1
B3PW91/6-311 + G(3df)	−22.8	43.7	−38.4	57.6	−17.1	32.2	−26.8	40.2
B3PW91/6-311 + G(3d2f)	−22.7	43.6	−38.0	57.2	−17.2	32.3	−26.6	40.0
B3PW91/aug-cc-pVQZ	−22.4	43.3	−41.4	60.6	−15.9	31.0	−27.3	33.4
mPW1PW91/6-311 + G(3df)	−21.5	42.4	−35.1	54.3	−16.7	31.8	−23.5	36.9
mPW1PW91/6-311 + G(3d2f)	−21.4	42.3	−34.7	53.9	−16.5	31.6	−23.0	36.4
mPW1PW91/aug-cc-pVQZ	−21.4	42.3	−36.2	55.4	−15.2	30.3	−23.6	36.3
B1LYP/6-311 + G(3df)	−21.7	42.6	−35.1	54.3	−14.2	29.3	−23.4	36.8
B1LYP/6-311 + G(3d2f)	−21.6	42.5	−34.8	54.0	−14.2	29.3	−23.0	36.4
B1LYP/aug-cc-pVQZ	−21.5	42.4	−30.3	49.5	−12.3	27.4	−22.6	35.3
G3(MP2)//B3LYP	−22.2	43.1	−36.0	55.2	−15.2	30.3	−24.5	37.9
G3(MP2)//B3LYP/6-311 + G(3d2f)	−20.9	41.8	−34.3	53.5	−15.3	30.4	−22.1	35.6
G3//B3LYP	−22.6	43.5	−36.1	55.3	−16.2	31.3	−24.4	37.8
G3//B3LYP/6-311 + G(3d2f)	−21.8	42.7	−35.1	54.3	−17.0	32.1	−23.5	36.9

methods, as well as the large basis set effects observed are notably diminished by using reactions (1)–(4). This improvement is mostly ascribed to compensation effects, which diminish the importance of the truncation in the one-electron basis set. Certainly, the $\Delta H_{f,298}$ values of 50.1 ± 10 , 66.6 ± 14 , 42.2 ± 12 and 53.6 ± 15 kcal mol⁻¹ resulting, respectively, for ClO₃, ClO₄, Cl₂O₃ and Cl₂O₄ after an average of the DFT data calculated with the 6-311 + G(3d2f) basis set, are dramatically reduced to 43.1 ± 1 , 55.6 ± 2 , 30.9 ± 1 and 38.2 ± 2 kcal mol⁻¹ when reactions (1)–(4) are employed. It should be noted that the latter set of values are, in average, only 1 kcal mol⁻¹ higher than those estimated from G3//B3LYP/6-311 + G(3d2f) isodesmic energies. A more detailed comparison between the DFT results consigned in Tables 1 and 3 indicates that the modified version of the Perdew–Wang gradient-corrected exchange functional proposed by Adamo and Barone [33], mPW1PW91, coupled to the 6-311 + G(3d2f) basis, leads to the more accurate predictions. It is interesting to note that the B1LYP model, which gives the worst results by atomization, performs very well when isodesmic reactions (1)–(4) are employed.

As mentioned above, forced by computational limitations, no G3//B3LYP and G3//B3LYP/6-311 + G(3d2f) calculations for Cl₂O₅, Cl₂O₆ and Cl₂O₇ were performed. However, based on the discussed results, the mPW1PW91/6-311 + G(3d2f) functional and the G3(MP2)//B3LYP and G3(MP2)//B3LYP/6-311 + G(3d2f) models are expected to give quite accurate results for these molecules. $\Delta H_{r,298}$ and $\Delta H_{f,298}$ values were determined using the following reactions



For this, a value of $\Delta H_{f,298} = 30.5 \pm 0.7$ kcal mol⁻¹ for ClOOCI [50,51] in conjunction with the $\Delta H_{f,298}$ values given above for the other species was employed. The resulting thermodynamic quantities are summarized in Table 4. Once more, isodesmic reaction schemes predict a higher stability for these higher chlorine oxides.

Table 5 lists the best $\Delta H_{f,298}$ values as calculated from the $\Delta H_{r,298}$ of the isodesmic reactions (1)–(7). The values for ClO₃, ClO₄, Cl₂O₃ and Cl₂O₄ are obtained as a mean of G3//B3LYP and G3//B3LYP/6-311 + G(3d2f) results. These values are very close to those obtained by averaging the G3(MP2)//B3LYP, G3(MP2)//B3LYP/6-311 + G(3d2f) heats of formation. Finally, the best values for Cl₂O₅, Cl₂O₆ and Cl₂O₇ were derived from G3(MP2)//B3LYP and G3(MP2)//B3LYP/6-311 + G(3d2f) calculations. It is interesting to note that the best $\Delta H_{f,298}$ values differ by only 0–1 kcal mol⁻¹ from those predicted at the mPW1PW91/6-311 + G(3d2f) level. In contrast, departures ranging from 0.8 to 7.2 kcal mol⁻¹ are observed when comparisons against B3LYP/6-311 + G(3d2f) calculations are done.

It should be noted that if more accurate $\Delta H_{f,298}$ values for the reference compounds were available, the current calculated thermodynamic data could be readily modified using the listed $\Delta H_{r,298}$ values of Tables 3 and 4. In this context, it can be seen that some of the data extracted from reactions (1) to (7) depend markedly (because of their large stoichiometric coefficients) on $\Delta H_{f,298}$ values of ClO and OCIO. Very small uncertainties remain for ClO (24.3 ± 0.02 [50,51], 24.4 [53], 24.3 ± 0.02 kcal mol⁻¹ [41]) but the value recommended in the last NIST-JANAF thermochemical tables for OCIO,

Table 4

Enthalpies of isodesmic reactions (5)–(7) and heats of formation (in kcal mol⁻¹) for Cl₂O₅, Cl₂O₆ and Cl₂O₇

Level of theory	Cl ₂ O ₅		Cl ₂ O ₆		Cl ₂ O ₇	
	$\Delta H_{r,298}$	$\Delta H_{f,298}$	$\Delta H_{r,298}$	$\Delta H_{f,298}$	$\Delta H_{r,298}$	$\Delta H_{f,298}$
B3LYP/6-311 + G(3d2f)	-30.4	55.8	-46.4	56.1	-60.4	68.7
mPW1PW91/6-311 + G(3d2f)	-28.0	53.4	-43.2	53.2	-53.2	61.5
G3(MP2)//B3LYP	-29.5	54.9	-43.3	53.3	-55.2	63.5
G3(MP2)//B3LYP/6-311 + G(3d2f)	-26.1	51.5	-41.1	51.1	-51.1	59.4

Table 5
Best values for the heat of formation (in kcal mol⁻¹)

Molecule	$\Delta H_{f,0}$	$\Delta H_{f,298}$
ClO ₃	43.9	43.1
ClO ₄	56.1	54.8
Cl ₂ O ₃	32.9	31.7
Cl ₂ O ₄	38.9	37.4
Cl ₂ O ₅	55.5	53.2
Cl ₂ O ₆	55.0	52.2
Cl ₂ O ₇	65.3	61.5

23 ± 2 kcal mol⁻¹ [41] is fairly higher than those reported in Refs. [50,51], 22.6 ± 0.02 kcal mol⁻¹, and in Ref. [53], 22.6 ± 1 kcal mol⁻¹. For instance, if the value 23 kcal mol⁻¹ instead of 22.6 kcal mol⁻¹ is employed in the Cl₂O₇ analysis, a heat of formation a 2.4 kcal mol⁻¹ larger is recovered. It appears interesting to note that an identical G3//B3LYP $\Delta H_{f,298}$ value of 55.9 kcal mol⁻¹ is calculated for ClO₄ by using either reaction (2) or the isodesmic reaction ClO₄ + 3Cl → 4ClO, which does not involve the OClO. This result suggests that the heat of formation for OClO given in Ref. [41] is slightly overestimated. These considerations and the stated uncertainties in the Gaussian-3 methods (close to 1 kcal mol⁻¹ [37]) allow to get conservative error estimates of ± 3 kcal mol⁻¹. Table 5 also shows the best $\Delta H_{f,0}$ values obtained from the $\Delta H_{f,298}$ values corrected for thermal effects. A comparison between previous and present results is given in Section 3.4.

3.3. Bond dissociation pathways for ClO₃, ClO₄, Cl₂O₃, Cl₂O₄, Cl₂O₅, Cl₂O₆ and Cl₂O₇

The knowledge of the energetic changes associated with making and breaking of molecular bonds is of central importance in many chemical fields such as atmospheric [50,51,53] and combustion modeling [54]. We presented here enthalpy values for relevant Cl–O bond fission processes of current molecules. To this end, the heat of formation values given in Table 5 in combination with values for O, Cl, ClO, OClO and ClOO of 59.0, 28.6, 24.2, 23.2 and 23.3 kcal mol⁻¹ at 0 K and of 59.6, 29.0, 24.3, 22.6 and 23.7 kcal mol⁻¹ at 298 K [50,51] were employed. For the Cl(O₃)OO radical, heat of formation values at 0 and 298 K of

36.9 and 36.2 kcal mol⁻¹ as derived from the Cl(O₃)–OO + 3ClO → 3OClO + ClOO isodesmic reaction with the G3(MP2)//B3LYP theory were employed to investigate the Cl₂O₅ dissociation energetics. On the other hand, the small Cl(O₃)–OO bond dissociation enthalpy estimated, 7 kcal mol⁻¹, is consistent with a short dissociative lifetime for this radical. The calculated bond dissociation enthalpies are listed in Table 6.

The present values for the reactions Cl₂O₃ → OClO + ClO, Cl₂O₄ → ClO₃ + ClO, Cl₂O₅ → ClO₃ + ClOO, Cl₂O₅ → ClO₄ + ClO, Cl₂O₆ → ClO₄ + OClO, Cl₂O₆ → ClO₃ + ClO₃ and Cl₂O₇ → ClO₄ + ClO₃ may be compared with those reported by Beltrán et al. [46]. These authors obtained from B3LYP/6-311 + G(3df) + ZPE energies, the following ΔH_0 values: 8.6, 19.9, 4.8, 23.5, 16.9, 24.2 and 25.3 kcal mol⁻¹, respectively. An inspection of Table 6 indicates that these values are up to 9 kcal mol⁻¹ smaller than ours. In order to elucidate the causes of such large differences, it should be noted that bond dissociation energies are not isogyric and, therefore, they constitute a difficult calculation test that could reveal systematic errors in the methods employed. This problem is largely diminished because the dissociation enthalpies given in Table 6 have been estimated from $\Delta H_{f,0}$ and $\Delta H_{f,298}$ values resulting from sound isodesmic and isogyric working reactions besides of other well-established thermodynamic data.

Table 6
Bond dissociation enthalpies (in kcal mol⁻¹) for ClO₃, ClO₄, Cl₂O₃, Cl₂O₄, Cl₂O₅, Cl₂O₆ and Cl₂O₇

Reaction	ΔH_0	ΔH_{298}
ClO ₃ → OClO + O	38.3	39.1
ClO ₄ → ClO ₃ + O	46.8	47.9
Cl ₂ O ₃ → OClO + ClO	14.5	15.2
Cl ₂ O ₃ → ClO ₃ + Cl	39.6	40.4
Cl ₂ O ₄ → ClO ₃ + ClO	29.2	30.0
Cl ₂ O ₄ → ClO ₄ + Cl	45.8	46.4
Cl ₂ O ₄ → Cl ₂ O ₃ + O	53.0	53.9
Cl ₂ O ₅ → Cl(O ₃)OO + Cl	10.0	12.0
Cl ₂ O ₅ → ClO ₃ + ClOO	11.7	13.6
Cl ₂ O ₅ → ClO ₄ + ClO	24.8	25.9
Cl ₂ O ₆ → ClO ₄ + OClO	24.3	25.2
Cl ₂ O ₆ → ClO ₃ + ClO ₃	32.8	34.0
Cl ₂ O ₇ → ClO ₄ + ClO ₃	34.7	36.4

Several values have been reported for the $\text{Cl}_2\text{O}_3 \rightarrow \text{OCIO} + \text{ClO}$ reaction. From static photolysis studies of the established equilibrium over the range 233–273 K, Hayman and Cox [11] have determined a value of $\Delta H_0 = 15 \pm 3 \text{ kcal mol}^{-1}$. Burkholder et al. [14], employed a laser flash photolysis technique to study the equilibrium between 232 and 258 K. From a second law analysis of their results along with those reported in Ref. [11], the value $\Delta H_0 = 11.1 \pm 1.2 \text{ kcal mol}^{-1}$ was obtained. A somewhat higher value of $12.3 \pm 3 \text{ kcal mol}^{-1}$ was derived by López et al. [55] from the thermal decomposition of OCIO at 318–333 K. More recently, the value $10.9 \text{ kcal mol}^{-1}$ was predicted by Clark and Francisco [19] using CCSD(T)/6-311 + G(3df)//B3LYP/6-311 + G(3df) calculations. Our value, $14.5 \pm 3 \text{ kcal mol}^{-1}$, agrees nicely with the data of Hayman and Cox [11] but it is, within the stated errors, in satisfactory agreement with those of other authors [14,19,55]. It should be noted that direct calculations performed at the G3//B3LYP/6-311 + G(3d2f) level give $\Delta H_0 = 15.2 \text{ kcal mol}^{-1}$. On the other hand, the present value of $\Delta H_0 = 39.6 \text{ kcal mol}^{-1}$ predicted for the $\text{Cl}_2\text{O}_3 \rightarrow \text{ClO}_3 + \text{Cl}$ decomposition channel, agrees reasonably with the CCSD(T)/6-311 + G(3df)//B3LYP/6-311 + G(3df) estimation of $37.7 \text{ kcal mol}^{-1}$ [20].

The formation of ClO_3 but not of ClO_4 in the vacuum flash pyrolysis of Cl_2O_4 at 673 K [56,57] is quite consistent with the energetics of the two decomposition channels given for this molecule in Table 6. Similar experiments carried out for Cl_2O_6 show that in agreement with our results, ClO_4 radicals are exclusively generated according to reaction $\text{Cl}_2\text{O}_6 \rightarrow \text{ClO}_4 + \text{OCIO}$ [58,59].

It appears interesting at this stage to compare the calculated $\text{Cl}(\text{O}_3)\text{--OCl}(\text{O}_3)$ bond strength against the value determined by Schumacher and co-workers [60] from the study of the thermal decomposition of this oxide. In that work, a high pressure limit activation energy measured at 373–393 K for reaction $\text{Cl}_2\text{O}_7 \rightarrow \text{ClO}_4 + \text{ClO}_3$ of $32.9 \pm 1.5 \text{ kcal mol}^{-1}$ was determined. This is consistent with our estimates of $E_{a,\infty} \approx \Delta_0 + RT = 35.3 \pm 3 \text{ kcal mol}^{-1}$.

No maxima in the electronic potentials for most of the feasible bond fission reactions of Table 6 are expected. Therefore, the consigned enthalpy changes are normally very close to the respective bond dissociation energy values. On thermodynamic

grounds, neither Cl_2O_3 nor Cl_2O_4 are probably formed by reaction of Cl atoms with either ClO_3 or ClO_4 . In fact, the highly vibrationally excited Cl_2O_3 and Cl_2O_4 species that could be initially formed, are surely short-lived enough to be collisionally stabilized. Therefore, they dissociate preferentially according to the following sequences: $\text{ClO}_3 + \text{Cl} \rightarrow \text{Cl}_2\text{O}_3^* \rightarrow \text{OCIO} + \text{ClO}$ ($\Delta H_{298} = -25.2 \text{ kcal mol}^{-1}$) and $\text{ClO}_4 + \text{Cl} \rightarrow \text{Cl}_2\text{O}_4^* \rightarrow \text{ClO}_3 + \text{ClO}$ ($\Delta H_{298} = -16.4 \text{ kcal mol}^{-1}$). Another, possible reactions that could play a role are: $\text{ClO}_4 + \text{ClO} \rightarrow \text{Cl}_2\text{O}_5^* \rightarrow \text{Cl}(\text{O}_3)\text{OO} + \text{Cl}$ ($\Delta H_{298} = -13.9 \text{ kcal mol}^{-1}$) and $\text{ClO}_4 + \text{ClO} \rightarrow \text{Cl}_2\text{O}_5^* \rightarrow \text{ClO}_3 + \text{ClOO}$ ($\Delta H_{298} = -12.3 \text{ kcal mol}^{-1}$). The less exothermic channel $\text{ClO}_3 + \text{ClO}_3 \rightarrow \text{Cl}_2\text{O}_6^* \rightarrow \text{ClO}_4 + \text{OCIO}$ ($\Delta H_{298} = -8.8 \text{ kcal mol}^{-1}$) does not appear to contribute significantly at normal conditions [5], being the collisionally mediated processes forming Cl_2O_6 dominant over unimolecular rates leading to $\text{ClO}_4 + \text{OCIO}$ products. To elucidate the interplay between collisional and dissociative processes in these complex-forming reactions, a quantitative analysis in terms of unimolecular reaction rate theories on reliable potential energy surfaces is required [61–64].

3.4. Comparison with previous heats of formation values

Most of the available heats of formation have been estimated from calculated atomization total energies [17–23] at different DFT and ab initio levels. However, data derived from theoretical analysis of experimental kinetics and equilibrium studies [11–14], from appearance energies of fragment ions from different chlorine oxides [15], and from valence additivity schemes [16] have been also reported. Therefore, the comparison of our calculated values for the ClO_3 , ClO_4 , Cl_2O_3 , Cl_2O_4 , Cl_2O_6 and Cl_2O_7 molecules against previous values appears appropriate at this stage.

ClO_3 . This is one of the most studied molecules. From an analysis in terms of the unimolecular reaction rate theory of measured low-pressure rate coefficients for the recombination reaction between O atoms and OCIO, a value of $55.6 \pm 4 \text{ kcal mol}^{-1}$ at 0 K was estimated by Colussi [12]. A reevaluation of those experiments by Zabel [9] is consistent with a smaller heat of formation value of 47 kcal mol^{-1} .

More recently Colussi et al. [13] suggested a value of $51.9 \pm 5 \text{ kcal mol}^{-1}$ from a theoretical analysis similar to the one employed in Ref. [12] of more detailed experiments. Different levels of quantum-chemical calculations have been employed to study the energetics of ClO_3 . By using the G1 theory [65, 66], Rathmann and Schindler [17] obtained a heat of formation of 48 kcal mol^{-1} at 0 K. A G2 model [67] with vibrational frequencies calculated at the MP2/6-311G(2df) level was employed by Rauk et al. [18] to estimate $\Delta H_{f,0} = 47.2 \text{ kcal mol}^{-1}$ and $\Delta H_{f,298} = 45.9 \text{ kcal mol}^{-1}$. More recently, the $\text{ClO}_3 + \text{Cl} \rightarrow \text{OCIO} + \text{ClO}$ reaction has been used by Workman and Francisco [20] to determine, at the CCSD(T)/6-311 + G(3df)/CCSD(T)/6-311G(2df) level of theory, the values $\Delta H_{f,0} = 46.0 \pm 3.0 \text{ kcal mol}^{-1}$ and $\Delta H_{f,298} = 44.6 \pm 3.0 \text{ kcal mol}^{-1}$. Besides, they have obtained values a 5 kcal mol^{-1} higher at the B3LYP/6-311 + G(3df) level. In contrast, as Table 3 shows a very good agreement between average $\Delta H_{f,298}$ values calculated with DFT and Gaussian-3 theories were here obtained. The value $\Delta H_{f,298} = 48.7 \text{ kcal mol}^{-1}$ has been calculated by Janoschek [21] with the B3LYP/cc-pV5Z functional. More recently, Zhu and Lin [23] employed a G2M/B3LYP/6-311 + G(3df) approach [68] to compute $\Delta H_{f,298} = 47.2 \pm 2.7 \text{ kcal mol}^{-1}$. The $\Delta H_{f,298}$ values determined from ClO_3 atomization in Refs. [17,18,21,23] agree within $\pm 2 \text{ kcal mol}^{-1}$ with the present G3//B3LYP/6-311 + G(3d2f) estimation of $47.7 \text{ kcal mol}^{-1}$.

Janoschek's $\Delta H_{f,298}$ values [21] for ClO , OCIO and ClO_3 of 23.1, 24.5 and $48.7 \text{ kcal mol}^{-1}$, respectively, have been used here to calculate $\Delta H_{r,298} = -22.8 \text{ kcal mol}^{-1}$ for reaction (1). The $\Delta H_{f,298} = 43.7 \text{ kcal mol}^{-1}$ thus obtained compares very well with our B3LYP/6-311 + G(3d2f) estimate of $43.9 \text{ kcal mol}^{-1}$ and our best value of $43.1 \text{ kcal mol}^{-1}$. Our recommended value for ClO_3 agrees reasonably well with a recent critical evaluation of $46 \pm 3 \text{ kcal mol}^{-1}$ [41]. However, it differs significantly from those reported in other data compilations of $52 \pm 4 \text{ kcal mol}^{-1}$ [53] and $55.6 \pm 4.1 \text{ kcal mol}^{-1}$ [50,51] which are respectively based on the results of Refs. [12] and [13].

ClO_4 . Colussi and Grela [16] have employed the activation energy value measured for $\text{Cl}_2\text{O}_7 \rightarrow \text{ClO}_3 + \text{ClO}_4$ [60] in conjunction with values of 65 and 48 kcal mol^{-1} for Cl_2O_7 and ClO_3 [17],

respectively, to estimate $\Delta H_{f,298} = 50 \text{ kcal mol}^{-1}$. In addition, these authors proposed for ClO_4 , a heat of formation of 47 kcal mol^{-1} based on electron impact data for Cl_2O_7 [69,70]. More recently, a $\Delta H_{f,298} = 66.3 \text{ kcal mol}^{-1}$ has been predicted by Janoschek from B3LYP/cc-pV5Z calculations [21]. This value agrees quite well with the present B3LYP/6-311 + G(3d2f) estimation of $66.4 \text{ kcal mol}^{-1}$ determined from ClO_4 atomization energies.

We have used reaction (2) and the Janoschek's data [21] for ClO , OCIO and ClO_4 (see above) to estimate $\Delta H_{f,298} = 58.2 \text{ kcal mol}^{-1}$, which compare very well with our B3LYP/6-311 + G(3d2f) value of $57.4 \text{ kcal mol}^{-1}$ and it is now in better agreement with our best estimation of $54.8 \text{ kcal mol}^{-1}$.

Cl_2O_3 . Aforementioned studies of this molecule lead to $\Delta H_{f,0}$ values of 34 ± 3 [11] and $36.5 \text{ kcal mol}^{-1}$ [14,19]. The first one compares better with our estimates of $32.9 \pm 3 \text{ kcal mol}^{-1}$. Recently, Li et al. [22] have employed G2 and G3 theories to investigate via atomization energies, the thermochemistry of several chlorine oxides. Using G3 theory [71], they calculated the heat of formation at 298 K to be $36.8 \text{ kcal mol}^{-1}$, close to our G3//B3LYP value of $37.8 \text{ kcal mol}^{-1}$ obtained from Cl_2O_3 atomization. We have used reaction (3) in conjunction with G3 enthalpies (H_{298}) for ClOCl and Cl_2O_3 given by these authors and computed values for ClO and OCIO of -535.116854 and -610.238712 hartree, to estimate $\Delta H_{f,298} = 30.5 \text{ kcal mol}^{-1}$. This value compares favorably with our best estimation of $31.7 \text{ kcal mol}^{-1}$ which in turns agrees with a recommended value of $33 \pm 3 \text{ kcal mol}^{-1}$ [72]. Recent recommended values of 37 ± 3 [53] and 37 kcal mol^{-1} [50,51] are based on experimental data from Ref. [14].

Cl_2O_4 . Colussi and Grela [16] have proposed a valence bond additivity scheme to estimate thermochemical data of a number of chlorine containing compounds. From this, they obtain for Cl_2O_4 a value of $37.2 \text{ kcal mol}^{-1}$, which is in excellent agreement with our best estimate of $37.4 \text{ kcal mol}^{-1}$. Rühl et al. [15] have performed photoionization mass spectrometry studies of several chlorine oxides. From measurements of the appearance energy for $\text{ClO}^+(^3\Sigma^-)$ formed according to the $\text{Cl}_2\text{O}_4 + h\nu \rightarrow \text{ClO}^+ + \text{ClO}_3 + e^-$ fragmentation process, a $\Delta H_{f,298} = 43 \pm 6 \text{ kcal mol}^{-1}$ was derived by using

values of 274 ± 2 and 52 ± 5 kcal mol⁻¹ for ClO⁺ and ClO₃, respectively. If instead of the latter, the current value of 43.1 kcal mol⁻¹ is used for ClO₃, a $\Delta H_{f,298} = 33 \pm 6$ kcal mol⁻¹ results, which is in better agreement with our best result. On the other hand, if the working reaction (4) is employed to interpret the data of Li et al. [22], a value of 35.6 kcal mol⁻¹ at 298 K is recovered. By contrast, the G3 value they derive from atomization energies for Cl₂O₄ is 44.5 kcal mol⁻¹.

Cl₂O₅. To our knowledge, only two heats of formation data have been reported for Cl₂O₅ peroxide to date. Colussi and Grela [16] suggests a value of 50.7 kcal mol⁻¹ based on additivity grounds, while a larger $\Delta H_{f,298} = 61.7$ kcal mol⁻¹ has been calculated by Li et al. [22] with the G3 model. As before, by using the isodesmic method (reaction (5)), a smaller value is recovered, 52.4 kcal mol⁻¹ from the latter study. Both, the data of Colussi and Grela [16] and the reevaluated value of Li et al. [22] are in remarkably agree with ours.

Cl₂O₆. The bond additivity method predicts a heat of formation value of 52 kcal mol⁻¹ for this molecule [16]. A larger value of 60 ± 8 kcal mol⁻¹ has been determined from the Cl₂O₆ photofragmentation process which yields the species ClO₃ and ClO₃⁺ (with assumed heats of formation of 52 and 310 kcal mol⁻¹, respectively) [15]. A smaller value of 52 kcal mol⁻¹ is obtained by using our estimate of 43.1 kcal mol⁻¹ for ClO₃. More recently, a $\Delta H_{f,298} = 66.6$ kcal mol⁻¹ derived from G3 calculations has been reported by Li et al. [22]. This value is dramatically reduced to 52.0 kcal mol⁻¹ if reaction (6) is used. The $\Delta H_{f,298}$ value of Colussi and Grela [16] and the reevaluated values of Rühl et al. [15] and Li et al. [22] are in excellent agreement with our best value of 52.2 kcal mol⁻¹.

Cl₂O₇. Additivity estimations lead to the $\Delta H_{f,298} = 54.8$ kcal mol⁻¹ [16]. However, repulsive interactions between the ClO₃ moieties are expected to increase this value. Rühl et al. [15] have determined the value $\Delta H_{f,298} = 65 \pm 4$ kcal mol⁻¹ from appearance energy measurements of ClO₃⁺, which is assumed to be generated in the photoionization reaction $\text{Cl}_2\text{O}_7 + h\nu \rightarrow \text{ClO}_3^+ + \text{ClO}_4 + \text{e}^-$. Although this value is in reasonable agreement with the present estimation of 61.5 kcal mol⁻¹, it is based on a heat of formation value for ClO₄ of 47 kcal mol⁻¹.

Thus, if instead of the latter, our value of 54.8 kcal mol⁻¹ is employed, a larger Cl₂O₇ heat of formation of 74 kcal mol⁻¹ is recovered. Finally, like for Cl₂O₃, Cl₂O₄, Cl₂O₅, Cl₂O₆ oxides, we have employed calculated G3 data by Li et al. [22] to estimate the heat of formation of Cl₂O₇ via reaction (7). In this way, the value of 76.8 kcal mol⁻¹ computed by atomization energies [22] is notably reduced to 59.5 kcal mol⁻¹. This value is quite consistent with the one estimated here.

4. Conclusions

A variety of theoretical procedures have been applied to estimate heats of formation values for ClO₃, ClO₄, Cl₂O₃, Cl₂O₄, Cl₂O₅, Cl₂O₆ and Cl₂O₇ molecules. Large basis set effects on $\Delta H_{f,298}$ determined from B3LYP atomization energies for ClO₃, ClO₄, Cl₂O₃, Cl₂O₄ have been observed. The values computed from DFT atomization energies are notably larger than those obtained using a selected set of isodesmic reactions which involve high-quality thermochemical data and lead to our best estimations. These $\Delta H_{f,298}$ values calculated from averaging G3//B3LYP and G3//B3LYP/6-311 + G(3d2f) results are 43.1, 54.8, 31.7 and 37.4 kcal mol⁻¹, respectively. For the larger Cl₂O₅, Cl₂O₆ and Cl₂O₇ molecules, values of 53.2, 52.2 and 61.5 kcal mol⁻¹ were derived using the G3(MP2)//B3LYP and G3(MP2)//B3LYP/6-311 + G(3d2f) models. The mPW1PW91/6-311 + G(3d2f) hybrid functional produce $\Delta H_{f,298}$ within 1 kcal mol⁻¹ with the values given above. Cl–O bond dissociation energies for all of the compounds are given. In addition, predictions for the occurrence of some reactions involving the formation of highly excited stable chlorine oxides are suggested. A detailed comparison of the obtained results with recent experimental and theoretical data allows to assume that the here reported heats of formation reduce significantly the uncertainties in the knowledge of this important property.

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