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Gaussian-2 and Gaussian-3 Study of the Energetics and Structures of Cl_2O_n and $Cl_2O_n^+$, $n = 1-7$

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The structures and energetics of the dichlorine oxides, Cl_2O_n, $n = 1-7$, and their cations have been investigated theoretically at the Gaussian-2 (G2) and the Gaussian-3 (G3) levels of theory. The G2 and G3 heats of formation obtained for both neutral and cationic species allow the interpretation of assigned appearance energies and ionization energies reported in a recent photoionization mass spectrometric study (Rühl et al. *Int. J. Mass Spectrom*. **1999**, *185*, 545) on these chlorine oxides. The calculations predict that $Cl_2O_6^+$ dissociates spontaneously to ClO_2^+ and ClO_4, in agreement with the nonobservation of $Cl_2O_6^+$ in the experimental study by Rühl et al. For systems with $n \leq 4$, the calculated and experimental thermochemical properties (such as heats of formation and ionization energies) are in good to excellent agreement with each other. However, this agreement deteriorates as the size of the molecular system increases or as n exceeds 4. Thus it appears that the G3 method may also suffer from "an unfavorable accumulation of component small errors," as has been found for the G2 method and its variants.

Introduction

Spectroscopic and photochemical techniques have been used to study various small chlorine oxides such as ClO,[1,2] ClO_2,[3,4] Cl_2O,[2] Cl_2O_2,[1,5−7] and Cl_2O_3.[8,9] However, the higher chlorine oxides, Cl_2O_n, where n ≥ 4, appear not to have been investigated extensively. In 1990, the composition, ultraviolet spectrum, and kinetics of the thermolysis of gaseous Cl_2O_6 have been reported.[10] Recently, Rühl et al. reported a photoionization mass spectrometric study of four dichlorine oxides, Cl_2O_n, $n = 1$, 4, 6, and 7, using monochromatic synchrotron radiation.[11] From the measured photoionization efficiency (PIE) spectra, Rühl et al. have assigned the adiabatic ionization energies (IEs) of these neutral dichlorine oxides and appearance energies (AEs) of fragment ions from these oxides. The IE and AE measurements have allowed them to deduce values for the heats of formation at 298 K (ΔH°_{f298}) for selected dichlorine oxide species and their cations. Interestingly, Rühl and co-workers[11] failed to detect the $Cl_2O_6^+$ cation in their study.

On the theoretical front, there are various studies on the thermochemical properties, such as ΔH°_{f298}, IEs, and electron affinities, as well as the structures of the gaseous Cl_2O_n and $Cl_2O_n^+$, for $n = 2-7$. The gaseous structures, spectroscopic properties, and relative energetics of the three different Cl_2O_2 isomers have been investigated at the CCSD(T)/TZ2P level by Lee et al.[12] as well as at the B3LYP/aug-cc-pVTZ+d level by Christen et al.[13] For several isomers of Cl_2O_3, the structures and energetics have been studied at the QCISD(T)/6-31G(d)//MP2/6-31G(d) level by Flesch et al.[14] The basis set effects on these isomers have also been investigated by using density functional theory (DFT) by Kim et al.[15] We note that the structure of Cl_2O_3 has been reported by Clark and Francisco[16] at the level of B3LYP/6-311+G(3df) as well. The structure of dimer $(ClO_2)_2$ has been calculated at the level of MP2/6-311+G(d)//MP2/6-311G(d) by Flesch et al.,[14] as well as by Harcourt[17] using the valence bond method with the STO-6G basis. In addition, the MP2(Full)/6-31G(d) optimized structures of Cl_2O_6[18] and Cl_2O_7[19] have been reported by Parthiban and co-workers. Very recently, the structure and bonding of Cl_2O_n, $n = 1-8$, have been investigated by Beltrán and co-workers.[20] Specifically, the structures of these compounds were optimized at the level of B3LYP/6-311+G(3df).

The present theoretical study is motivated by the PIE study[11] of Rühl et al. The primary goal of this PIE experiment is to obtain thermochemical data for cationic and neutral fragments produced in photoionization processes involving dichlorine oxides. It is well-known that the accuracy for AE and IE values of polyatomic species measured in such experiments may be limited by the kinetic shift effect. The structures of a neutral polyatomic species and its cation are sometimes very different. Since the Franck−Condon factors for photoionization transitions in such a case are small at the ionization threshold, the observed ionization onset may represent an upper limit for the true IE value. In a more extreme case, such as in the photoionization

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of SF_6, only the SF_5^+ fragment is observed,[21] indicating that SF_6^+ is not stable at the ionization onset. To examine the reliability of the AE and IE values observed in a PIE study of polyatomic species such as the dichlorine oxides, it is highly profitable to perform a reliable theoretical investigation on the energetics and structures of the neutrals and cations involved. The previous comparisons between the results of PIE experiments and the energetic predictions based on Gaussian-2 (G2)[22] and Gaussian-3 (G3)[23] ab initio calculations have provided much chemical insights concerning the photoionizations and dissociative photoionizations of many polyatomic molecules.[24,25] Second, in this work, we try to assess the performance of the newly developed G3 and G3-based methods for a molecular system as large as $Cl_2O_7^+$.

To sum up, we present G2 and G3 results for species Cl_2O_n and $Cl_2O_n^+$, $n = 1-7$. A similar G2 study on Cl_2O_n and $Cl_2O_n^+$,[26] for $n = 1$ and 2, has been published previously. The present calculations yield $\Delta H°_{f298}$ values of Cl_2O_n and $Cl_2O_n^+$, as well as IEs of Cl_2O_n, $n = 1-7$, which may be compared with the available experimental results. Such a comparison makes the rationalization of these experimental data possible. In addition, a brief assessment of the G3 method is made.

Theoretical Methods

Our calculations were carried out on a variety of computers: SGI10000 workstation, DEC500au and DEC600au workstations, SGI Origin 2000 High Performance Server, using the Gaussian 94 and Gaussian 98 packages of programs.[27] We have carried out full G2[22] calculations only for Cl_2O_n and $Cl_2O_n^+$, $n = 1-4$. At the G2 level, all structures have been optimized at the second-order Møller−Plesset theory (MP2) using the 6-31G(d) basis set with all electrons included, i.e., the MP2(Full)/6-31G(d) level. The G2 theoretical procedure[22] is an approximation to the ab initio level of QCISD(T)/6-311+G(3df,2p). It involves single-point energy calculations at the QCISD(T)/6-311G(d,p), MP4/6-311G(d,p), MP4/6-311+G(d,p), MP4/6-311G(2df,p), and MP2/6-311+G(3df,2p) levels based on the optimized geometry at MP2(Full)/6-31G(d). A small empirical correction is added to include high-level correlation (HLC) effects in the calculation of the total electronic energies (E_e). Unless specified, the HF/6-31G(d) harmonic vibrational frequencies, scaled by 0.8929, were applied for the zero-point vibrational energy (ZPVE) correction at 0 K ($E_0 = E_e$ + ZPVE) in the G2 and G2-based calculations.

On the other hand, two economical variants of the conventional G2 theory, G2(MP2)[28] and G2(MP2,SVP),[29] which provide substantial savings in computational time and resources, have been employed in the calculations of Cl_2O_n and $Cl_2O_n^+$, $n = 5-7$. In the G2(MP2) method, only two single-point energy calculations at the QCISD(T)/6-311G(d,p) and MP2/6-311+G(3df,2p) levels are required, while the G2(MP2,SVP) theory needs single points at the QCISD(T)/6-31G(d) and MP2/6-311+G(3df,2p) levels. Both G2(MP2) and G2(MP2,SVP) theories have been tested on the same set of 125 molecular systems used for the validation of the G2 theory, and the mean absolute deviation of the G2(MP2) and G2(MP2,SVP) methods from experimental values are 6.6 kJ mol^{-1} [28] and 6.8 kJ mol^{-1},[29] respectively, compared with 5.0 kJ mol^{-1} for the G2 method.[22]

Besides performing the G2 and G2-based calculations, we have also carried out G3[23] calculation on all species under study. In the G3 model, geometry optimization and ZPVE correction are also done at the MP2(Full)/6-31G(d) level. It entails single-point energy calculations at the QCISD(T)/6-31G(d), MP4/6-31G(d), MP4/6-31+G(d), MP4/6-31G(2df,p), and MP2(Full)/G3large levels, where G3large is a triple-ζ basis proposed by Curtiss et al.[23] In addition, this model includes HLC and spin−orbit coupling correction (the latter only for monatomic species). For the set of 125 molecular systems used to validate the G2 method, the average absolute deviation from experiment for the G3 model is 4.5 kJ mol^{-1},[23] as compared with 5.0 kJ mol^{-1} for the G2 method.[22]

The G3(MP2) theory,[30] a variation of the G3 theory and analogous to the G2(MP2) theory with the G2 theory, has been employed in the calculation of Cl_2O_n and $Cl_2O_n^+$, $n = 5-7$. It is less demanding computationally than the G3 method. The G3(MP2) theory involves single-point energy calculations at the QCISD(T)/6-31G(d) and MP2/G3MP2large levels. The latter single-point calculation includes only valence electrons in treatment of electron correction, i.e, frozen core, accompanied with a specially designed G3MP2large basis set. For the previously mentioned 125 molecular systems, the average absolute deviation of the G3(MP2) method from experiments is 5.4 kJ mol^{-1}.[30] In our G3 and G3(MP2) calculations, unless specified, the MP2(full)/6-31G(d) harmonic frequencies, scaled by 0.9646,[23] were employed to account for the ZPVE and thermal corrections.

In this work, the MP2(Full)/6-31G(d) harmonic frequencies, scaled by 0.9646,[31] were used for ZPVE and thermal corrections of $Cl_2O_7^+$, as we were unable to obtain the optimized structure for this cation at the HF/6-31G(d) level. Also, for species Cl_2O^+ and Cl_2O_3, the optimized QCISD(Full)/6-31G(d) structures were used for single-point calculations and their corresponding QCISD(Full)/6-31G(d) harmonic frequencies, scaled by 0.95, were used for ZPVE and thermal corrections.

Additionally, it is noted that the calculated heats of formation in this work are obtained in the following manner.[32] For molecule AB, its G2/G3 $\Delta H°_{f298}$ is calculated from the G2/G3 heat of reaction ΔH_{r298} ($A + B \rightarrow AB$) and the respective experimental $\Delta H°_{f298}(A)$ and $\Delta H°_{f298}(B)$ for elements A and B.

Before we proceed to present and discuss the results, we note that the G2 and G3 predictions for $\Delta H°_f$ and IE values are usually within ±0.10 eV (or about ±10 kJ mol^{-1}) of the experimental data. So far we have applied the G2 method to determine the $\Delta H°_f$'s of C_2H_5S[32,33] and $C_2H_5S^+$ [34] isomers, $CH_3S_2^+$, CH_3S_2, and CH_3S_2 isomers,[35,36] CH_3O^+, CH_3O, and CH_3O^- isomers,[37−39] SF_n^+, SF_n, and SF_n^-, $n = 1-6$,[40,41] CH_3SF and CH_3SSCH_2,[42] and Cl_2O_2 and $Cl_2O_2^+$ isomers as well as their fragments.[26] We have also applied the same method to determine the energies of the dissociation reactions involving CH_3S, CH_2SH, and their cations and anions,[43] $HSCH_2CH_2SH$,[44] C_2H_3Cl, and $C_2H_3Cl^+$,[45] as well as Cl_2O_2 and $Cl_2O_2^+$ isomers.[26] In all instances, the calculated results are in good to excellent agreement with the experimental data. Indeed, there are also cases where we used the G2 results to suggest preferred values where the experimental data are either not very accurate or in conflict with each other.[43] There are also examples where the G2 results were used to revise experimental data.[46] As the G3 method is relatively new, we have only applied it to hydrochlorofluoromethanes and their cations[25] as well as to CClO, $(CClO)_2$, and their cations.[47] The results obtained are very satisfactory. However, this method has not been applied to many large systems. In this work, we are applying it to Cl_2O_6 and Cl_2O_7, as well as to their cations. It will be of interest to see if this method can lead to satisfactory results for such large systems.

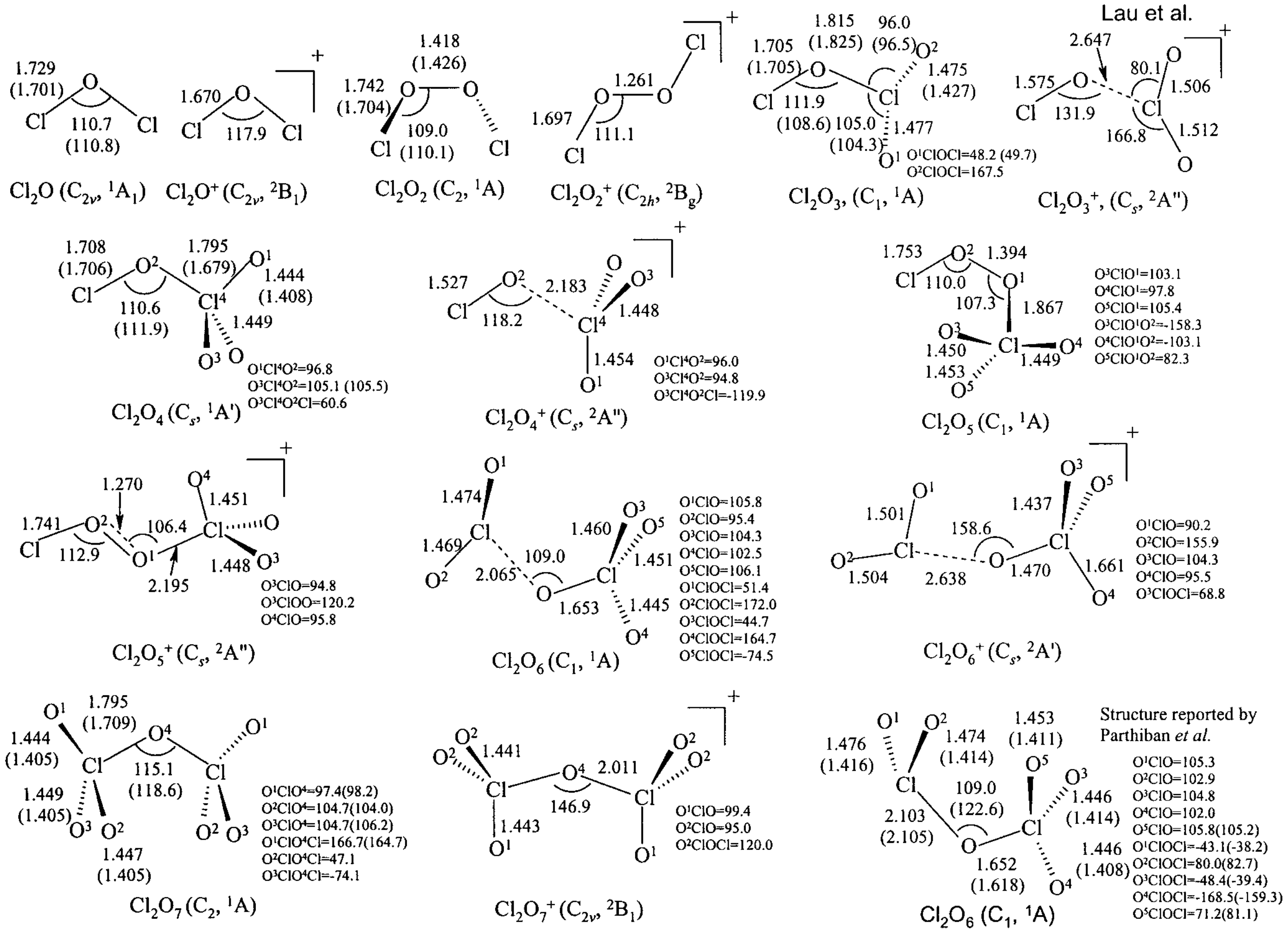

Figure 1. Geometrical parameters of Cl_2O_n and $Cl_2O_n^+$, $n = 1-7$, optimized at the MP2(Full)/6-31G(d) level, except that the structures of Cl_2O^+ and Cl_2O_3 are obtained at QCISD(Full)/6-31G(d) and that of Cl_2O_2 is optimized at HF/6-31G(d). All bond lengths are in angstroms and angles are in degrees. Experimental values, where available, are given in brackets. Also shown is the structure for Cl_2O_6 reported by Parthiban et al.[18]

Results and Discussion

The structures of Cl_2O_n and $Cl_2O_n^+$, $n = 1-7$, optimized at MP2(Full)/6-31G(d), are displayed in Figure 1. Also shown in this figure is the Cl_2O_6 structure reported by Parthiban et al.[18] Experimental parameters, where available, are given as well. The G2 and G3 total energies at 0 K (E_0), enthalpies at 298 K (H_{298}), and $\Delta H°_{f298}$ values for both series of Cl_2O_n and $Cl_2O_n^+$, as well as the IEs of Cl_2O_n, are summarized in Table 1. Experimental values for these quantities are also included in the table for ready comparison.

Before discussing the results of individual Cl_2O_n species and its cation, we first briefly compare our optimized structures of the neutral Cl_2O_n with those determined by Beltrán et al.[20] using DFT methods. In general, these two sets of results are in good agreement with each other, even though minor disagreements remain. When these two sets of results are compared with the known experimental data, we find that our results are better for $n = 2$ and 3. While there are no experimental structural data for Cl_2O_5, our results are slightly inferior for $n = 1$, 4, 6, and 7. But, as mentioned previously, the disagreements between the two calculated sets of results are small. Also, for Cl_2O_6, the optimized structures suggest an ionic mixed-valent dimer of the form $[ClO_2]^+[ClO_4]^-$ (see below) and the experimental data have been obtained by X-ray diffraction. Since crystal packing effects may distort the structure with respect to the isolated species, it is not totally appropriate to compare the calculated results of Cl_2O_6 with the solid-state experimental findings.

Cl_2O and Cl_2O^+. From Figure 1, it is seen that the optimized bond length in Cl_2O (1.729 Å), is in good agreement with the experimental value[48] of 1.701 ± 0.020 Å. From our previous study on Cl_2O and Cl_2O^+,[26] the G2 and G3 $\Delta H°_{f298}$ values for Cl_2O are 76.0 and 80.7 kJ mol^{-1}, respectively, in very good agreement with the three experimental results of 78.2 ± 6,[11] 80,[49] and 82.8 ± 2[50] kJ mol^{-1}.

Turning to Cl_2O^+, its G2 and G3 $\Delta H°_{f298}$ values of 1127.3 and 1131.7 kJ mol^{-1}, respectively, are also in very good accord with the recent experimental result of 1128 ± 7 kJ mol^{-1}.[11] We note that, in our previous study,[26] the experimental $\Delta H°_{f298}$ of Cl_2O^+ was reported as 1136 kJ mol^{-1},[49] which is almost 10 kJ mol^{-1} higher than the latest experimental value.[11] Besides the excellent agreement between the G2/G3 and experimental $\Delta H°_{f298}$ values for both Cl_2O and Cl_2O^+, the G2/G3 IEs (both at 10.89 eV) of Cl_2O obtained are consistent with the experimental value (10.88 ± 0.02 eV).[11]

Cl_2O_2 and $Cl_2O_2^+$. Neutral dichlorine dioxide, Cl_2O_2, has a hydrogen peroxide structure with C_2 symmetry. The optimized geometrical parameters are in good agreement with the experimental data obtained by rotational spectroscopic analysis.[5] It is also worth mentioning that isomer ClOOCl we used in the calculations here has the lowest energy among the three Cl_2O_2 isomers reported in the literatures.[12,13] The G2 and G3 $\Delta H°_{f298}$ values for ClOOCl are 125.7 and 132.3 kJ mol^{-1}, respectively. The G3 value is in better accord with the experimental data of 133 ± 8 kJ mol^{-1}.[50]

TABLE 1: G2^a and G3^b Total Energies (E_0), Enthalpies (H_{298}), and Standard Heats of Formation at 298 K (ΔH°_{f298}) for Cl_2O_n and $Cl_2O_n^+$, $n = 1-7$, as Well as the Ionization Energies (IEs) of Cl_2O_n

species	E_0, hartree	H_{298}, hartree	ΔH°_{f298},^{b} kJ mol^{-1}	IE,^{b} eV
Cl_2O	−994.49098^c	−994.48659^c	76.0^c	10.89^c
	−995.16687	**−995.16240**	**80.7**	**10.89**
			(78.2 ± 6)	(10.88 ± 0.02)
			(80)^d	
			(82.8 ± 2)^e	
Cl_2O^+	−994.09078^c	−994.08617^c	1127.3^c	
	−994.76660	**−994.76212**	**1131.7**	
			(1128 ± 7)	
			(1136)^d	
Cl_2O_2	−1069.54762^c	−1069.54226^c	125.7^c	10.98^c
	−1070.27188	**−1070.26633**	**132.2**	**11.00**
			(133 ± 8)^e	(11.05 ± 0.05)^f
$Cl_2O_2^+$	−1069.14409^c	−1069.13851^c	1185.7^c	
	−1069.86748	**−1069.86191**	**1194.0**	
			(1199 ± 12)^f	
Cl_2O_3	−1144.61287^c	−1144.60627^c	153.4^c	11.13^c
	−1145.38816	**−1145.38156**	**154.1**	**11.09**
			(137 ± 13)^e	
			(142 ± 13)^g	
			(153)^h	
$Cl_2O_3^+$	−1144.20399^c	−1144.19560^c	1231.7^c	
	−1144.97827	**−1144.97005**	**1234.5**	
Cl_2O_4	−1219.67143^c	−1219.66483^c	195.5^c	11.04^c
	−1220.49989	**−1220.49291**	**186.1**	**11.11**
			(155.6)^i	(11.23 ± 0.05)
			(178 ± 27)	
$Cl_2O_4^+$	−1219.26580^c	−1219.25768^c	1264.5^c	
	−1220.09174	**−1220.08413**	**1259.3**	
			(1262 ± 30)	
Cl_2O_5	−1294.69625^j	−1294.68855^j	212.8^j	10.17^j
	−1294.69727^k	−1294.68957^k	233.2^k	10.76^k
	−1295.59738	**−1295.58894**	**258.3**	**10.88**
	−1294.77649	*−1294.76804*	*277.6*	*10.87*
$Cl_2O_5^+$	−1294.32262^j	−1294.31334^j	1193.7^j	
	−1294.30188^k	−1294.29260^k	1271.3^k	
	−1295.19773	**−1295.18900**	**1308.4**	
	−1294.37720	*−1294.36847*	*1326.7*	
Cl_2O_6	−1369.75983^j	−1369.75096^j	232.9^j	
	−1369.76184^k	−1369.75297^k	254.4^k	
	−1370.71413	**−1370.70480**	**278.5**	
	−1369.84973	*−1369.84040*	*303.8*	
			(218)^i	
			(250 ± 35)	
$Cl_2O_6^+$ ^{l}	−1369.32752^j	−1369.31648^j	1367.9^j	
	−1369.33289^k	−1369.32185^k	1380.6^k	
	−1370.28200	**−1370.27195**	**1414.9**	
	−1369.41956	*−1369.40951*	*1435.1*	
			(1470 ± 38)	
Cl_2O_7	−1444.81343^j	−1444.80426^j	279.2^j	12.34^j
	−1444.81567^k	−1444.80651^k	303.8^k	12.33^k
	−1445.82181	**−1445.81203**	**321.3**	**12.37**
	−1444.91296	*−1444.90318*	*355.1*	*12.34*
			(272 ± 17)	(12.15 ± 0.05)
$Cl_2O_7^+$	−1444.35981^j	−1444.34910^j	1470.2^j	
	−1444.36243^k	−1444.35171^k	1493.8^k	
	−1445.36709	**−1445.35637**	**1517.7**	
	−1444.45959	*−1444.44888*	*1547.9*	
			(1444 ± 23)	

[a] The G2 and G2-based results are given in normal font, while the G3 and G3(MP2) results are in bold and italic fonts, respectively. [b] Unless specified, all experimental results (given in parentheses) are taken from ref 11. [c] Calculated at the G2 level. [d] Taken from ref 49. [e] Taken from ref 50. [f] Taken from ref 1. [g] Taken from ref 51. [h] Taken from ref 52. [i] Taken from ref 54. [j] Calculated at the G2(MP2) level. [k] Calculated at the G2(MP2,SVP) level. [l] Dissociates readily to ClO_2^+ and ClO_4 (see text).

When Cl_2O_2 is ionized, the $Cl_2O_2^+$ cation having C_{2h} symmetry is formed. However, we were unable to locate the cationic structure at MP2(Full)/6-31G(d), so the single-point calculations of $Cl_2O_2^+$ were based on the HF/6-31G(d) structure. At HF/6-31G(d), the O−O bond of $Cl_2O_2^+$ is 1.261 Å in length and exhibits some double bond character. The respective G2 and G3 ΔH°_{f298} values for $Cl_2O_2^+$ are 1185.7 and 1194.0 kJ mol^{-1}. Again, the G3 value is in better accord with the experimental value of 1199 ± 12 kJ mol^{-1}.[1] The G2 and G3 IEs (10.98 and 11.00 eV, respectively) are in good agreement with the experimental IE (11.05 ± 0.05 eV).[1] Here, it is noted that our G3 results are found to be in better agreement with the experimental data, when compared with our previous G2 study of Cl_2O_2 and its cation.[26]

Cl_2O_3 and $Cl_2O_3^+$. The stability and structure of dichlorine trioxide, Cl_2O_3, have been calculated by Flesch et al.,[14] Kim et al.,[15] Clark and Francisco,[16] and Beltrán and co-workers.[20] The most stable structure is found to be ClOCl(O)O. We have obtained this structure at the MP2(Full)/6-31G(d) level. However, the ClO−Cl(O)O bond is found to be very long (2.322 Å). As suggested by Clark and Francisco,[16] the MP2 perturbation may be inadequate for the determination of the Cl_2O_3 structure. Also, all the aforementioned calculations on Cl_2O_3, based on DFT with various basis sets, yielded the calculated ClO−Cl(O)O bond lengths of about 0.1 Å off the experimental value of 1.825 Å.[9] As a result, we have optimized the structure at the higher level of QCISD(Full)/6-31G(d), which leads to a bond length of 1.815 Å. Together with other structural parameters shown in Figure 1, our calculated results are in excellent agreement with experimental data.[9] So, the G2 and G3 single-point calculations for Cl_2O_3 were carried out based on the structure optimized at QCISD(Full)/6-31G(d).

For Cl_2O_3, the G2 and G3 ΔH°_{f298} values are 153.4 and 154.1 kJ mol^{-1}, respectively. Both values are in very good agreement with three independent experimental values of 137 ± 13,[50] 142 ± 13,[51] and 153 kJ mol^{-1}.[52] The G2 and G3 ΔH°_{f298} values for $Cl_2O_3^+$ are 1231.7 and 1234.5 kJ mol^{-1}, respectively, and the respective G2 and G3 IE for the neutrals are calculated to be 11.13 and 11.09 eV. With the good agreement obtained between experimental and calculated results for Cl_2O/Cl_2O^+, $Cl_2O_2/Cl_2O_2^+$, and Cl_2O_3, it may be concluded that the G2/G3 ΔH°_{f298} of $Cl_2O_3^+$ and IE value of Cl_2O_3 are accurate estimates.

Cl_2O_4 and $Cl_2O_4^+$. As illustrated in Figure 1, the eclipsed structure of neutral dichlorine tetraoxide, Cl_2O_4, has C_s symmetry and a $^1A'$ ground state. The MP2(Full)/6-31G(d) structure is in good accord with the experimental findings.[53] For its cation, $Cl_2O_4^+$, we obtained a staggered structure with a significantly elongated Cl^4−O^2 bond (2.183 Å), as compared with the corresponding bond (1.795 Å) in Cl_2O_4. The structure of cation $Cl_2O_4^+$ may be regarded as a tight complex of the form $ClO\cdots ClO_3^+$. Another structure of Cl_2O_4, in a dimer form of ClO_2 ($O_2Cl\cdots OClO$), has been reported by Flesch and coworkers[14] as well as Harcourt.[17] But this species is not related to our work.

The G2 and G3 ΔH°_{f298} values for Cl_2O_4 are 195.5 and 186.1 kJ mol^{-1}, respectively, which are within the error range of the experimental result, 178 ± 27 kJ mol^{-1}.[11] For this species, we find that the G3 result is in better agreement (by about 10 kJ mol^{-1}) with the experimental data. We note that there is an estimation of ΔH°_{f298} for Cl_2O_4 (155.6 kJ mol^{-1}), by Colussi and Grela.[54] Meanwhile, the G2 and G3 ΔH°_{f298} values for the dichlorine tetraoxide cation, $Cl_2O_4^+$, are 1264.5 and 1259.3 kJ mol^{-1}, respectively. They are very close to the experimental value of 1262 ± 30 kJ mol^{-1} reported by Rühl et al.[11] In addition, the G2 and G3 IE values (11.04 and 11.11 eV, respectively) for Cl_2O_4 are in fair agreement with the experimental IE value (11.23 ± 0.05 eV).[11] Since the geometries predicted for Cl_2O_4 and $Cl_2O_4^+$ are very different, the experimental IE for Cl_2O_4 should be an upper bound. The close agreement between the experimental and theoretical $\Delta H^\circ_{f298}(Cl_2O_4^+)$ values is likely to be fortuitous, resulting from a low experimental $\Delta H^\circ_{f298}(Cl_2O_4)$ and a high experimental IE(Cl_2O_4).

Cl_2O_5 and $Cl_2O_5^+$. Dichlorine pentaoxide, Cl_2O_5, was found to have a peroxide structure of $ClOOClO_3$ in trans conformation across the peroxide bond. In our investigation, we found this structure to be more stable than isomers $O_2ClOClO_2$ (with C_2 symmetry) and $OClOClO_3$ (C_1) at the levels of MP2(Full)/6-31G(d) and MP2(Full)/6-311G(df). Rather surprisingly, for $Cl_2O_5^+$, we have obtained a cis structure with C_s symmetry. Similar to $Cl_2O_4^+$ with Cl_2O_4, cation $Cl_2O_5^+$ has a elongated $Cl-O^1$ bond of 2.195 Å compared with 1.867 Å in Cl_2O_5. No experimental data on the structures of Cl_2O_5 and $Cl_2O_5^+$ are available for comparison, nor have other relevant theoretical results been found in the literature (except the aforementioned work carried out by Beltrán and co-workers[20]).

We have carried out calculations on Cl_2O_5 and $Cl_2O_5^+$ at four levels of theory: G2(MP2), G2(MP2,SVP), G3, and G3(MP2). As seen in Table 1, the values of ΔH°_{f298} for Cl_2O_5 vary from 212.8 at G2(MP2) to 277.6 kJ mol^{-1} at G3(MP2). Moreover, the variations for the ΔH°_{f298} values of the cation are even more pronounced, ranging from 1193.7 at G2(MP2) to 1326.7 kJ mol^{-1} at G3(MP2). In view of the lack of experimental ΔH°_{f298} data for both Cl_2O_5 and $Cl_2O_5^+$, reliable calculated results would provide us with valuable estimates. However, at the various G2 and G3 levels of theory, we are unable to achieve a consistent set of results for these quantities. The disparity between the results obtained at these levels may be due to the inherent deficiencies of the theoretical methods employed (see further discussion below).

Cl_2O_6 and $Cl_2O_6^+$. At the MP2(Full)/6-31G(d) level, neutral dichlorine hexoxide, Cl_2O_6, is found to have an oxygen-bridged structure with C_1 symmetry. As one of the bridging Cl−O bonds is 2.065 Å, qualitatively speaking, this structure has the ionic mixed-valent dimer form of $[ClO_2]^+[ClO_4]^-$, as suggested by Tobias et al. in an X-ray crystallographic study,[55] and in an infrared spectroscopic analysis.[56] Quantitatively, by natural population calculations, the atomic charges for ClO_4 and ClO_2 fragments are found to be −0.49 and +0.49, respectively. As mentioned previously, the structures of Cl_2O_6 have also been studied by Parthiban and co-workers.[18] They have reported five structures for Cl_2O_6, with symmetries C_1, C_2, C_s, D_{2h}, and D_{3d}, at the HF/6-31G(d) level. Among these structures, the one with D_{2h} symmetry is a fifth-order saddle point. Also, at the MP2/6-31G(d) level, both the C_1 and C_2 structures dissociate into smaller fragments, and the D_{3d} structure is ruled out due to its high energy. For the remaining C_s structure, four possible conformers are found, however they are either first-order or second-order saddle points. Upon relaxing symmetry from C_s to C_1, an equilibrium structure is obtained. This structure differs from ours by a rotation around one of the bridging Cl−O bonds. At the MP2(Full)/6-31G(d), our structure is more stable by 2.9 kJ mol^{-1}. As seen from Figure 1, the structure for Cl_2O_6 by Parthiban et al. is in better agreement with the X-ray crystal data[55] than ours. On the other hand, since our structure is relatively more stable, we have carried out the G2 and G3 energy calculations for Cl_2O_6 based on our structure.

As reported by Rühl and co-workers,[11] when Cl_2O_6 is ionized, it fragments into lighter ionic species, instead of yielding the corresponding cation, $Cl_2O_6^+$. In other words, the $Cl_2O_6^+$ cation appears to be unstable. Despite this, we have located the gaseous structure for $Cl_2O_6^+$ at the MP2(Full)/6-31G(d) level. As seen from Figure 1, this structure has C_s symmetry and a $^2A'$ ground state. From the structure shown, $Cl_2O_6^+$ may be viewed as a weak complex of the form $O_2Cl^+\cdots OClO_3$, or $O_2Cl^+\cdots ClO_4$, with a long Cl···O "bond" of 2.638 Å. From the natural population analysis for the $Cl_2O_6^+$ cation, it is clear that the positive charge is mainly on the ClO_2 moiety.

We have performed the G2(MP2), G2(MP2,SVP), G3, and G3(MP2) calculations for both Cl_2O_6 and $Cl_2O_6^+$, the respective ΔH°_{f298} values for Cl_2O_6 are calculated to be 232.9, 254.4, 278.5, and 303.8 kJ mol^{-1}. The G2(MP2,SVP) result is in excellent agreement with the experimental value of 250 ± 35 kJ mol^{-1},[11] while the other three values are within the error range. On the other hand, an earlier experimental ΔH^o_{f298} for Cl_2O_6 is 218 kJ mol^{-1}, by Colussi and Grela,[54] which is in fair agreement with the G2(MP2) result.

As stated above, due to the unstable nature of the $Cl_2O_6^+$, it is experimentally undetectable. At the G3 level, it is found that $Cl_2O_6^+$ will dissociate readily into fragments ClO_2^+ and ClO_4. Our calculations indicate that ClO_4 exists in three forms with different symmetries: in decreasing order of stability, $C_s > C_{3v} > T_d$. The G3 heat of reaction at 0 K (ΔH_{r0}) for $Cl_2O_6^+ \rightarrow ClO_2^+ + ClO_4(C_s)$ is −5.7 kJ mol^{-1}. This value implies that $Cl_2O_6^+$ will spontaneously dissociate into ClO_2^+ and $ClO_4(C_s)$. However, the dissociation of $Cl_2O_6^+$ into ClO_2^+ and either $ClO_4(T_d)$ or $ClO_4(C_{3v})$ is less likely to occur, as the $\Delta H_{r0}(Cl_2O_6^+ \rightarrow ClO_2^+ + ClO_4(C_{3v}))$ and $\Delta H_{r0}(Cl_2O_6^+ \rightarrow ClO_2^+ + ClO_4(T_d))$ are calculated to be 15.1 and 37.0 kJ mol^{-1}, respectively, at the G3 level. In our optimized structure for $Cl_2O_6^+$ shown in Figure 1, it is difficult to determine the local symmetry for the ClO_4 moiety. In any event, with these three ΔH_{r0} values obtained, it is seen that $Cl_2O_6^+$ can readily dissociate to ClO_2^+ and ClO_4. Such a conclusion is consistent with the nonobservation of the $Cl_2O_6^+$ cation reported by Rühl and co-workers.[11]

Cl_2O_7 and $Cl_2O_7^+$. As depicted in Figure 1, the structure of Cl_2O_7 has C_2 symmetry. The optimized geometrical parameters are in very good agreement with the electron diffraction results.[57] The dichlorine heptoxide cation, $Cl_2O_7^+$, has C_{2v} symmetry with a $Cl-O^4$ distance of 2.011 Å compared to 1.795 Å in the neutral structure. The $Cl_2O_7^+$ structure with C_{2v} symmetry is a minimum at the MP2(Full)/6-31G(d) level, whereas it is a first-order saddle point at the HF/6-31G(d) level. These results are similar to these obtained by Parthiban et al.[19]

For Cl_2O_7 and $Cl_2O_7^+$, we again have performed calculations at the G2(MP2), G2(MP2,SVP), G3, and G3(MP2) levels. As shown in Table 1, the calculated ΔH°_{f298} value at the G2(MP2) level (279.2 kJ mol^{-1}) for Cl_2O_7 is in excellent agreement with the experimental value (272 ± 17 kJ mol^{-1}),[11] while the results obtained at the other three levels are becoming less and less satisfactory. For the cation $Cl_2O_7^+$, the ΔH°_{f298} values obtained at G2(MP2), G2(MP2,SVP), G3, and G3(MP2) are 1470.2, 1493.8, 1517.7, and 1547.9 kJ mol^{-1}, respectively. The G2(MP2) result is in fair agreement with the experimental data of 1444 ± 23 kJ mol^{-1},[11] while the remaining results are significantly larger than the experimental value by about 50−100 kJ mol^{-1}. Our calculations on $Cl_2O_7/Cl_2O_7^+$, together with $Cl_2O_5/Cl_2O_5^+$ and $Cl_2O_6/Cl_2O_6^+$, are by far the largest systems tested for the newly proposed G3 and G3(MP2) models, our calculated G3 and G3(MP2) results (especially the latter) are significantly deviated from the available experimental values. Even if we can ignore the experimental data, we are still faced with a lack of consistency among our calculated results. Based on the admittedly limited results discussed here, it appears that the G3 and G3(MP2) methods may also suffer from "an unfavorable accumulated of component small error," as has been found for G2 and its variants.[58]

Surprisingly, we obtained very similar IEs (12.33−12.37 eV) for Cl_2O_7 at the four levels of theory. All of these values are about 0.2 eV larger than the experimental IE of 12.15 ± 0.05 eV.[11]

Geometrical Changes between Cl_2O_n and Its Cation. Before concluding the discussion, we briefly review the geometrical variation between a given Cl_2O_n species and its corresponding cation. Inspecting the wave function of the highest occupied molecular orbital (HOMO) of Cl_2O, it is found that this wave function has b_1 symmetry, with antibonding interaction between oxygen and chlorine orbitals. Hence, upon removing an electron from this orbital of Cl_2O to yield Cl_2O^+, the Cl−O distances will be reduced, as indeed was found in our results. Likewise, for ClOOCl, the HOMO has antibonding character between the orbitals on the peroxide oxygens. Hence, by ionizing ClOOCl to form $ClOOCl^+$, the peroxide bond is shortened in length. A similar situation is found in $ClOOClO_3$, which also has a peroxide bond. This O−O bond is shortened as well when the neutral species is ionized. For both ClOCl(O)O and ClOCl(O)O′O, the HOMO's have an antibonding interaction between the terminal chlorine and bridging oxygen. When both of these neutrals undergo ionization, a shortening of the corresponding Cl−O bonds is resulted. Since this ClO moiety in both $ClOCl(O)O^+$ and $ClOCl(O)O'O^+$ carries significant positive charge, these cations may be viewed as weak complexes between the ClO^+ moiety and the remaining radical fragments, i.e., $ClO^+\cdots ClO_2$ and $ClO^+\cdots ClO_3$, respectively. For Cl_2O_6, the HOMO of $O_2Cl'O'ClO_3$ has bonding character between Cl′ and O′ orbitals. Hence, upon ionizing an electron from this orbital, the $O_2Cl-OClO_3$ bond is significantly lengthened and a weakly bound structure of the form $O_2Cl^+\cdots OClO_3$ is resulted. Finally, it is noted that our analysis presented here is similar to the one carried out by Schaefer et al. in their study of BrF_n ($n = 1-7$) and their anions.[59]

Conclusions

We have carried out a study, using three G2-based models as well as two G3-based theories, on the structures and energetics of Cl_2O_n and $Cl_2O_n^+$, $n = 1-7$. The G2/G3 energies are used to calculate the $\Delta H°_{f298}$ values of the species and the IE values of the neutrals, to compare with the various experimental data in the literature as well as the results of a very recent photoionization mass spectrometric study[11] by Rühl et al. Also, the performance of the G3-based methods has been briefly assessed. Based on the results obtained, we have arrived at the following conclusions.

The G2 and G3 results for Cl_2O/Cl_2O^+, $Cl_2O_2/Cl_2O_2^+$, and Cl_2O_3 are in excellent agreement with the available experimental data. Hence, the results for $Cl_2O_3^+$ should be accurate estimates.

Our G2 and G3 $\Delta H°_{f298}$ and IE values for Cl_2O_4 are in good agreement with the experimental result after taking into account the experimental uncertainties. The theoretical calculations suggest that the excellent agreement found between the G2 and experimental $\Delta H°_{f298}$ values for $Cl_2O_4^+$ is most likely to be fortuitous, resulting from a low experimental $\Delta H°_{f298}$ value and a high experimental IE value for Cl_2O_4.

For Cl_2O_5 and $Cl_2O_5^+$, there are no experimental data available for comparison with our calculated results. However, the various G2- and G3-based methods fail to arrive at a consistent set of data for these two species.

At both G2(MP2) and G2(MP2,SVP) levels, the results for Cl_2O_6 yield fair agreement with the experimental value. But the G3 and G3(MP2) models yield less satisfactory values. Our results on the $Cl_2O_6^+$ cation indicate that it will readily dissociate into ClO_2^+ and ClO_4, in accord with a recent experimental observation.

At the G2(MP2) level, the calculated results for both Cl_2O_7 and $Cl_2O_7^+$ are in fair to good agreement with the reported experimental values. But the G3 and G3-based models once again do not lead to good results.

Our calculations on Cl_2O_n and $Cl_2O_n^+$, $n = 5-7$, are by far the largest systems tested for the newly proposed G3 model. Based on our limited results, it appears that, when this model is applied to relatively large systems, it may also suffer from "an unfavorable accumulation of component small errors," as has been found for the G2 theory and its variants.[58]

The geometrical variation for a given Cl_2O_n with its corresponding cation may be rationalized by examining the HOMO wave function of the neutral species.

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