

The study of Cl₂O₄: Implications for the Ozone Hole

Student XYZ, Chemistry Department, Macalester College, 1600 Grand Avenue, St.Paul, MN 55105.

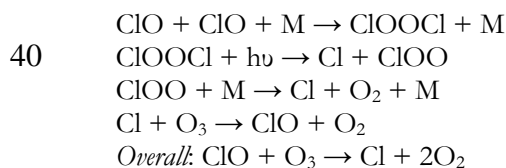
5 **Abstract:**

10 Ozone depletion occurs when the natural balance between the production and destruction of stratospheric ozone is tipped in favor of destruction. Observations of an Antarctic ozone "hole" and atmospheric records indicating seasonal declines in global ozone levels provide strong evidence that global ozone depletion is occurring. Although natural phenomena can cause temporary ozone loss, chlorine and bromine released from synthetic compounds are now accepted as the main cause of this depletion. The aim of this lab is to study Cl₂O₄ and its implications for the ozone hole. The experiment has employed *MacSpartan Pro* to carry out the analysis. The equilibrium structures of both Cl₂O₄ and Cl₂O₆ have been determined using the computational methods and calculated the bond length and angle. The experimental observations have proved that the HF/6-31G* is the most accurate method of determining the bond length and strength with percentage error of 0.07 - 5.59. Δ_rH was calculated to be -4.466kcalmol⁻¹ and -4.412kcalmol⁻¹ and Δ_rG was -4.301kcalmol⁻¹ and -3.87kcalmol⁻¹.

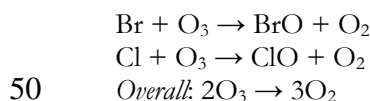
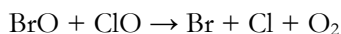
20 **Introduction:**

Over the past years, the chemistry involving the study of the destruction of ozone within the Antarctic polar vortex has played a significant role in many scientific studies. Several observations have been made and the concentrations of ClO, BrO and O₃ have been monitored to determine their effect. Reports suggest that the two main mechanisms, shown below, account for the major part of the ozone destruction in the stratosphere¹. Mechanism 3 accounts for a small portion of the ozone destruction.

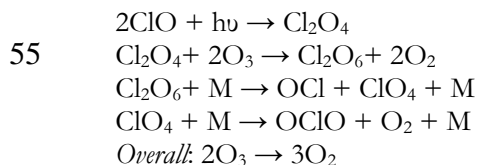
35 **Mechanism 1:**



45 **Mechanism 2:**



Mechanism 3:



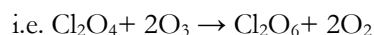
60 From mechanism 3, we can see that Cl₂O₄ is the major photolysis product in the 1st step. The formation of Cl₂O₄ in the stratosphere is very important since it takes part in the ozone destruction cycles. This can be clearly seen from the 2nd step where Cl₂O₆ is formed from the reaction between Cl₂O₄ and the ozone layer in the stratosphere.

70 In order to have a solid understanding on the study of Cl₂O₄ and its implications for the Ozone hole, the experiment will be divided into two important parts

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- To determine the equilibrium geometry of Cl₂O₄ at several different levels of theory, by using both ab initio and semi-empirical computational methods.

¹ The class lab handout.

- 80 • To apply thermodynamics to analyze the 2nd elementary step in mechanism 3;



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Computational Methods:

90 The computational method on this experiment employed the *MacSpartan Pro*. Hartree-Fock self-consistent field (HF-SCF) molecular orbital calculations with the 6-31G* basis function and Semi-empirical method PM1 were performed on both Cl₂O₄ and Cl₂O₆.

95 In order to have a clear study of Cl₂O₄, both the Lewis structure of the molecules under investigation had to be built in *MacSpartan Pro*. This was followed by the minimization of the structures we built as to have the best confirmation of the structures at lower energy. 100 Using the calculations mode, on the set up menu, it enabled us to determine both the bond lengths and angles for the desired atoms on the Cl₂O₄ molecule as shown on table 1. 105 The values calculated were then compared to the experimental value provided.

110 For the second part of the experiment, we again employed *MacSpartan Pro* to determine both the enthalpy and free energy of the reaction under investigation. Calculations mode was again selected under the Set-Up menu, HF/3-21G* and AM1 for Cl₂O₆ were used to calculate the values of enthalpy and free energy. 115 Note that the program assumes that T = 298K and basically uses a set of equations to carry out the calculations of vibrational frequencies and hence calculates ΔH and ΔG values for all the species i.e. Cl₂O₄, O₃, Cl₂O₆ and O₂. The multiplicity state of oxygen was taken into account determining the Δ_rH and Δ_rG values as shown in the appendix. 120

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Results:

Please refer to the appendix for the calculations of Δ_rH and Δ_rG. The results from *MacSpartan* from part one of the experiment have been tabulated as shown in table 1 which provided us with the opportunity to analyze carefully computational methods employed by allowing us to compare the experimental values and the calculated values by the basis set. 130 135

Table 1: The calculated values of bond length, bond angle and percentage error for Cl₂O₄.

	Experimental	AM1	%Error	PMB	%Error	MNDO	%Error
Cl=O	1.408	1.761	25.07102	1.444	2.556818	1.485	5.46875
		1.807	28.33807	1.441	2.34375	1.482	5.255682
Cl ₁ -O	1.706	1.701	0.293083	1.618	5.158265	1.621	4.982415
O-Cl ₂	1.679	1.806	7.564026	1.766	5.181656	1.705	1.548541
Angle O=Cl=O	115.9	119.8	3.36497	113.7	1.898188	114.3	1.3805
		113.2	2.329594	112	3.36497	114.8	0.949094
Angle O-Cl=O	105.5	99.6	5.592417	101.2	4.075829	104.8	0.663507
Angle O-Cl ₂ =O	111.9	97.6	12.77927	108.7	2.859696	101.3	9.472744
		113.3	1.251117	124.3	11.08132	134	19.74978

	Experimental	STO-3G*	%Error	6-31G*	%Error	3-21G*	%Error
Cl=O	1.408	2.386	40.9891	1.407	0.071023	1.417	0.639205
		2.341	66.2642	1.411	0.213068	1.412	0.284091
Cl ₁ -O	1.706	1.755	2.792023	1.671	2.051583	1.696	0.586166
O-Cl ₂	1.679	1.739	3.450259	1.642	2.203693	1.634	2.680167
Angle O=Cl=O	115.9	115.1	0.695048	113.9	1.725626	113.9	1.725626
				115.1	0.69025	115.3	0.517688
Angle O- Cl=O	105.5	96.1	9.781478	99.6	5.592417	99.9	5.308057
						40.6	61.51659
						34.3	67.48815
Angle O- Cl ₂ =O	111.9	109.3	2.378774	115	2.770331	117.1	4.647006

The percentage error was calculated as follows:

$$\text{Percentage error} = \left| \frac{e_{\text{value}} - c_{\text{value}}}{e_{\text{value}}} \right| \times 100\%$$

Where e_{value} = expt. value

c_{value} = calc. value

Discussion:

The Hartree-Fock self-consistent field (SCF) equations as we have seen, are based on the fact that the molecular orbital is a single product of the component one-electron orbital. The energy of the system is therefore the sum of the one-electron energies (kinetic energies and electron-nuclear attractions) and coulomb interactions between the charge clouds of all pairs of electrons.

Furthermore, equations for a system are derived by finding where this energy is at a minimum. This is done through an iterative process adding different amounts of the atomic orbitals to build the one-electron orbitals, calculating the energy of the resulting set of one-electron orbitals, then summing the energy of the occupied orbitals. Eventually $dE = 0$ and at this point the SCF has converged.

Part 1: Referring to table 1, we can see that the Hartree-Fock equations gave more accurate values relative to others when compared to the experimental data. The 6-31G* and 3-21G* level of theory basis sets gave percentage errors of 0.07 - 5.59 and 0.28 - 5.31 respectively. For the angle calculations (O-Cl=O) using the 3-21G* basic set has a high %error of 61.5 and 67.5 suggesting that those two values might have been wrongly calculated. Even though both were demonstrated to be more accurate, 6-31G* seems to be more accurate of all. The least accurate basis set is STO-3G due to higher percentage error.

One thing to notice is that there are underlying limitations for the Hartree-Fock calculations. These calculations approximate the wave function of electron-electron repulsion such that the energy due to repulsion is assumed to be zero or very small. But the neglected energy is equivalent to the discrepancy between the given experimental values and the calculated values. In addition, this energy participates in the stabilization of the electron bonding; thus a simplified model will be inaccurate as it neglects the above effect.

On the other hand, The Semi-Empirical equations employ a different path with another set of assumptions. Semi-empirical assumes that the central orbital has no effect on the electron bonding thus neglecting the orbital overlap. From the class lecture, we can deduce

215 that this will lead to the 'zero differential overlap approximation' i.e. as the overlap integral becomes smaller, the electron repulsion values becomes smaller too, which ends up simplifying the integrals.

220 **Part 2:** Referring to the appendix, we can see the calculated values of $\Delta_r H$ and $\Delta_r G$ for the crucial reaction in the ozone destruction. For the enthalpy of the reaction, both values suggests that the reaction is exothermic i.e. $\Delta_r H$ equals to $-4.466 \text{ kcal mol}^{-1}$ and $-4.412 \text{ kcal mol}^{-1}$. For the triplet oxygen molecule, it is more exothermic, which suggests that the reaction is thermodynamically feasible. The AM1 was employed to facilitate the procedure. Both values of $\Delta_r G$ are spontaneous, i.e. $-4.301 \text{ kcal mol}^{-1}$ and $-3.87 \text{ kcal mol}^{-1}$. This proves the importance of this reaction to the destruction of stratospheric ozone. Thus the more Cl that goes into the atmosphere the more the ozone is damaged.

235 *Conclusion:*

In conclusion, this experiment has demonstrated the simplest and the most direct method for the study of Cl_2O_4 and its implication to the ozone hole. The equilibrium structures of both Cl_2O_4 and Cl_2O_6 have been determined using the computational methods. The experimental observations have proved that the HF/6-31G* is the most accurate method of determining the bond length and strength. The experiment has also demonstrated the importance of Cl_2O_4 on the ozone depletion thus more studies have to be done to have a solid understanding and to formulate a method to stop further destruction of ozone.

Reference:

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