



Research paper

Theoretical study of the thermochemistry of chlorine oxyfluorides



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ABSTRACT

There is a lack of experimental thermochemical values for most chlorine oxyfluorides. Previous high level theoretical, CCSD(T), results showed uncommonly large errors in the standard heats of formation calculated through the atomization method. We propose that the differences are due to unusually large contributions to energy from higher excitations within the coupled cluster framework, and we tackle the problem by using a calculation scheme based on isodesmic reactions. Our suspicions are supported by results of static correlation diagnostics. Our final recommended values are in better agreement with the experimental data available. Other thermodynamic properties are also calculated.

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1. Introduction

Halogen oxyfluorides (ClF_mO_n) are an interesting field of study because they exhibit a large range of oxidation states, from $-I$ to $+VII$ [26], and coordination numbers. These overvalent species are very reactive and they are mainly used as fluorinating agents and strong oxidizers [1,27]. A consequence of this is the lack of experimental values for their thermodynamic properties. A common approach to solve this is to estimate these values computationally.

Previous attempts to calculate standard Heats of Formation (HOF) for ClO_mF_n series [26] by the total atomization energy (TAE) method [17] at the CCSD(T) [19] level of theory, resulted in abnormally inaccurate values, compared to CCSD(T) mean error [12]. This is also the case for composite methods [5].

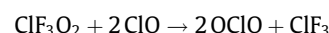
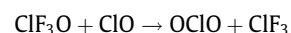
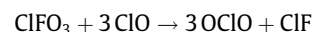
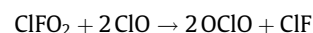
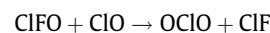
In this work the compounds of the ClF_mO_n family were analyzed. They were suspected to have a similar behavior to those belonging to the Cl_mF_n family, not only due to their similar composition and chemical reactivity, but also due to the previous results by Dixon [26] which show errors of $4.0 \text{ kcal}\cdot\text{mol}^{-1}$ for ClF_3O and $2.8 \text{ kcal}\cdot\text{mol}^{-1}$ for ClFO_3 when compared to experimental values. These errors are substantially higher than the mean error for the method used, approximately $0.4 \text{ kcal}\cdot\text{mol}^{-1}$ for CCSD(T)/CBS [12], for well behaved medium sized molecules. The available tests suggest that the contribution due to the superior excitations to the TAE must be large for these compounds. For example Karton estimated [9] that when the value of %TAE(T) diagnostic is greater than 10%, the post-CCSD(T) contribution to the total atomization energy can surpass the $1 \text{ kcal}\cdot\text{mol}^{-1}$ for a considerable amount.

These contributions which are unaccounted for at the CCSD(T) level of theory can lead to the discrepancies observed by Dixon. Therefore in this work, the HOF values were calculated using an isodesmic reaction scheme [32], that, thanks to an important compensation of the systematic errors, results in better estimates.

2. Methods

The A_k [7] and the %TAE(T) diagnostics [10] were used in order to test our hypothesis about the large contribution of superior excitations to the TAE. The standard enthalpy of formation were calculated by using several composite methods (G3MP2B3, G3B3, CBS-QB3 and G4) via atomization reaction scheme. The result would go in support of our hypothesis if they present large differences among them. Here, every electronic structure calculation was performed with the ORCA program [14], except those of composite methods for which Gaussian09 [8] was used.

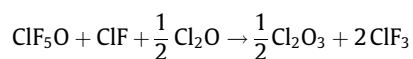
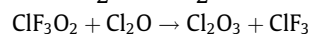
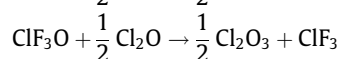
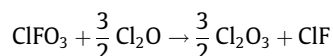
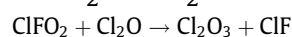
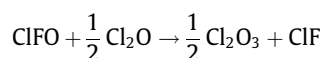
The best values of this work were obtained through the isodesmic reactions procedure in conjunction with the CCSD(T) method. For each molecule two different isodesmic reactions were considered. The whole reaction pool was divided into two sets, the first of which consist in the following reactions



while the second one is made up the reactions listed below

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To be able to perform the isodesmic calculation scheme, the following accepted HOF were used, all in units of $\text{kcal}\cdot\text{mol}^{-1}$: 23.45 ± 0.14 for OCIO [3]; 24.3086 ± 0.0084 for ClO [23,22]; -13.3088 ± 0.0143 for ClF [23,22]; -39.6 for ClF_3 [24]; 19.43 ± 0.43 for ClOCl [3] and 33.5 ± 1.2 for Cl_2O_3 [3].

The results reported in the supporting information of the reference [10] were used in order to estimate the HOFs for F_2 , O_2 and Cl_2 at a level of theory similar to the one employed in the reference [26], that is $\text{CCSD(T)}/\text{CBS}$. With these estimates and the results from Dixon's work, the HOF were recalculated by using the formation reaction and the Hess's law.

The final recommended values correspond to a weighted average of the those from isodesmic and formation reactions.

The equilibrium geometries were obtained at the $\text{B3LYP}/\text{def2-TZVPP}$ [2,11,30,25,31] level of theory. The vibrational and rotational constants were obtained at the $\text{B3LYP}/6-311+\text{G}(3\text{d}2\text{f})$ [13,4] level of theory. For the calculation of zero point energy corrections the unscaled harmonic frequencies were used. They were also employed in conjunction with the rotational constants for the calculation of thermal corrections to energy. Basis set convergence difficulties were encountered for ClF_n [20,24]. In order to ensure that the results are not overly compromised by the basis set truncation error, in this work the different contributions to electronic energy of the isodesmic reactions were calculated by employing different basis sets, and their convergence was examined. For the CCSD(T) calculations the def2-SVP , def2-TZVPP and def2-QZVPP basis sets [31] were used. For the SCF part [21,18] calculations employing the cc-pV6Z [29,33] basis set were also performed, by using the chain-of-spheres algorithm [16] with the corresponding auxiliary basis set. The latter are in fact the final values used for this contribution to the energy.

For the sake of completeness, the isodesmic procedure was also applied in conjunction with the composite methods on the two sets of reactions.

3. Results and discussion

The results of the static correlation diagnostic tests are compiled in Table 1.

According to the results of $\%TAE[T]$ and A_i tests, all the molecules have a large contribution of static correlation. As $\%TAE[T]$

Table 1

All tests were conducted using results calculated with the def2-QZVPP basis set. For reference the thresholds for each of the tests are, according to their authors: (a) $\%TAE[T] > 10\%$ indicates a severe to pathological case; (b) A_i value close to unity indicates significant static correlation.

	$\%TAE[T]$	A_i
ClFO	14.9	0.90
ClFO_2	13.0	0.78
ClFO_3	11.5	0.69
ClF_3O	15.0	0.90
ClF_3O_2	14.9	0.88
ClF_5O	16.1	0.95

and A_i are proportional to each other, and the $\%TAE[T]$ diagnostic is based of its linear relationship to the superior excitations, we prefer to take a more conservative stance and just state that: The test results suggest that the contribution of the superior excitations to the TAE is quite likely to be large.

In order to ensure that $\%TAE[T]$ results are not basis set dependent for these cases, the test was also run with the def2-TZVPP basis set, resulting in very small differences, around 0.1%.

The results for the HOF at 298.15 K calculated using the composite methods are compiled in Table 2. Those obtained by using the atomization energy method exhibit a large dispersion for each molecule. This dispersion is greatly decreased by employing isodesmic reactions, this is a testament to the large systematic errors compensation that takes place under this procedure.

3.1. HOF calculations

Finally the HOFs were calculated by using the Dunning's sextuple zeta basis sets (cc-pV6Z) for the SCF part, while the correlation energies were obtained by employing the Ahlrich's def2-TZVPP and def2-QZVPP basis sets in conjunction with a Helgaker's like extrapolation scheme with an exponent of 2.97 as was suggested in Ref. [15].

The values obtained through the formation reactions, by using the results by Karton and Dixon, are a marked improvement over those originally obtained through the atomization method. They are also consigned in Table 2.

3.1.1. Reliability of the results

In order to examine the degree of proximity to CBS values, the isodesmic reaction electronic energies were decomposed into their components obtained for a number of basis sets which belong to the Ahlrich's family, ranging from double to quadruple zeta. The results for both sets of isodesmic reactions are compiled in Tables 3 and 4.

The very small difference between the results for def2-QZVPP and those of the $3/4\zeta$ basis set extrapolation, around 0.40 for the largest cases, indicates that they are very near the CBS limit.

The core-valence effects are small, the errors that arises due to neglecting these effects are already relatively small within the atomization method, in the order of $0.3\text{--}0.9 \text{ kcal}\cdot\text{mol}^{-1}$ [26]. They are further compensated in the isodesmic framework therefore they were not taken into account.

In the case of ClFO_2 there is not any reliable experimental value available. One of the cited in the references seems to be a very coarse estimate obtained by comparison with bond energies of well characterized Cl-O and Cl-F containing compounds.

For ClFO_3 the contribution of the perturbative triples is quite large, as can be seen in Tables 3 and 4, which seems to indicate that the contribution of higher excitations could be important. The experimental values for this molecule are -5.12 ± 0.68 , -5.3 ± 4 , and $-5.6 \pm 1.2 \text{ kcal}\cdot\text{mol}^{-1}$. It is clear from Table 2 that the atomization method is outperformed by the other calculation schemes for the gold standard method. This is remarkable because ClFO_3 is the best experimentally characterized specie of the series.

The ClF_3O is an interesting case as the results seem to be among the least disperse, and with very small contributions from doubles and triple excitations. Although it could be said that they are very accurate, when compared with the experimental value of $-35.4 \pm 1.5 \text{ kcal}\cdot\text{mol}^{-1}$, they seem to be systematically overestimated. Considering the large uncertainty of the measured value and the apparent accuracy of our result, it is likely that the former value is slightly underestimated.

In general terms, the results obtained by the isodesmic and formation reaction methods are fairly similar to each other. By comparing our results with those informed by Dixon, the latter tend

Table 2
Heats of formation at 298.15 K (in kcal·mol⁻¹).

	ClFO	ClFO ₂	ClFO ₃	ClF ₃ O	ClF ₃ O ₂	ClF ₅ O
			<i>Atomization</i>			
G3MP2B3	3.1	-8.3	2.0	-31.9	-2.8	-27.3
G3B3	2.5	-9.6	-1.0	-34.1	-6.4	-31.5
CBS-QB3	0.5	-12.8	-6.6	-36.2	-17.0	-34.8
G4	0.5	-13.3	-8.4	-38.9	-13.7	-38.5
CCSD(T) ^a	5.8	-8.2	-2.3	-31.4	-5.1	-27.2
			<i>Isodesmic 1</i>			
G3MP2B3	3.2	-9.4	-0.4	-33.6	-5.6	-30.7
G3B3	3.9	-8.4	-0.1	-33.1	-5.6	-30.9
CBS-QB3	6.1	-4.9	3.6	-31.2	-9.6	-30.3
G4	4.8	-7.9	-1.8	-32.8	-6.4	-30.6
CCSD(T)	5.6	-8.1	-2.9	-32.9	-8.0	-32.6
			<i>Isodesmic 2</i>			
G3MP2B3	3.5	-8.8	0.5	-33.3	-5.1	-30.4
G3B3	3.7	-8.8	-0.7	-33.4	-6.0	-31.1
CBS-QB3	4.4	-8.4	-1.6	-32.9	-13.1	-32.1
G4	3.9	-9.6	-4.4	-33.7	-8.2	-31.5
CCSD(T)	4.5	-10.2	-6.0	-34.0	-10.0	-33.6
			<i>Formation Reaction^b</i>			
CCSD(T)	4.9	-9.4	-3.8	-33.0	-7.0	-29.6
			<i>Best estimates^c</i>			
	4.7	-9.8	-5.2	-33.7	-9.2	-32.8

^a Results from Dixon's work.^b Obtained by combining Dixon and Karton's values.^c Following the description given in the Recommended Values subsection.**Table 3**
Energy contributions (in kcal·mol⁻¹) at different basis levels for the first set of isodesmic reactions.

	ClFO	ClFO ₂	ClFO ₃	ClF ₃ O	ClF ₃ O ₂	ClF ₅ O
HF/def2-SVP	1.23	32.87	64.93	9.62	19.16	-1.53
HF/def2-TZVPP	-10.01	21.27	49.08	4.56	6.14	-8.06
HF/def2-QZVPP	-10.75	19.71	46.07	3.34	3.39	-10.88
HF/cc-pV6Z	-10.87	19.42	45.46	3.13	2.86	-11.35
			<i>Contributions to correlation energy</i>			
CCSD/def2-SVP	-8.99	-24.93	-51.58	-9.98	-30.93	-17.01
CCSD/def2-TZVPP	-8.28	-22.47	-46.56	-9.09	-27.97	-15.50
CCSD/def2-QZVPP	-8.68	-22.83	-47.20	-9.33	-28.55	-15.96
(T)/def2-SVP	-0.48	-2.50	-7.69	-0.46	-4.41	-3.00
(T)/def2-TZVPP	-0.46	-2.89	-8.80	-0.71	-5.49	-4.29
(T)/def2-QZVPP	-0.44	-2.98	-9.25	-0.76	-5.83	-4.68
CCSD(T)/def2-SVP	-9.47	-27.44	-59.27	-10.44	-35.34	-20.01
CCSD(T)/def2-TZVPP	-8.75	-25.36	-55.36	-9.80	-33.46	-19.79
CCSD(T)/def2-QZVPP	-9.12	-25.82	-56.45	-10.09	-34.38	-20.64
Extrapolation (3 ζ /4 ζ)	-9.40	-26.15	-57.27	-10.30	-35.06	-21.27

Table 4
Energy contributions (in kcal·mol⁻¹) at different basis levels for the second set of isodesmic reactions.

	ClFO	ClFO ₂	ClFO ₃	ClF ₃ O	ClF ₃ O ₂	ClF ₅ O
HF/def2-SVP	-9.01	12.39	34.21	-0.62	-1.32	-11.77
HF/def2-TZVPP	-12.12	17.05	42.74	2.45	1.92	-10.17
HF/def2-QZVPP	-11.99	17.23	42.35	2.10	0.90	-12.12
HF/cc-pV6Z	-11.93	17.31	42.29	2.08	0.74	-12.41
			<i>Contributions to correlation energy</i>			
CCSD/def2-SVP	1.05	-4.85	-21.45	0.07	-10.84	-6.97
CCSD/def2-TZVPP	0.69	-4.52	-19.64	-0.11	-10.02	-6.52
CCSD/def2-QZVPP	0.53	-4.40	-19.56	-0.12	-10.12	-6.74
(T)/def2-SVP	-0.27	-2.09	-7.08	-0.26	-4.00	-2.79
(T)/def2-TZVPP	-0.10	-2.16	-7.70	-0.35	-4.76	-3.93
(T)/def2-QZVPP	-0.05	-2.21	-8.09	-0.37	-5.06	-4.29
CCSD(T)/def2-SVP	0.78	-6.94	-28.52	-0.19	-14.85	-9.76
CCSD(T)/def2-TZVPP	0.59	-6.68	-27.33	-0.46	-14.78	-10.45
CCSD(T)/def2-QZVPP	0.48	-6.61	-27.65	-0.49	-15.17	-11.03
Extrapolation (3 ζ /4 ζ)	0.40	-6.56	-27.88	-0.51	-15.47	-11.47

Table 5

Standard molar entropies ($S_m^\circ(T)$ in $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) and standard molar heat capacities at constant pressure ($C_{p,m}^\circ(T)$ in $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), difference between molar standard enthalpy at temperature T and molar standard enthalpy at 298.15 K ($H_m^\circ(T^*)$ in $\text{kJ}\cdot\text{mol}^{-1}$).

Specie	Property	200 K	298.15 K	400 K	500 K	600 K	700 K	800 K
ClFO	$H_m^\circ(T^*)$	−4.3	0.0	4.8	9.9	15.1	20.5	26.0
	$C_{p,m}^\circ(T)$	41.1	45.7	49.2	51.6	53.2	54.3	55.1
	$S_m^\circ(T)$	246.7	264.0	278.0	289.2	298.8	307.1	314.4
ClFO ₂	$H_m^\circ(T^*)$	−5.2	0.0	6.2	12.8	19.8	27.2	34.7
	$C_{p,m}^\circ(T)$	47.9	57.1	63.8	68.5	71.9	74.3	76.0
	$S_m^\circ(T)$	258.7	279.7	297.4	312.2	325.0	336.3	346.3
ClFO ₃	$H_m^\circ(T^*)$	−5.8	0.0	7.3	15.4	24.1	33.3	42.8
	$C_{p,m}^\circ(T)$	51.6	66.0	76.8	84.3	89.7	93.6	96.4
	$S_m^\circ(T)$	256.3	279.7	300.7	318.7	334.6	348.7	361.4
ClF ₃ O	$H_m^\circ(T^*)$	−7.1	0.0	8.5	17.6	27.2	37.0	47.1
	$C_{p,m}^\circ(T)$	64.0	78.8	88.0	93.6	97.2	99.7	101.4
	$S_m^\circ(T)$	277.6	306.1	330.7	351.0	368.4	383.5	397.0
ClF ₃ O ₂	$H_m^\circ(T^*)$	−7.7	0.0	9.7	20.3	31.6	43.3	55.4
	$C_{p,m}^\circ(T)$	67.4	87.8	101.3	109.8	115.5	119.4	122.2
	$S_m^\circ(T)$	276.8	307.7	335.6	359.2	379.7	397.9	414.0
ClF ₅ O	$H_m^\circ(T^*)$	−9.2	0.0	11.8	24.7	38.3	52.6	67.1
	$C_{p,m}^\circ(T)$	78.4	106.2	123.4	133.5	139.9	144.2	147.1
	$S_m^\circ(T)$	279.2	316.1	350.0	378.7	403.6	425.5	445.0

to be systematically overestimated, and in some cases greatly so. It is reasonable if the superior excitations, which are almost uncompensated in atomization reactions, are large.

3.2. Recommended values

Values from the second set of isodesmic reactions are closer to available experimental data than those from the first one and the formation reaction set. They all clearly improve upon the atomization reaction scheme.

Given the different values obtained with the three reactions used to obtain the HOFs, two isodesmics and the formation reaction, and the lack of experimental references, a linear combination of these results would allow to mitigate the deviation of each individual result, giving an overall more robust result. We propose to use the following weights: 0.7 for isodesmic 2, 0.15 for isodesmic 1 and 0.15 for the formation reaction. Notice that due to the accuracy of the three methods there is no risk in the choice of the numerical coefficients. Our best theoretical estimates are summarized in Table 2.

The final results of standard enthalpies of formation at 298.15 K were also calculated by using the correlation energies obtained by employing correlation consistent basis sets. The cc-pV(T+d) Z [6] and cc-pV(Q+d) Z [34] basis sets were used in conjunction with the previously employed extrapolation scheme, now with an exponent of 3.05 [15]. These electronic structure calculations were performed with the PSI4 program [28]. The results obtained are 5.0, −9.5, −5.6, −33.9, −9.8 and −33.8 $\text{kcal}\cdot\text{mol}^{-1}$ for ClFO, ClFO₂, ClFO₃, ClF₃O, ClF₃O₂ and ClF₅O respectively. The comparison with the results presented in Table 2 is fairly good with a mean absolute deviation of 0.47 $\text{kcal}\cdot\text{mol}^{-1}$ and a largest absolute deviation of 1.0 $\text{kcal}\cdot\text{mol}^{-1}$ (for ClF₅O). Even if these differences seem large for the method it is still a great improvement upon the atomization scheme values.

3.3. Other thermodynamic parameters and their variation with temperature

Standard heat capacities at constant pressure and standard entropies were calculated based on statistical thermodynamics at

temperatures between 200 and 800 K. All usual approximations were used, i.e. separability of movements contributions, ideal gas law behavior, replacement of summation over the discrete levels by integration over continuous levels when feasible, neglect of degeneracies to nuclear spins etc. Thermal changes in enthalpy were also computed and reported as the difference between its value at the temperature T and the corresponding to 298.15 K. The previously computed rotational constants and unscaled harmonic vibrational frequencies were used for these calculations. The results are presented in Table 5.

The results are in very good accordance with available experimental values and are, in general, superior to those previously reported [5].

4. Summary

The standard heats of formation of oxides of chlorine fluorides were studied. Previous high level theoretical, CCSD(T), results showed an uncommonly large error for the calculation of HOFs through the atomization method. We proposed that this was caused by large higher excitations contributions to the energy not accounted by CCSD(T). The static correlation diagnostics strongly suggest that these contributions are significant. To address this the HOFs were calculated by using the isodesmic reaction scheme which provides better systematic error compensation. The differences between our final recommended values and those obtained by CCSD(T)–TAE method range from 1.1 to 5.6 $\text{kcal}\cdot\text{mol}^{-1}$. Our results are in better agreement with the two experimental values available. These considerations lead us to conclude that our results are more reliable on the whole.

Standard heat capacities at constant pressure and standard entropies were calculated at temperatures between 200 and 800 K. The values are in good accordance with available experimental values.

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