

EXPERIMENTAL AND **THEORETICAL STUDIES OF ATMOSPHERIC INORGANIC
CHLORINE CHEMISTRY**

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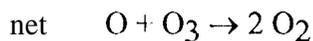
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I. introduction

The role of chlorine-containing species in stratospheric processes has been actively investigated since 1974 when Rowland and Molina¹ drew attention to the potential impact of chlorofluorocarbons on stratospheric ozone. From 1974 until 1985 the center of atmospheric chemical interest was on the ozone-depleting catalytic cycle involving atomic chlorine and chlorine monoxide (ClO), namely



The quantitative effect of this cycle on the stratospheric ozone layer has been the subject of numerous atmospheric modeling efforts. Such studies have demonstrated the critical importance of chemical processes that control the partitioning between Cl, ClO and other catalytically inactive forms (or reservoirs) of chlorine in the atmosphere. By 1985 laboratory and field measurements had identified I-I Cl, HOCl, and ClONO₂ as important atmospheric chlorine reservoirs. Substantial efforts were made to understand the physical and chemical properties of these species as well as to quantify the important atmospheric reactions that interconnect them.

The discovery in 1985 of dramatic ozone depletion in the Antarctic stratosphere² followed by the observation of tremendously elevated ClO levels^{3,4} in the same region led to the suggestion of a causal relation between the two phenomena. The canonical mechanism for chlorine catalyzed ozone destruction (equations 1 - 3) cannot account for the observations, however, due to the lack of significant oxygen atom concentrations under Antarctic springtime conditions. Instead, recent attempts to explain the loss of ozone have focused on new chemical mechanisms, occurring at temperatures below 220 K, which involve poorly known molecular characteristics of inorganic chlorine species.

Over the last five years substantial progress has been made in defining the realm of new chlorine chemistry in the polar stratosphere. Application of existing experimental techniques to potentially important chlorine-containing compounds has yielded quantitative kinetic and spectroscopic data as well as qualitative mechanistic insights into the relevant reactions. In addition, the emergence of improved ab initio theoretical methods has provided valuable guidance regarding the feasibility of postulated reaction mechanisms and intermediates. As a result of these efforts atmospheric reaction schemes have been proposed that can semi-quantitatively account for the observed loss of polar ozone. However, many questions remain unanswered about the mechanistic aspects of these schemes. Moreover, the possible impact of these new schemes on the coupling between chemical families, ie. ClO_x , NO_x , and IO_x , remains to be fully explored.

In this chapter we review recent (post 1985) studies on chlorine-containing inorganic compounds of possible relevance to the gas-phase chemistry of the polar stratosphere. This review is not intended to be comprehensive but rather to highlight compounds which have received significant attention only recently. Emphasis is placed on thermochemical data that relate directly to the atmospheric roles of the species. Physical chemical data on aspects such as reaction dynamics are not included. This chapter also seeks to emphasize the increasing value of ab initio theory in atmospheric chemical assessments. In particular, ab initio predictions of the energetic of reactions involving chlorine-containing species are presented.

The chlorine-containing species discussed in this review are organized by chemical family. Three chemical families are included, namely, ClO_x , ClO_x , and ClNO_x . The general experimental and theoretical approaches that have been used to study these compounds are summarized in the next section. The summary of ab initio methods is greatly expanded in order to adequately address the rapid advances made in this field.

11. Experimental and **Theoretical** Methods

Model calculations of atmospheric processes require as input the rates of all relevant atomic and molecular production and loss processes. For a given atmospheric constituent the relevant in situ loss processes typically include thermal decomposition, photolytic decomposition, and reaction with other atmospheric species. The in situ production of any particular atmospheric species is related to the corresponding loss processes of others.

Laboratory experiments attempt to quantify competing loss processes and to quantitatively identify the resulting products. The range of temperature and pressure conditions that are relevant to atmospheric processes extend from 300 K to 180 K and 760 torr to 1 torr. Recent experimental investigations of polar stratospheric processes have focused on the lower temperature regimes and intermediate pressures.

A variety of spectroscopic techniques, including, UV, visible, IR, SMM-wave, and microwave absorption, resonance and laser-induced fluorescence, and mass spectrometry have been employed in the laboratory to monitor species of interest. Photolytic decomposition rate calculations are based on quantitative measurements of UV and visible absorption cross sections. For studies of thermal decomposition and chemical reaction kinetics the spectroscopic techniques are combined with a variety of experimental kinetics techniques, most notably, discharge flow and flash photolysis. The essential features of the kinetic techniques are well known^{5,6}; flash photolysis is characterized by rapid formation of reactants (i.e. pulsed laser or lamp induced dissociation) followed by real time observation of the reaction kinetics; discharge flow is characterized by the mixing and subsequent reaction over a controlled distance, of two gaseous flows. Both techniques have been further adapted, recently, to study the chemistry of inorganic chlorine compounds. One example is studies of the photolysis products of OCIO and ClONO₂ that were accomplished by combining the laser photolysis technique with a molecular beam - mass spectrometer.^{7,8} Another example is a study of ClOOC1 that relied on a modification of the flow tube technique to include both a low (<100 mtorr) and high pressure (> 1 torr) region.⁹

In the following sections of this chapter we will attempt to further highlight the spectroscopic and kinetic techniques that have been applied in recent studies of inorganic chlorine species.

Experimental data are scarce or nonexistent for many potentially important reactions. Initial assessments of the possible importance or atmospheric consequences of these reactions benefit greatly from *ab initio* calculations. In the past ten years, both the quality and quantity of theoretical predictions of the energetics of chemical reactions for inorganic chlorine compounds have improved markedly. Ten years ago, most of the few theoretical papers that dealt with chlorine chemistry used minimal basis set *ab initio* or semi-empirical self-consistent field (SW) calculations. These papers dealt with predictions of molecular and electronic structures, Very few dealt with energetics of reactions. Significant advances have been made recently both in methods for the prediction of reaction energetics and the computer technology that makes use of these methods. Consequently, it is now possible to predict energetics related to reactions of molecules of small to medium size. In the following subsections we summarize the progress made in theoretical methods for calculation of electronic structure and reaction energetics.

A. Electronic Structure Calculations

The two essential ingredients in an *ab initio* electronic structure calculation are the basis set and the level of theory used in the calculation. For the prediction of energetic properties of molecules and reactions, high quality basis sets and correlation corrections to the Hartree-Fock (HF) self-consistent field (SCF) molecular orbitals are both essential. The basis sets must be of at least double zeta plus polarization (DZP) quality. Such basis sets contain two functions for each formal atomic orbital on each atom plus one set of functions (polarization functions) on each atom with quantum number one higher than required in the isolated atoms. Commonly used basis sets at this level are those due to Dunning and Hay¹⁰ and the well-known 6-31 G(d) and 6-31G(d,p) basis sets developed by Pople and co-workers^{11,12}. Note that we will use 6-31 G(d) and the older 6-31 G* notation interchangeably. These two basis sets are the ones most commonly used for the predictions of molecular geometries and vibrational frequencies. For the

prediction of energetic properties, much larger basis sets are required, with at least triple zeta plus polarization quality ('I-H'). Examples are 6-311 G(d,p) and larger basis sets such as 6-311G(3df,3pd)[references 13, 14]. The latter basis set includes three sets of functions and one set of *f* functions on each heavy atom and three sets of *p* functions and one set of *d* functions on each hydrogen. Several studies have indicated that in order to provide an adequate description of chlorine compounds a second set of polarization functions should be added to the chlorine,¹⁵

'here are several ways in which correlation corrections can be added into an electronic structure calculation. At present, the most popular approaches are: (1) Many body perturbation theory as popularized by Pople and co-workers within the Moller-Plesset (MP) formalism,^{16>17}. To second, third and fourth order, these are referred to as MP2, MP3 and MP4, respectively. MP4 calculations can be performed with (SDTQ) or without (SDQ) the inclusion of triple excitations. Triples can be quite important for the prediction of energetics, but they are also quite computationally expensive, (2) A variational treatment of correlation comes from the singles and doubles excitation configuration interaction method (CISD)^{18~19}. (3) Coupled cluster theory²⁰ is closely related to many body perturbation theory and has become increasingly popular. It is commonly formulated with the inclusion of single and double excitations (CCSD), single, double and triple excitations (CCSDT), or through quadruples (CCSDTQ). A closely related method is the quadratic configuration interaction methods (QCI) developed by Pople and co-workers²¹. (4) Multi-reference. configuration interaction (MRCI) calculations are particularly important when there is significant diradical character at important points on a potential energy surface. In such cases MP and CC approaches frequently break down. A common approach to MRCI calculations is to first perform a fully optimized reactions (FORS)SCF (or CASSCF) calculation, followed by a singles and doubles CI from all the FORS reference configurations.²²⁻²⁴

B. Computational Procedures for Predicting Energetics

Theoretical heats of formation can be obtained from calculated bond dissociation energies and heats of reactions. Semi-empirical molecular orbital calculations provide useful insights, but

they are often not sufficiently reliable for accurate estimates of the heats of formation. A detailed discussion of the performance of ab initio molecular orbital theory can be found in the book by I. Lehn, Radom, Schleyer and Pople.¹⁷ Even high level ab initio calculations can be inadequate if measures have not been taken to control the systematic errors. Unless reactions are chosen carefully to cancel errors, the various levels of ab initio theory that are currently practical all require some degree of empirical correction in order to achieve chemical accuracy (± 1 kcal/mole). Two factors determine the quality of a given level of ab initio molecular orbital calculation: the basis set and the treatment of electron correlation. However, increasing the size of the basis set or improving the treatment of correlation is expensive (computational cost is proportional to n^4 to n^7 , where n is the number of basis functions).²⁵ For most work, the basis set must be at least double zeta plus polarization or 6-31 G* quality, preferably triple zeta plus polarization or 6-311 G**. Depending on the reaction, it is often necessary to add extra polarization functions and diffuse functions (e.g. 6-31 ++G(2dfp)). Electron correlation energy should be calculated at an appropriately high level, such as fourth order perturbation theory (including triple excitations, e.g. MP4SDTQ) or by an iterative method like CISD (with corrections for higher excitations), QCISD or CCSD (with corrections for triples). Even at the MP4SDTQ/6-31 G** level, direct calculations of bond dissociation energies can be in error by as much as 10-29 kcal/mole. One method to control the errors arising from basis set deficiencies and inadequacies in the treatment of electron correlation energy is to choose reactions so that the systematic errors tend to cancel. A class of reactions of this type is the isodesmic reaction, i.e. a reaction in which the number of bonds of each type is conserved. Depending on how carefully the bonding environments are preserved in an isodesmic reaction, the errors in the computed heats of reaction can range from 1 to 5 kcal/mole at the MP4SDTQ/6-31 G* level. A homodesmic reaction takes this idea one step further by conserving not just bonds but entire groups and bonding environments. Errors in homodesmic reactions can be ± 5 kcal/mole at the MP4SDTQ/6-31 G** level. For open shell systems, unrestricted Hartree-Fock and Moller-Plesset perturbation theory are often used to calculate energy differences. These methods can suffer from

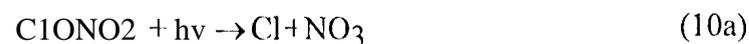
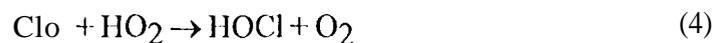
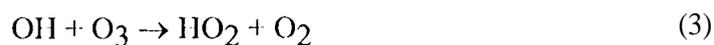
spin contamination that can cause errors of 1 kcal/mole in heats of reaction for systems where the contamination is small to errors of 15 kcal/mole in activation energies if the spin contamination is large. An isogyric reaction is one that conserves spin and eliminates a substantial fraction of the spin contamination error, provided the contamination is small. When perturbative methods are used for systems with substantial spin contamination, spin projection can be used to remove most of the error.²⁶ To compute the heat of formation of a particular compound via an isodesmic, isogyric or homodesmic reaction requires the heats of formation of all the other compounds in the reaction used,

Pople and co-workers²⁷⁻²⁹ have used theoretical atomization energies to calculate heats of formation without resorting to specific corrections for individual bonds. The atomization energies are computed using isogyric reactions by adding sufficient hydrogen atoms so that the total spin on both sides is the same. The computed heat of reaction is combined with the experimental dissociation energy for H₂ to obtain a theoretical estimate of the heat of formation. This eliminates the need for a set of reference compounds (other than H₂) for which the heat of formation is well known. To control the computational expense, various assumptions are made concerning the additivity of basis set effects. The systematization and extension of this approach lead to the G-1 and G-2 levels of theory³⁰⁻³¹. The G-1 approach³⁰ uses MP2/6-31 G* optimized geometries, QCISD(T)/6-311 G** energies with the effects of diffuse functions (6-311 G+G* *) and extra polarization functions (6-311 G(2df,p)) calculated at the MP4 level and assumed additive, with small empirical corrections for the number of paired and unpaired electrons. The G-2 level of theory³¹ improves on G-1 by removing most of the additivity assumptions. The G-1 level of theory is accurate to ± 2 kcal/mole for first and second row singly bonded two heavy atom systems³⁰. The mean absolute deviation for the G-2 level is 1.2 kcal/mole for the set of 125 molecules that includes multiply bonded systems³¹.

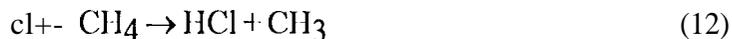
III. Review of **Experimental** and Theoretical Studies of **ClO_x Species**

A. Cl and ClO

As mentioned in the introduction, reactions involving Cl and ClO are central to the catalytic destruction of stratospheric ozone. In addition to the ClO_x-only cycle (reactions 1 and 2), at least three other cycles which couple the ClO_x, IO_x, and NO_x families are important in mid-latitude stratospheric ozone chemistry.



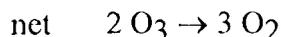
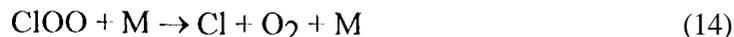
The reaction of atomic chlorine with ozone is common to all of the cycles. The chain lengths of the atomic cycles are limited by the reaction



which effectively sequesters atomic chlorine in the form of hydrogen chloride, a relatively unreactive (in the gas phase) atmospheric constituent. The rate constants for the reactions of atomic chlorine with ozone and methane have been extensively studied above 220 K. Recently, DeMore has measured the ratio of $k(\text{Cl} + \text{O}_3)$ to $k(\text{Cl} + \text{CH}_4)$ at temperatures characteristic of the polar stratosphere.³² The ratio obtained at 196 K, for example, is within 10% of the value calculated by extrapolation down to 196 K of the two Arrhenius expressions that characterize the kinetics data above 220 K.

Reactions involving ClO in the above catalytic cycles serve to couple the ClO_x, HO_x, and NO_x families. These coupling reactions are particularly important in the lower stratospheres³ and have received a tremendous amount of attention over the past 15 years. Although the overall kinetics of these reactions have been well studied above 220 K, the data base is incomplete both below 220 K and in terms of some of the product branching ratios. Several poorly characterized product channels will be discussed in the following sections of this chapter.

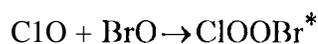
A coupling reaction between ClO and BrO is the key step in a recently proposed mechanism for polar ozone depletion,³⁴ namely



The kinetics of the ClO + BrO reaction have been characterized experimentally by Friedl and Sander,³⁵⁻³⁷ Turnipseed et al.,³⁸ and Poulet et al.,³⁹ (see Table I) Three product channels are observed, specifically,



The inverse temperature dependences of the observed rate coefficients for each of the reaction channels strongly indicate that the reaction proceeds via formation of metastable intermediates.

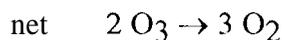
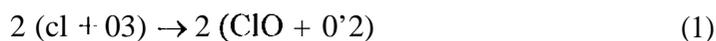
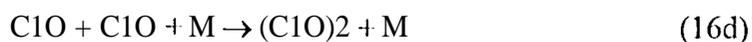


By invoking the existence of short-lived intermediates the temperature dependence can be rationalized in terms of the competition between product formation and reactant re-formation during dissociation of the intermediate. Based on the absence of a pressure dependence in the observed rate constants, Sander and Friedl³⁷ have concluded that decomposition of the excited intermediates is substantially faster than collisional stabilization. Consequently, the formation of a long-lived ClBrO₂ molecule in the atmosphere is unlikely.

Another reaction in which metastable intermediates play an important role is the ClO self reaction:



The termolecular addition reaction of ClO to form (ClO)₂ is the rate-limiting step in a proposed mechanism for polar ozone destruction.⁴⁰



The rate coefficients for formation of $(\text{ClO})_2$ from the ClO self reaction have been studied extensively in the last several years. The results of those studies will be presented in a later section of this chapter.

ClO has long been a favorite subject of ab initio theoretical methods. Most theoretical studies of the ClO radical have focussed mainly on the structural characterizations of ClO using high level calculations CASSCF, MRCI, and MP2 methods⁴¹⁻⁴⁵. The heat of formation for ClO, which is an important quantity for determining ClO reaction enthalpies, can be determined from the dissociation energy of ClO combined with the enthalpies of formation for Cl(g) and O(g) at OK. Using the G1 methods of Pople et al.,²⁹ the dissociation energy of ClO has been determined as $60.9 \text{ kcal mol}^{-1}$. Curtiss et al.,⁴⁶ re-determined the dissociation energy and obtained $61.5 \text{ kcal mol}^{-1}$ using G2 theory. The dissociation energy of ClO has been determined spectroscopically by Coxon and Ramsay⁴⁷ from the convergence limit of the $\Lambda \leftarrow X$ subbands assuming dissociation into the $^2P_{3/2}$ of O and 1D of Cl. The dissociation energy value obtained is $63,427 \text{ kcal mol}^{-1}$. Based on this value an experimental heat of formation for gaseous ClO is derived as $24.15 \pm 0.02 \text{ kcal mol}^{-1}$ at OK and 24.30 ± 0.02 at 298K. Deviation of the results between experiment and the G2 theory is only $1.9 \text{ kcal mol}^{-1}$. (see Table 11)

B. ClO₂ Isomers

The important polar stratospheric reactions $\text{ClO} + \text{BrO}$ and $\text{ClO} + \text{ClO}$ both generate products with the chemical formula ClO₂. There are two isomers having the chemical composition ClO₂. One of these, OC1O, is a well known species which is kinetically stable at

room temperature, while the other, ClOO, is highly reactive and has only been observed at low temperatures. In the next two subsections we review experimental and theoretical work on both isomers.

B1. Symmetric OCIO

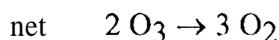
One of the channels of the ClO + BrO reaction has been shown to produce OCIO. Subsequent to this finding, OCIO has been observed in the atmosphere in both the south and north polar regions by Solomon and coworkers,⁴⁸ Wahner et al.,⁴⁹ and Perner et al.,⁵⁰ using the ultraviolet absorption technique. These measurements provide qualitative confirmation of the atmospheric importance of the BrO + ClO reaction. However, several investigators have raised the possibility of significant OCIO formation from the ClO + ClO reaction. Nickolaisen et al.,⁵¹ and Simon et al.⁵² have recently measured reaction rate coefficients for formation of OCIO from the ClO self reaction, (Table I) Based on a comparison of the kinetics of the ClO + ClO and ClO + BrO reactions and a knowledge of the polar atmospheric abundances of ClO and BrO (Toohey et al.⁵³), the current consensus is that atmospheric OCIO is primarily produced from BrO + ClO.

A number of OCIO loss processes have been investigated. The primary path is photolysis since OCIO absorbs strongly in the near UV and visible regions. Wahner et al.⁵⁴ have recently measured the absorption cross section of OCIO with a resolution of 0.25 nm at 204, 296, and 378 K, in the wavelength range 240 to 480 nm. (see Figure 1)

A significant controversy has developed recently concerning the quantum yields of OCIO photolysis. The photochemistry of OCIO is known to occur on the excited A2A2 potential energy surface,⁵⁵⁻⁶¹ which can lead to dissociation via both the ClO (X211) + O(³P) and O₂ + Cl(²P) pathways.



The atmospheric effects of the two photolysis channels are potentially quite different. The production of atomic oxygen in channel 18a ultimately leads to regeneration of O₃ via the O + O₂ reaction. In contrast the production of atomic chlorine in channel 18b enables catalytic ozone destruction to occur by the following mechanism:



Theoretical calculations on OCIO may provide valuable insight into the photochemical branching. Unfortunately, only a few previous theoretical calculations on OCIO have been carried out and these have not included the effects of electron correlation. The most extensive self-consistent field (SCF) calculations have been those of Golc and Hayes,^{62,63} Peterson and Werner,⁶⁴ using the internally contracted multireference configuration (CMRCI) method with a restricted full valence active space. These authors used a large Gaussian basis set (a Dunning correlated polarized valence quadruple zeta set supplemented with f-functions—the basis set was denoted as a 3d2f). The CMRCI, including corrections for higher order excitations (CMRCI+Q), yielded a dissociation energy of 53.0 kcal mol⁻¹ for the dissociation of OCIO into ClO + O. The experimental bond energy⁶⁵ has been measured to be 55.2 ± 2 kcal mol⁻¹. (Table 11)

Many experimental investigations of OCIO photolysis have been performed recently, but no consensus has been reached regarding the photochemical behavior of OCIO as a function of photolysis wavelength. Colussi et al.,⁶⁶ employing the laser photolysis - resonance fluorescence technique, reported an oxygen atom yield of unity and a chlorine atom yield of less than 0.01 at 308 nm. This finding was supported by laser photolysis - Xe phototitration experiments of Lawrence et al.⁶⁷ that covered the 359- 368 nm range. However, Vaida et al.⁶

and Ruhl et al.⁶⁸ reported detection of chlorine atom production from OCIO photolysis at 368 nm upon application of resonance enhanced multiphoton ionization (REMPI) as a technique for atomic chlorine detection. Bishenden et al.⁶⁹ reported a chlorine atom yield of 0.15 ± 0.10 from experiments similar in approach to those of Vaida and coworkers. Very recently, Davis and Lee⁷⁰ reexamined the photodissociation of OCIO in a molecular beam using photofragment translational energy spectroscopy between 350 and 475 nm. They found strong evidence for a non zero yield of Cl, however, the maximum Cl quantum yield was only 0.039 at 404 nm, decreasing to <0.002 under the absorption peaks in the wavelength region of the previous REMPI experiments. A summary of the photochemical data for OCIO is given in Table III.

B2. Unsymmetrical ClOO

The ClO₂ peroxy radical was first proposed by Porter and Wright⁷¹ in order to account for ClO production in the flash photolysis of Cl₂/O₂ mixtures. Subsequent work by Burns and Norrish⁷² supported the claim. Identification of ClOO as a product of the atmospherically important BrO + ClO reaction (reaction 13a) has been inferred from kinetics experiments by Friedl and Sander.³⁵ In that experiment Cl and O₂, not ClOO, were observed as the reaction products. However, the observed negative temperature dependence of the reaction rate coefficient supports the identification of ClOO + Br, not Cl + Br + O₂, as the nascent product set for this channel. Direct production of Cl, a process approximately 2 kcal mole⁻¹ endothermic, would manifest itself as a significant positive temperature dependence for k_{13a}. An analogous argument can be used to infer ClOO production in the ClO + ClO reaction (reaction 16a).⁵¹

The apparently rapid decomposition of ClOO in the laboratory studies of reactions 13a and 16a can be rationalized in terms of thermal decomposition if ClOO is only weakly bound. The first estimate of the Cl-OO bond dissociation energy resulted from the thermochemical estimate of Benson and Buss⁷³. They estimated it to be 8.0 kcal mol⁻¹. The kinetic studies of Johnston⁷⁴, Wagner and Garvin⁷⁵, and Clyne et al.⁷⁶ have led to an experimental estimate for the ClO₂ heat of formation. These studies lead to the conclusion that ClO₂ is

thermodynamically more stable than OClO by $3.1 \text{ kcal mol}^{-1}$. Several more recent thermochemical studies have been initiated in response to the increased recognition of the role of ClOO in the polar stratosphere, Nicovich et al.⁷⁷ redetermined the heat of formation of ClO₂ rigorously. Their newly derived value is $23.4 \pm 0.5 \text{ kcal mol}^{-1}$ (at 298 K), Baer et al.⁷⁹ determined a value of $23.3 \text{ kcal mol}^{-1}$ (at 298 K), while Mauldin et al.⁸⁰ measure the heat of formation to be $24.0 \pm 0.4 \text{ kcal mol}^{-1}$ (at 0 K). (see Table 11) The major conclusion of these studies is that the fate of ClOO in the stratosphere is dominated by thermal decomposition under all pressure and temperature conditions.

Theoretical studies largely corroborate the experimental findings. Golc⁶³ performed the first SCF calculations on ClO₂ radical using constrained geometry optimization. This was later followed by full geometry optimization at the SCF level using large sp basis set without polarization functions by Hinchliffe⁸⁰. The first high level optimization of the ClO₂ radical was done by Jafri⁸¹ using a double-zeta plus polarization basis set and MC SCF-CI wave functions. This work led to the first theoretical estimate of the bond dissociation energy (Cl + O₂) of $7.5 \pm 4 \text{ kcal mol}^{-1}$. Peterson and Werner in their study of the energetics of the OClO radical also obtained a bond dissociation energy of $2.46 \text{ kcal mol}^{-1}$. Francisco and Sander⁸² have re-examined the bond dissociation energy and heat of formation using QCIST(1) methods with large basis sets (6-3 11 ++G(3df,3pd) basis set) and isodesmic schemes. They estimate the bond dissociation energy to be $4.0 \pm 2 \text{ kcal mol}^{-1}$. This is in reasonable agreement with the experimental measurements of Nicovich et al. ($4.76 \pm 0.49 \text{ kcal mol}^{-1}$), Baer et al. ($4.983 \pm 0.005 \text{ kcal mol}^{-1}$), and Mauldin ($4.6 \pm 0.4 \text{ kcal mol}^{-1}$). Francisco and Sander estimated the heat of formation for ClO₂ to be $24.2 \pm 2 \text{ kcal mol}^{-1}$ at the QCISD(T) level as compared to the experimental estimate of $23.4 \pm 0.1 \text{ kcal mol}^{-1}$ that was determined by Nicovich et al.. The difference can be attributed to the fact that a small basis set and moderate correlation are included, Rathman and Schindler⁸³ using G 1 theory estimated the heat of formation to be 29 kcal mol^{-1} .

C. ClO₃

The reaction of O₂ with ClO could potentially reduce the catalytic efficiency of the ClO_x cycle towards the destruction of O₃. In experimental studies that have examined the reaction of ClO with O₂, the formation of a long-lived ClO-O₂ complex has been suggested⁸⁴, but the evidence is controversial.⁸⁵⁻⁸⁷ Ilandwerk and Zellner⁸⁸ examined the reaction of O₂(¹Δ_g) + ClO by following the loss of ClO. From their data they suggested that the barrier to the formation of ClO₃ should be large because the reaction was slow,

Indirect evidence for the existence of ClO₃ has been obtained by Colussi et al.⁸⁹ Using a laser photolysis - resonance fluorescence technique, they observed a negative temperature and a positive pressure dependence for the reaction of atomic oxygen with OCIO. (see Table 1) Both results were interpreted in terms of the formation of a ClO₃ complex.^{66,89}



Gleason et al.,⁹⁰ using a discharge flow - mass spectrometric technique also found the reaction to be negative] y dependent on temperature, but only below 240 K. Above 240 K, the observed reaction rates abruptly increased with temperature. This latter observation suggests that, at least at low pressure, an abstraction channel is competitive with adduct formation, i.e.



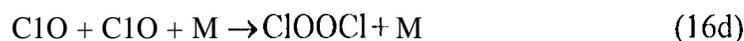
One significant discrepancy between the two investigations is that the termolecular rate constant, k₁₀, derived by Gleason et al. on the basis of their low temperature data is not consistent with the data obtained by Colussi et al..

To date there has been no direct experimental evidence for the existence of ClO₃. Nevertheless, there are three possible ClO₃ isomers: (1) ClOO₂; (2) OCIO₂; and (3) sym-ClO₃ structures. Rathman and Schindler⁹¹ optimized the structures of ClO₃ using second-order Moller-Plesset perturbation theory (MP2) using the medium set 6-31 G* basis set. All the structures were found to be bound. Using G1 theory, the heats of formation at 0K were determined for the three isomers as 41 kcal mol⁻¹ for ClOOO, 58 kcal mol⁻¹ for OCIOO; and 48 kcal mol⁻¹ for sym-ClO₃. However, there is a large discrepancy between the value for sym-

ClO₃ calculated using G1 theory and that determined using thermochemical additivity (55.6 ± 4 kcal mol⁻¹)⁶⁶. This latter value has been revised by Colussi et al.⁸⁹ to 51.9 kcal mol⁻¹ which brings the G1 theory as the experimental estimates in closer agreement. (see Table 11)

D. Cl₂O₂

in recent years, three isomers of Cl₂O₂ (ClOOC1, ClOC1O and ClC1O2) have been studied extensively using a variety of kinetic, spectroscopic and theoretical techniques. Chlorine peroxide has been examined the most thoroughly because of its likely role in the catalytic depletion of ozone (reactions 16d, 17, 14, and 1) in the region of the polar stratosphere that has been perturbed by heterogeneous reactions occurring on cloud particles:



The ClO + ClO reaction is partially rate-determining in the above cycle, along with the photolysis of ClOOC1. Rate coefficients for the termolecular component of the ClO + ClO reaction (reaction 16d) have been obtained by Basco and Hunt,⁹² Hayman et al.,⁹³ Sander et al.,⁹⁴ Trolrier et al.⁹⁵ and Nickolaisen et al.,⁵¹ and the results are summarized in Table 1. Sander et al. and Trolrier et al. studied the reaction under conditions of pressure and temperature relevant to the polar stratosphere and the results are in reasonably good agreement, although Trolrier et al. observed non-zero intercepts in the rate coefficient falloff curves which were not observed by Sander et al. Subsequent work by Nickolaisen et al. showed that the results of Trolrier et al. were probably affected by the large apparent collision efficiency of Cl₂ which was present in high concentrations in their system. Nickolaisen et al. suggested that the effect was due to the

formation of a weakly bound ClOOCI₂ complex which acts as a “chaperone” in the ClO recombination.

Under nighttime or twilight conditions when ClOOC1 photolysis is slow, the atmospheric partitioning of chlorine-containing species is determined by the rates and branching ratios for the thermal decomposition of ClOOC1,



Unimolecular rate constants for reaction 21 have been measured directly or inferred by Basco and Junj⁹² and Cox and Derwent⁹⁶ at room temperature, by Cox and Hayman⁹⁷ over the temperature range 233-303 K, and by Nickolaisen et al.⁵¹ over the temperature range 260-310 K. Nickolaisen et al. obtained a larger temperature dependence for $k_{21 \text{ a}}$ than Cox and Hayman which is reflected in a somewhat larger inferred O-O bond energy in ClOOCI (18.8 kcal mole⁻¹ vs 17.3 kcal mole⁻¹). While this difference is relatively small, it results in a difference of a factor of five in the extrapolated ClOOCI thermal lifetime under polar stratospheric conditions (T= 195 K). There are no direct measurements of rate constants for the unimolecular decomposition pathways 21 b and 21 c. Nickolaisen et al. measured the activation energies for the bimolecular channels for the ClO + ClO reaction and obtained values of 3.2 ± 0.2 kcal mole⁻¹, 4.9 ± 0.9 kcal mole⁻¹ and 2.7 ± 0.3 kcal mole⁻¹ for the Cl₂ + O₂, ClOO + Cl and OC1O + Cl channels, respectively. (see “Table 1) The magnitude of these activation barriers indicates that the only significant pathway for ClOOCI unimolecular decomposition under atmospheric conditions is the one forming ClO + ClO.

As indicated above, photolysis of ClOOCI,



is a key process in the catalytic destruction of ozone in the polar stratosphere. While pathway a results in ozone destruction, pathway b leads to a null cycle, hence wavelength resolved quantum

yield measurements are extremely important for atmospheric modelling. Quantum yields for ClOOCl photolysis have been measured by Cox and Hayman⁹⁷ and by Molina et al.⁹⁸ (see Table 111) Cox and Hayman inferred a value of 1 ± 0.4 for ϕ_a at 254 nm using steady-state photolysis and time-resolved ultraviolet absorption spectroscopy to monitor Cl₂O₂. Molina et al. derived a value for ϕ_a of 0.6 ± 0.07 using 308 nm laser photolysis of Cl₂O₂ followed by time-resolved laser-induced fluorescence of Cl (both the Cox and Hayman, and Molina et al. results have been corrected using the currently accepted absorption cross sections of Cl₂O and Cl₂O₂). In view of the differences in the results from the two studies, and the additional uncertainties in both the relative and absolute cross sections of Cl₂O₂, additional wavelength-resolved measurements of both ϕ_a and ϕ_b are clearly needed.

Ab initio methods also have been applied to the characterization of the photolytic behavior of ClOOCl. In particular, theory has been used to examine the excitation energies and associated oscillator strengths of electronic transitions of ClOOCl. The earliest attempt was by Jensen and Oddershede⁹⁹ who utilized the random phase approximation (RPA) to evaluate the low-lying transitions in ClOOCl. The calculations were performed at the MCSCF level using a 6-31 G* basis set and MP2/6-31 G * optimized geometries. The principal conclusion of that investigation was that the UV spectrum of ClOOCl above 200 nm is too weak to be readily observed. This finding called into question the assignment of the experimentally obtained absorption spectrum to ClOOCl, Jensen and Oddershede suggested that chloryl chloride, ClC102, which is predicted by the RPA method to have strong absorption in the 200-300 nm region might be responsible for the spectrum obtained from ClO + ClO reaction mixtures. Stanton and Bartlett¹⁰⁰ have examined the low-lying singlet electronic states of ClOOCl at the coupled-cluster singles and doubles level. They find that transitions to the \tilde{D} and \tilde{F} electronic states occur at approximately 240 nm and have sizeable oscillator strengths. Transition probabilities for these states were not reported by Jensen and Oddershede since the RPA calculations predicted that the states lie more than 6 eV above the ground state. Stanton and Bartlett have investigated this discrepancy and have concluded that the RPA model severely

overestimates excitation energies for transitions to the E and F states of ClOOCl. The coupled-cluster calculations predict an electronic spectrum for ClOOCl that is in qualitative agreement with that observed experimentally. The molecular orbital description of the process involves the promotion of an electron to a ClO antibonding sigma orbital. The electron promotion is likely to result in significantly weakened Cl-O bonds or spontaneous decomposition of the ClOOCl to give Cl and ClOO.

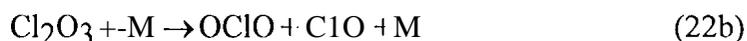
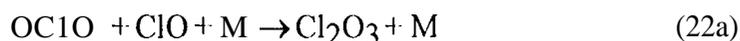
Considerable progress has been made recently in the experimental and theoretical characterization of the thermochemical properties of the (ClO)₂ isomers. The ClO + ClO reaction surface has a fairly deep potential well (≈ 17 kcal mol⁻¹) corresponding to the most stable form of (ClO)₂. Using a discharge-flow reactor with submillimeter absorption spectroscopy, Birk et al.⁸ identified this molecule as chlorine peroxide, ClOOCl, and determined its structure. Another isomer of (ClO)₂, chloryl chloride (ClClO₂) has been identified by Mueller and Willncr1013102 using matrix and gas-phase infrared and ultraviolet absorption spectroscopy, but its thermal stability and barriers toward isomerization are not well established. Because of the extensive rearrangement required in the direct formation of chloryl chloride from the ClO self-reaction, the A-factor for this process is expected to be small. The isomer ClOCIO has not yet been identified spectroscopically but would be expected to play a role in the ClO + ClO reaction channel leading to Cl + OClO.

Physical properties of Cl₂O₂ isomers have also been studied extensively using *ab initio* methods. McGrath et al.¹⁰³³¹⁰⁴ using a Moller-Plesset theory (MP2, MP4) with 6-31 G and 6-31 +G(3d) basis sets found that the lowest structure of the three isomeric forms is the straight-chain structure, ClOOCl. The structures ClClO₂ and ClOCIO were found to be 1 and 7 kcal mol⁻¹ above the ClOOCl structure, respectively. At the MP2/6-31 +G(3d) level of theory, the heat of formation was determined to be 32.6 kcal mol⁻¹ at 0 K for ClOOCl; 33.8 kcal mol⁻¹ for ClClO₂; and 40.0 kcal mol⁻¹ for ClOCIO. Lee et al.¹⁰⁵ have reexamined the relative energies of the isomers of Cl₂O₂ using coupled cluster theory including singles, doubles, and incorporating effects of triplet excitations (CCSD(T)) using large basis sets that include g-type functions. The

computed heat of formation at 0 K is 34.2 kcal mol⁻¹. The heat of formation value determined by McGrath et al. is lower than that determined by Lee et al. which is attributed to the fact that a small basis set and moderate correlation is included. The relative energies of the C1C1O2 and ClOC1O isomers lie 0.9 ± 2.0 and 10.1 ± 4.0 kcal mol⁻¹ higher in energy at 0 K, respectively, above the straight-chain form. (see Table II)

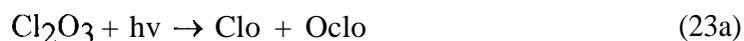
E. Cl₂O₃

The reaction of OC1O with C1O was initially recognized as a complication in studies of the C1O self reaction that utilized OC1O as a precursor. Later, Sander et al.¹⁰⁶ and Anderson et al.¹⁰⁷ pointed out that the formation of a stable C1O-OC1O adduct could lead to sequestering of atmospheric C1O, and subsequent inhibition of O₃ loss, in the polar stratosphere.



A number of spectroscopic investigations of reaction 9 have been conducted and have confirmed adduct formation at temperatures below 240 K. These include discharge flow - UV + IR absorption studies by Burkholder et al.,¹⁰⁸ (Figure 1) steady state photo] ysis - IR absorption studies by Zabel¹⁰⁹ and discharge flow - submillimeter wave spectroscopic studies by Friedl et al.¹¹⁰ The equilibrium constant between reactions 9a and 9b has been examined by Hayman and Cox¹¹¹ and Burkholder et al.¹¹² The enthalpy of reaction derived from these studies is approximately 12 kcal mole⁻¹. The association rate constant has been measured by Parr et al.¹¹³ at 226 K and by Burkholder et al.¹¹² over the range 200-260 K. (Table I) The observed rate constants are more than a factor of three greater than the corresponding C1O + C1O constants.

On account of the small C1O-C1O2 bond energy the stratospheric fate of Cl₂O₃ is dominated by thermal decomposition. However, under some atmospheric conditions photolysis of Cl₂O₃ may compete with thermal decomposition.



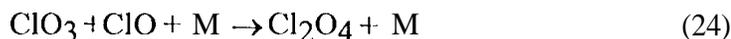
The photochemical quantum yields have, as yet, not been characterized by theoretical or experimental methods. The possible occurrence of channel 23b may result in the formation of higher oxide of chlorine in the atmosphere. This possibility is discussed in the next section.

F. Cl₂O₄, Cl₂O₆, and Cl₂O₇

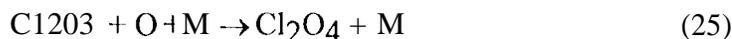
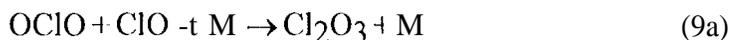
The discovery of dramatically elevated concentrations of ClO and OClO in the polar stratosphere has focused increased attention not only on Cl₂O₃ but on the possible formation of higher oxides, such as Cl₂O₄, Cl₂O₆, and Cl₂O₇. These higher oxides of chlorine have been known for a long time and are typically discussed in inorganic textbooks. However, many of the structural, spectroscopic, and chemical properties of these compounds remain poorly known or controversial. In addition, the reaction data base on gas phase formation of the higher oxides is nearly nonexistent.

Although chlorine perchlorate (ClOClO₃) was synthesized in 1970 by Schack and Pilipovich,¹¹⁴ the gas phase ultraviolet spectrum has been obtained only recently by Lopez and Sicre.¹¹⁵ (Figure 1) The UV spectrum is significantly shifted to the blue compared to smaller dichlorine oxides such as Cl₂O and ClOOC1. In addition, the absorption cross sections of Cl₂O₄ are uniformly smaller than the corresponding ones of ClOOC1. Accordingly, Cl₂O₄ is substantially more stable with respect to atmospheric photochemical decomposition than ClOOC1 and could, therefore, function as a reservoir of inorganic chlorine provided that it is also relatively stable thermally and chemically.

The method used by Lopez and Sicre to generate ClOClO₃ was based on results obtained by Schell-Sorokin et al.¹¹⁶ and involved static photolysis of OClO followed by a series of fractional condensation and distillation steps designed to remove OClO, Cl₂, and Cl₂O₆. Zabel¹⁰⁹ has attempted, using a static photolysis - IR Fourier transform spectrometer technique, to investigate the reaction mechanism responsible for ClOClO₃ formation in the photochemical decomposition of OClO. The results of his study suggest two possible mechanisms, namely



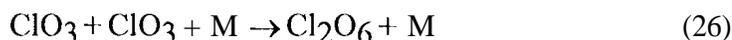
or



The mechanism involving ClO_3 provides the best explanation for the weak temperature dependence and strong pressure dependence of the Cl_2O_4 yield observed by Zabel.

The possibility of in situ atmospheric formation of Cl_2O_4 by reaction 14 has been discussed by Sander et al.⁹⁴ This reaction is expected to occur most readily in the polar stratosphere during the springtime when there exists high ClO concentrations, low temperatures, and moderate pressures. However, formation of ClO_3 by reaction 10 is not expected under these conditions due to the lack of significant oxygen atom concentrations. Consequently, other mechanisms for the generation of ClO_3 are presently being investigated.

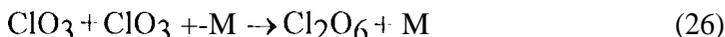
The chemistry of ClO_3 is intimately connected with that of Cl_2O_6 through the reaction



Recently, Jansen et al.¹¹⁷ have demonstrated, using IR spectroscopy, that the original gas phase spectrum of ClO_3 reported in 1937 is probably due to Cl_2O_6 . Both Jansen et al. and Lopez and Sire¹¹⁸ find no UV or IR spectroscopic evidence for the presence of monomeric ClO_3 in gas phase samples of Cl_2O_6 . Accordingly, the reverse of reaction 26 is apparently slow and the equilibrium between ClO_3 and Cl_2O_6 must greatly favor the dimeric form. The experimental results have been supported by theoretical estimates of the heats of formation of ClO_3 and Cl_2O_6 . (Table II) Rathman and Schindler⁸³ have derived a value of 48 kcal mole⁻¹ for $\Delta H_f(\text{sym-ClO}_3)$ from ab initio calculations performed at the Hartree-Fock level. Meanwhile, Colussi and Grela¹¹⁹ have estimated a value for $\Delta H_f(\text{Cl}_2\text{O}_6)$ of 52 kcal mole⁻¹ using a valence

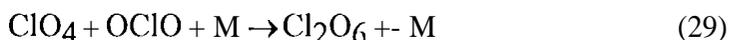
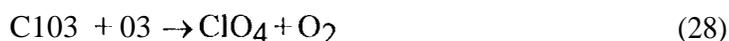
bond additivity approach. Combining these two estimates results in a predicted enthalpy for reaction 16 of -44 kcal mole⁻¹.

Cl₂O₆ has been produced in the laboratory by reaction of OCIO with O₃. The presumed mechanism is



Lopez and Sire and Jansen et al. have observed that formation of Cl₂O₆ from OCIO and O₃ is followed by slow decomposition of the Cl₂O₆ to yield Cl₂O₄ and trace amounts of Cl₂O₇. A barrier to Cl₂O₄ formation of approximately 20 kcal mole⁻¹ has been derived from kinetic data obtained at temperatures between 300 and 360 K. Combination of the Cl₂O₆ decomposition barrier height data with the calculated enthalpies of formation for ClO₃ and Cl₂O₆ (Table 11) suggests that the presumed mechanism for Cl₂O₆ formation is incorrect. In particular, the Cl₂O₆ decomposition barrier energy is substantially lower than the potential energy of two ClO₃ radicals. Consequently, the preferred reaction path from ClO₃ should be directly to Cl₂O₄ rather than to Cl₂O₆.

One alternative Cl₂O₆ formation mechanism involves the ClO₄ radical as an intermediate



The enthalpy of formation of ClO₄ has been estimated to be 50 kcal mole⁻¹ by Colussi and Grela based on literature data for the kinetics of Cl₂O₇ decomposition. Using this estimate for ΔH_f°(ClO₄) the calculated enthalpy change for reaction 29 is roughly equivalent to the energy barrier for Cl₂O₆ decomposition into Cl₂O₄. Consequently, the likely fate of the excited intermediate formed from the addition of ClO₄ to OCIO is collisional stabilization to yield Cl₂O₆ rather than rearrangement followed by O₂ elimination to yield Cl₂O₄.

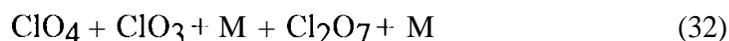
Attempts to model the possible formation of Cl₂O₆ in the stratosphere are hampered by uncertainties in the above-mentioned chemical mechanisms. Regarding atmospheric Cl₂O₆ loss processes UV absorption cross sections of Cl₂O₆ have been recently measured by Lopez and Sicre. (Figure 1) Although the more recent spectrum is qualitatively similar to one obtained by Good eye and Richardson ¹²⁰ (and erroneously ascribed to ClO₃) the newly reported cross section values are significantly higher than the earlier values. Based on the recently obtained absorption cross section values the atmospheric lifetime of Cl₂O₆ with respect to photolysis will be quite short, ranging from minutes to hours. The photolysis products have not been determined yet. The likely photolysis channels are



Chemical loss mechanisms of Cl₂O₆ have been suggested by Jansen et al. and Lopez and Sicre. The reaction of Cl₂O₆ with O₃ represents a potentially important atmospheric sink of inorganic chlorine since the product, Cl₂O₇, is thermally and photolytically stable.



Alternatively, Cl₂O₇ may be formed following the thermal or photolytic decomposition of Cl₂O₆ by the reaction of ClO₃ with ClO₄.



IV. Review of Experimental and **Theoretical** Studies of **HClO_x** Species

A. HOCl

The significance of hypochlorous acid (HOCl) in stratospheric chemical processes has been the subject of considerable debate. Although it is involved in a catalytic cycle (reactions 1, 3, 4, and 5) that destroys ozone, the cycle is less efficient than those involving other chlorine species. Consequently, HOCl is generally considered a temporary reservoir of stratospheric chlorine. The atmospheric reaction primarily responsible for HOCl formation, i.e. HO₂ + ClO,

has resisted a satisfactory experimental characterization. Stimpfle et al.,¹²¹ using discharge flow - laser magnetic resonance, found that the temperature dependence of the reaction was described by non-linear Arrhenius behavior. The data suggested that two different mechanisms are manifest in the reaction. However, mass spectrometric studies of the products of the reaction by Leu¹²² and Leek et al.¹²³ reported no evidence for any chlorine containing species other than 110Cl . Upper limits of less than 3% were placed by all of the investigators on the channel producing 1Cl .

Recent ab initio studies by Toohey and Anderson¹²⁴ have considered the possible formation of a HClO_3 adduct in the $\text{H}_2 + \text{ClO}$ reaction. In order to pursue this suggestion ab initio calculations are required on the energetic of all of the species involved in the reaction. The heat of formation, $\Delta H_f^{\circ,298}$, of gaseous HOCl is listed as -17.8 ± 0.5 kcal/mole in the JANAF thermochemical tables¹²⁵. This value is based on the ultraviolet photometric equilibrium measurement of Knauth et al.¹²⁶ who measured the heat of formation for HOCl as -17.8 ± 0.5 kcal/mole. Subsequent measurements by Molina and Molina¹²⁷, of -18.0 kcal/mole and those of Niki and co-workers¹²⁸ of -17.9 kcal/mole show good consistency with the adopted JANAF value. More recently, Ennis and Birks¹²⁹ reported a value of -18.0 ± 0.9 kcal/mole (298 K). The first theoretical prediction of the heat formation comes from the studies of Hirsch et al.¹³⁰. Using multireference double excitation (M RCI) methods, Hirsch and co-workers determined a heat of formation of -19.2 ± 4 kcal/mole as predicted from calculation of IOCl bond dissociation energies. Francisco and Sander¹³¹ more recently determined the heat of formation of HOCl using the isodesmic reaction scheme with Moller-Plesset perturbation methods (MP2 and MP4) and the single-configuration based quadratic configuration interaction method in the single and double-space with perturbation inclusion of triple substitutions method QCISD(T). The heat of formation using Moller-Plesset methods and isodesmic schemes (PMP4/6-311++G(3df,3pd)//UMP2/6-311G(2d,2p)) predict a value of -22.9 ± 1 kcal mol⁻¹. While QCI SD(T) methods used in conjunction with isodesmic schemes yield a heat of formation

value of $-19.9 \pm 1 \text{ kcal mol}^{-1}$. In the case of HOCl, theoretical predictions and experimental determinations of the heat of formation are in remarkably good agreement. (see Table 11)

Ab initio methods have also been applied in order to assist in the understanding of the photodissociation of HOCl in the atmosphere. Bruna et al.¹³² have examined ground and various valence and Rydberg excited states of HOCl using MRDCI methods. Only vertical excitation energies are given for low-lying states of HOCl. Potential energy surfaces connecting the states of HOCl to its separated products (i.e. O₁ and Cl or to H and ClO or to HCl and O) show that for the first four excited states of HOCl which show strong repulsive character, the dissociation strongly favors dissociation into HO radicals and Cl atoms.

B. HClO₂

In addition to reaction 12 (Cl + CH₄) the reactions of Cl + H₂O and HO + ClO are recognized as possible important steps for the conversion of reactive chlorine (Cl and ClO) to inactive HCl. The potential energy surfaces for these two reactions are obviously intimately connected. Not at all obvious is the role of intermediate formation in the reaction mechanisms. A host of recent studies have attempted to further characterize these reactions.

Experimental characterizations of the kinetics of the Cl + HO₂ reaction were accomplished by Lcu and DeMore¹³³ using a flow discharge mass spectrometric method and Burrows et al.¹³⁴ using a discharge flow system coupled instead to a laser magnetic resonance (LMR) detection system. The total rate constants showed no temperature dependence. Y-P. Lee and C. J. Howard¹³⁵ discovered that the Cl + HO₂ reaction possesses two product channels, namely



Using a discharge flow system with far infrared laser magnetic resonance detection of HO₂, O₁, and ClO, Lee and Howard determined the branching for these reactions to be approximately 0.79 and 0.21 for 33a and 33b, respectively. Benson and co-workers¹³⁶ using a thermochemical

analysis suggested that the measured rates could not result from a direct hydrogen abstraction process. Instead, they reasoned that due to the strong attractiveness of the chlorine to the terminal oxygen, a HOOCl complex could be responsible for the observed rates. Mozurkewich¹³⁷ using a RRKM analysis showed that the direct hydrogen abstraction is likely to predominate over HOOCl intermediate formation. Toohcy et al.¹³⁸ showed that although experimental activation barriers for a set of hydrogen abstraction reactions from H₂O₂ were small, they were not inconsistent with predictions based on an extension of the bond energy-bond order (BEBO) analysis, which likely proceed by direct mechanisms. Toohcy and Anderson¹²⁴ were the first to perform ab initio calculations of the Cl + H₂O₂ potential energy surface, although their examination did not completely map the potential energy surface of this reaction. Only the direct hydrogen abstraction process was explored with unrestricted Hartree-Fock (UHF) and unrestricted second-order perturbation (UMP2) methods. At the UMP2/6-31 G** level of theory, the activation energy for the Cl + H₂O₂ reaction was predicted to be 8.4 kcal mol⁻¹. At the Hartree-Fock level, the activation energy barriers were predicted to be 21.1 kcal mol⁻¹. Clearly, electron correlation is needed to explore the potential energy surfaces for this reaction. Calculating the energies at the fourth-order MP level, including single, double, and quadruple excitations (MPP4SDQ) with the UMP2 geometries, yielded an estimated activation energy barrier of 8.9 kcal mol⁻¹.

The reaction of OH radicals with ClO radicals can also proceed by two reaction pathways:



There have been two detailed experimental studies of this reaction. Leu and Lin¹³⁹ first studied this reaction in 1979 and reported a room temperature rate of $9.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Ravishankara et al.¹⁴⁰ found that the reaction was temperature independent over the range 248 to 335 K. Hills and Howard¹⁴¹, using discharge flow /far infrared laser magnetic resonance kinetic studies, measured a branching ratio ($k_{34a}/k_{34b} = 0.86 \pm 0.14$) for this reaction. The total

rate measurement showed a temperature dependence over the range of 219 to 373 K. Burrows et al.¹⁴² explored the reaction using resonance fluorescence detection in a flow tube reactor over the temperature range 242 to 298 K. Their temperature dependence did not agree with that observed by Hills and Howard. A later study by Poulet et al.¹⁴³ measured the branching ratio (0.98 ± 0.12) for the reaction using a discharge flow system coupled with laser-induced fluorescence and modulated molecular beam mass spectrometry detection systems. Their results implied that the channel (reaction 34b) that produced $\text{HCl} + \text{O}_2$ could not be significant for converting ClO into inactive HCl .

Recent ab initio studies of the HClO_2 potential energy surface by Francisco, Sander, Lee, and Rendell^{144,145} lend some perspective to the experimental findings. They find for the reaction of Cl atoms with HO_2 radicals that a dual mechanism dominated by the direct hydrogen abstraction channel may occur. The direct hydrogen channel takes place on the triplet surface. On the singlet surface the only pathway available is formation of stable HOCl . This species has not been detected in the laboratory, but could be a new atmospheric chlorine reservoir species. In contrast to the suggestion of Benson, that the HOCl intermediate spontaneously dissociates, ab initio studies suggest that it remains stable. At the PMP4/6-311++G(3df,3p)/UMP2/6-311G(2d,2p) level of theory, the heat of formation for HOCl is predicted to be $-86.0 \text{ kcal mol}^{-1}$. In the reaction of HO_2 radicals with ClO radicals, the ab initio studies of Francisco and Sander find that this reaction may involve two intermediates, HOCl and HOClO . The pathway leading through the HOCl intermediate should yield HO_2 and Cl as products since dissociation of the HOCl through a four-center transition state to form HCl and O_2 is energetically unfavorable. The pathway leading to the HOClO intermediate leads to an oxygen exchange process.

C. HClO_3

Under low pressure conditions the $\text{ClO} + \text{HO}_2$ reaction is thought to yield primarily HOCl and O_2 . Toohcy and Anderson¹²⁴ have raised the possibility of ClO_3 formation at low

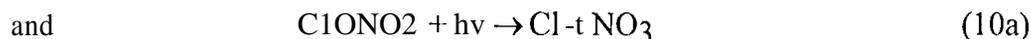
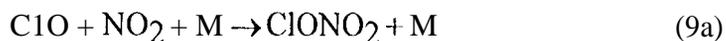
temperatures and/or high pressures, Indirect evidence for complex mechanistic behavior in the $\text{HO}_2 + \text{ClO}$ reaction has been provided by the unusual temperature dependence observed for the reaction, ^{146,147} This behavior has been interpreted as an indication of the occurrence of two different mechanisms in the $\text{ClO} + \text{HO}_2$ reaction. Stimpfle et al. ¹⁴⁷ suggested that an IClO_3 collision complex could possibly explain the experimental observations. No observation of the products of the $\text{ClO} + \text{HO}_2$ has been performed in order to provide more insight into the details of the mechanism. Toohey and Anderson made a partial examination of the $\text{ClO} + \text{HO}_2$ potential energy surface. Using second order Moller-Plesset perturbation theory with the 6-31 G** basis set, they found that the activation energy for the direct hydrogen abstraction process is $1.4 \text{ kcal mol}^{-1}$. At the UMP4SDQ/UMI'2/6-31 G** level of theory including corrections for zero-point, thermal energy, basis set superposition errors, and the $\Delta(\text{PV})$ terms, they predicted a barrier of $0.3 \text{ kcal mol}^{-1}$. Toohey and Anderson then argued that the $\text{ClO} + \text{HO}_2$ reaction may have two mechanisms; one the direct attack at the hydrogen atom, which should dominate at high temperatures; while the other involves an HClO_3 intermediate, which dominates at the lower temperature,

Another examination of the potential energy surface of the $\text{HO}_2 + \text{ClO}$ system comes from the experimental studies of the $\text{OH} + \text{OClO}$ reaction conducted by Poulet et al. ¹⁴⁸ HOCl was observed as a product of the reaction. HOCl and OClO concentrations were followed over the temperature range of 293 to 473 K. As in the case of the $\text{ClO} + \text{HO}_2$ reaction, an unusual temperature dependence was found for the $\text{OH} + \text{OClO}$ reaction. Poulet et al. suggested that a HOClO_2 intermediate maybe involved,

V. Review of Experimental and Theoretical Studies of ClNO_x Species

A. ClONO₂

The potential importance of chlorine nitrate as an atmospheric reservoir of inorganic chlorine was recognized by Rowland and Molina in 1976.¹⁴⁹ The principal production and loss mechanisms at mid latitudes were identified in laboratory experiments as



Chlorine nitrate has now been detected in the atmosphere by high resolution infrared solar absorption spectroscopy. The atmospheric feature attributed to ClONO₂ is the 780 cm⁻¹ band Q branch. Ballard et al.¹⁵⁰ and Davidson et al.¹⁵¹ have measured the absolute absorption cross section of ClONO₂ at 780 cm⁻¹ as a function of temperature and found it to increase with decreasing temperature. Absolute atmospheric column abundances of ClONO₂ have been derived from the field data using the laboratory cross section data.¹⁵² The retrieved ClONO₂ column abundances confirm that ClONO₂ is a major reservoir of inorganic chlorine at levels comparable to HCl.

Recent laboratory and theoretical studies of the gas phase chemistry of ClONO₂ have reexamined the details of reactions 23 and 24. McGrath et al.¹⁵³ have examined the possible formation of chlorine nitrate isomers in the reaction of ClO with NO₂.



Since normal chlorine nitrate is unusually resistant to photodecomposition due to its small absorption cross sections at wavelengths greater than 300 nm, it is possible that other isomers may be substantially more photochemically labile. An assessment of the role of these other isomers in atmospheric process would require a further knowledge of the precise photolysis routes and chemical reactions of the isomeric species.

McGrath et al. have calculated energies of the chlorine nitrate isomers at the RHF/6-31 G* level. Relative to chlorine nitrate the isomers (in the reaction order 23 a - c) are 23.2, 58.6, and 66.0 kcal mole⁻¹ higher in energy. The calculated energy difference between chlorine nitrate and the most stable alternative isomer chlorine peroxyxynitrite, ClOONO, is found to increase as the RHF basis set is improved. At the RMP2/6-31 G* level the energy difference is 30.0 kcal mole⁻¹ which implies that the theoretical association reaction to yield chlorine peroxyxynitrite is endothermic. The theoretical results, therefore, support previous laboratory experiments that failed to observe any other product besides chlorine nitrate in the gas-phase reaction of ClO and NO₂.

Minton et al.⁷ have recently made a direct observation of ClO production from the photolysis of chlorine nitrate at 248 nm.



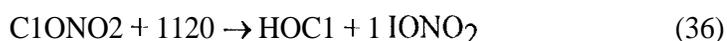
The experiment utilized the technique of photofragment translational energy spectroscopy and was performed using a crossed laser/molecular beam apparatus. This method has not been used extensively in the past to measure quantitative photolysis yields. The results of the experiment are contrary to recent work by Burrows et al.¹⁵⁴ who measured a unity yield of NO₃. The ClO quantum yield derived from the Minton et al. experiment, 0.43, is also substantially different from earlier measurements by Margitan¹⁵⁵ at 266 nm that identified Cl as the primary photolysis product and placed an upper limit of 0.2 on the ClO yield. (see Table III)

Although there are no obvious explanations for the discrepancies between the studies, one possibility may be related to the substantially lower pressure conditions employed by Minton et al. relative to those used by Margitan or Burrows et al. The differences in pressure may manifest themselves in the partitioning of the product yields if the photochemical mechanism involves excited intermediates, such as ClO* or NO₃*. The subsequent fate of the intermediates could then involve a competition between collisional stabilization and unimolecular decomposition.

Atmospheric models predict that the branching ratio in ClONO₂ photolysis has little effect on ozone depletion in the unperturbed stratosphere because ClO and Cl interconvert

rapidly. However, Minton et al. suggest that the lack of selective bond photolysis in the ClONO₂ case raises the possibility of multiple product channels in the photolysis of ClOOCl. A substantial yield of ClO in the ClOOCl case would significantly reduce the calculated amount of polar ozone depletion by chlorine catalyzed chemistry,

Other potential atmospheric ClONO₂ loss processes which have received a great deal of attention recently are the reactions with HCl and H₂O.



These reactions serve to convert ClONO₂ into photolytically labile Cl₂ and HOCl and hence to increase the fraction of catalytically active chlorine in the atmosphere. A variety of experimental techniques have been employed to study the homogeneous gas phase component of these reactions. 156-159 They have all demonstrated that the homogeneous reactions are too slow to have any significant effect on atmospheric chemistry. However, more recent studies have discovered a rapid heterogeneous component. The characterization of the heterogeneous reactions between ClONO₂ and HCl and H₂O and the importance of these processes to atmospheric processes are discussed in another chapter of this volume.

B. 02 ClONO₂

The correlated removal of ClONO₂ and NO₂ that has been observed in the polar vortex has been attributed to heterogeneous processes occurring on polar stratospheric clouds. Some effort has been directed at the alternative possibility of additional gas-phase reservoir species of ClO_x and NO_x. Friedl et al.¹⁶⁰ have recently observed the low temperature (< 250 K) formation of an adduct in the reaction of OCIO with NO₃.



The reaction was studied using the discharge flow technique and the adduct was observed by Fourier transform infrared and ultraviolet diode array absorption spectroscopy. The observed infrared band frequencies suggest that the adduct is chloryl nitrate. The experimentally derived

value of the rate coefficient for adduct formation was used in conjunction with unimolecular reaction theory to estimate the strength of the bond between N03 and OC1O in O2C1ONO2. The bond strength derived from this method is $18 \pm 3 \text{ kcal mol}^{-1}$. This value is similar to that of C1OOC1 but substantially less than that of C1ONO2. (see Table II) Consequently the thermal stability of chloryl nitrate in the atmosphere should approach that of chlorine peroxide. Friedl et al. have modeled the effect of reaction 37 on polar chlorine chemistry using a one-dimensional photochemical model. They find that chloryl nitrate may exist in significant concentrations in the polar stratosphere. However, uncertainty in the experimental chloryl nitrate bond strength severely hampers the model effort. In particular, a variation of $\pm 2 \text{ kcal mol}^{-1}$ in the chloryl nitrate bond strength translates to a 105 fold variation in the atmospheric number density. Inclusion of other chemical routes would also affect the predicted amounts of atmospheric chloryl nitrate. For instance, Friedl et al. propose that the reaction of C1O3 with N02 will produce O2 C1ONO2



At higher temperatures Friedl et al. have observed the production of ClO from the OC1O + NO3 reaction,



According to Friedl et al. the competition between the reaction channels favors adduct formation at temperatures below 240 K. The reaction rate constant derived by Friedl et al. for the abstraction channel is consistent with a recent upper limit reported for the reaction rate by Becker et al.¹⁶¹ However the rate coefficient is two orders of magnitude larger than an upper limit placed on the reaction by Biggs et al.¹⁶² (see Table 1) The discrepancy between the two studies awaits further investigation.

VI. Summary and Conclusions

The transformation of substantial fractions of inorganic chlorine from inactive to active forms via heterogeneous reactions on polar stratospheric clouds is now recognized as the catalyst for a wide variety of atmospheric reactions. Experimental and theoretical studies conducted over the last ten years have succeeded in defining the general scope of the gas-phase chemical processes initiated by the PSC processing. In addition, these studies have provided sufficient data to allow for semiquantitative analysis of ozone destruction in the springtime polar stratosphere. The current understanding of inorganic chlorine chemistry, as summarized in this chapter, is depicted in Figure 2.

Recent experimental and theoretical attempts to understand the chemistry of chlorine in the polar stratosphere have recognized the fundamental importance of adduct formation in a wide variety of reactions. In some cases, such as ClOOCl , the adduct is sufficiently stable thermodynamically to exist in substantial atmospheric abundance. In other cases, such as BrOOCl , the adduct decomposes rapidly through a myriad of possible product channels. In either case, a fundamental physical chemical understanding of the reaction potential energy surface, especially in the energy region corresponding to that of the adduct, is required in order to allow for reliable predictions of atmospheric consequences. The need for further theoretical and experimental studies is especially critical as regards the stability of HClO_x adducts such as HClO_2 and HClO_3 .

The experimental and theoretical studies reviewed in this chapter have served to identify a number of new and possibly important atmospheric reactions and species. A great deal of work remains to be done in order to quantitatively assess the role of these species in atmospheric processes. The greatest challenges will be provided by the newly identified large polyatomic chlorine-containing species. For example, additional thermochemical and kinetics parameters are needed for chloryl nitrate, O_2ClONO_2 , the chlorine oxyacids, HClO_2 and HClO_3 , and the higher oxides of chlorine, i.e. ClO_3 , ClO_4 , Cl_2O_4 , and Cl_2O_6 . Improved experimental and computational methodologies will be required in order to effectively characterize these species.

As described in this chapter, recent photochemical studies of the chlorine-containing compounds OCIO and ClONO₂ have resulted in surprising discrepancies in the measured quantum yields. Clearly, future experiments that span a wide range of pressure conditions and photolysis wavelengths are required to understand the photodynamics of these apparently complex Systems. In addition, photochemical yield measurements on Cl₂O₃, Cl₂O₄, and Cl₂O₆, for which none currently exist, are required in order to assess the atmospheric chemistry of these species. All of these endeavors will greatly benefit from future ab initio studies aimed at identifying and quantifying the energetics of excited states associated with these molecules.

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Table I: Kinetics Data for Selected ClO and OClO Reactions

| Reaction | Buffer | Temp (K) | A-Factor (cm ³ S ⁻¹) | n | Es/R (kcal/mole) | Order | k(298 K) (cm ³ S ⁻¹) | Ref. |
|--|----------------|----------|---|-------|------------------|-------|---|------|
| ClO + ClO → Cl ₂ O ₂ | N ₂ | 268-338 | 6.00 x 10 ⁻³² | -2.10 | | 3 | 6.00 x 10 ⁻³² | 93 |
| | N ₂ | 200-300 | 1.34 x 10 ⁻³² | -3.90 | | 3 | 1.34 x 10 ⁻³² | 95 |
| | N ₂ | 194-247 | 1.80 X 10 ⁻³² | -3.60 | | 3 | | 94 |
| | N ₂ | 194-247 | 6.0 X 10 ⁻¹² | | | 2 | | 94 |
| ClO + ClO → Cl ²⁴ O ₂ | | 260-390 | 1.01 x 10 ⁻¹² | | 1590 | 2 | 4.87x 10 ⁻¹⁵ | 51 |
| | | 298 | 4.5 x 10 ⁻¹⁵ | | | 2 | 4.5 x 10 ⁻¹⁵ | 88 |
| ClO + ClO → cl + ClOO | | 260-390 | 2.98 X 10 ⁻¹² | | 2450 | 2 | 8.0 x 10 ⁻¹⁵ | 51 |
| | | 298 | 3.1 x 10 ⁻¹⁵ | | | 2 | 3.1 x 10 ⁻¹⁵ | 88 |
| ClO + ClO + cl + OClO | | 260-390 | 3.5 OX10 ⁻¹³ | | 1370 | 2 | 3.5 x 10 ⁻¹⁵ | 51 |
| | | 298 | 1.5 x 10 ⁻¹⁵ | | | 2 | 1.5 x 10 ⁻¹⁵ | 88 |
| ClO + BrO + BrCl + O ₂ | | 220-400 | 5.8 X 10 ⁻¹³ | | -334 | 2 | 1.02X 10 ⁻¹² | 35 |
| | | 298 | 1.4X10 ⁻¹² | | | 2 | 1.4X 10 ⁻¹² | 39 |
| | | 234-406 | 1.9 X10 ⁻¹³ | | -1019 | 2 | 1.06 X 10 ¹² | 38 |
| ClO + BrO → Br + ClOO | | 220-400 | 2.9 X 10 ⁻¹² | | -431 | 2 | 6.00 X 10 ¹² | 35 |
| | | 234-406 | 1.9X10 ⁻¹² | | -513 | 2 | 4.99x 10 ⁻¹² | 38 |
| ClO + BrO → Br + OClO | | 220-400 | 1.60 x 10 ⁻¹² | | -847 | 2 | 6.68 x 10 ⁻¹² | 35 |
| | | 234-406 | 6.70 x 10 ⁻¹³ | | -1236 | 2 | 5.40X 10 ⁻¹² | 38 |
| | | 298 | 4.80 X 10 ⁻¹² | | | 2 | 4.80 X 10 ¹² | 39 |
| | | 298 | 7.61 X 10 ⁻¹² | | | 2 | 7.61 X 10 ⁻¹² | 36 |
| | | 220 | 1.27 x 10 ⁻¹¹ | | | 2 | | 36 |

| | | | | | | | |
|--|----------------|---------|-------------------------|-------|---|-------------------------|-----|
| ClO + OClO | N ₂ | 200-260 | 6.2 x 10 ⁻³² | -4.7 | 3 | 6.2 x 10 ⁻³² | 112 |
| → Cl ₂ O ₃ | N ₂ | 200-260 | 2.4 x 10 ⁻¹¹ | | 2 | | 112 |
| | N ₂ | 226 | 2.8 x 10 ⁻³¹ | | 3 | | 113 |
| OCIO + O | N ₂ | 248-312 | 1.86X10 ⁻³¹ | -1.12 | 3 | 1.86X 10 ⁻³¹ | 89 |
| → ClO ₃ | N ₂ | 248-312 | 3.1 x 10 ⁻¹¹ | 0 | 2 | 3.1 X1 0 ⁻¹¹ | 89 |
| OCIO + O | | 298 | 1.60 x10 ⁻¹³ | | 2 | 1.60 x10 ⁻¹³ | 66 |
| → ClO + O ₂ | | | | | | | |
| OCIO + NO ₃ | He | 220 | 1x 10 ⁻³¹ | | 3 | | 160 |
| + ClNO ₅ | | | | | | | |
| OCIO + NO ₃ | | 220 | 2X10 ⁻¹⁵ | | 2 | | 160 |
| → ClO + NO ₂ + O ₂ | | 298 | 2x 10 ⁻¹⁴ | | 2 | 2 x 10 ⁻¹⁴ | 160 |
| | | 298 | <7 x 10 ⁻¹⁴ | | 2 | <7 x 10 ⁻¹⁴ | 161 |
| | | 298 | <1 x 10 ⁻¹⁵ | | 2 | <1 x 10 ⁻¹⁵ | 162 |

Table 11: Thermochemical Data for Selected Inorganic Chlorine Compounds

| Molecule | $\Delta H_f(0\text{ K})$ (kcal/mole) | $\Delta H_f(298\text{ K})$ (kcal/mole) | D_0 (kcal/mole) | Method | Reference |
|----------------------|---|---|----------------------|----------------------|-----------|
| ClO | 24.15 | 24.30 | 60.9 | Ab Initio/G1 | 30 |
| | | | 61.5 | Ab Initio/G2 | 46 |
| | | | 63.4 | 13xpt./Spcctroscopic | 47 |
| | | | | | |
| OCIO | | | 53.0 | Ab Initio/CMRCI | 64 |
| | | | 55.2 | Expt./ | |
| Cl ₂ O | | 23.4 | 4.76 | 1;xpt./Kinetics | 85 |
| | | | 23.3 | Expt ./Kinetics | 86 |
| | | | 24.0 | Expt./Kinetics | 87 |
| | | | 8 | Est./Bond Additivity | 81 |
| | | | 7.5 | Ab Initio/MCSCF-CI | 90 |
| | | | 2.5 | Ab Initio/CMRCI | 64 |
| | | | 24,2 | Ab Initio/QCIST(T) | 82 |
| | | | 29.0 | Ab Initio/G1 | 83 |
| sym-ClO ₃ | 55.6 51.9 48.0 | | | Expt ./Kinetics | 66 |
| | | | | Expt./Kinetics | 89 |
| | | | | Ab Initio/G1 | 91 |
| ClOOO | 41.0 | | | Ab Initio/G1 | 91 |
| OCIOO | 58.0 | | | Ab Initio/G1 | 91 |
| ClOOCi | | | 17.3 | 1{xpt./Kinetics | 51 |
| | | | 18,8 | Expt./Equilibrium | 97 |
| | | | 32.6 | Ab Initio/MP2 | 103,104 |
| | | | 34.2 | Ab Initio/CCSD(T) | 105 |
| ClClO ₂ | 33.8 35.1 | | | Ab Initio/MP2 | 103,104 |
| | | | | Ab Initio/CCSD(T) | 105 |
| ClOCIO | 40.0 44.3 | | | Ab Initio/MP2 | 103,104 |
| | | | | Ab Initio/CCSD(T) | 105 |

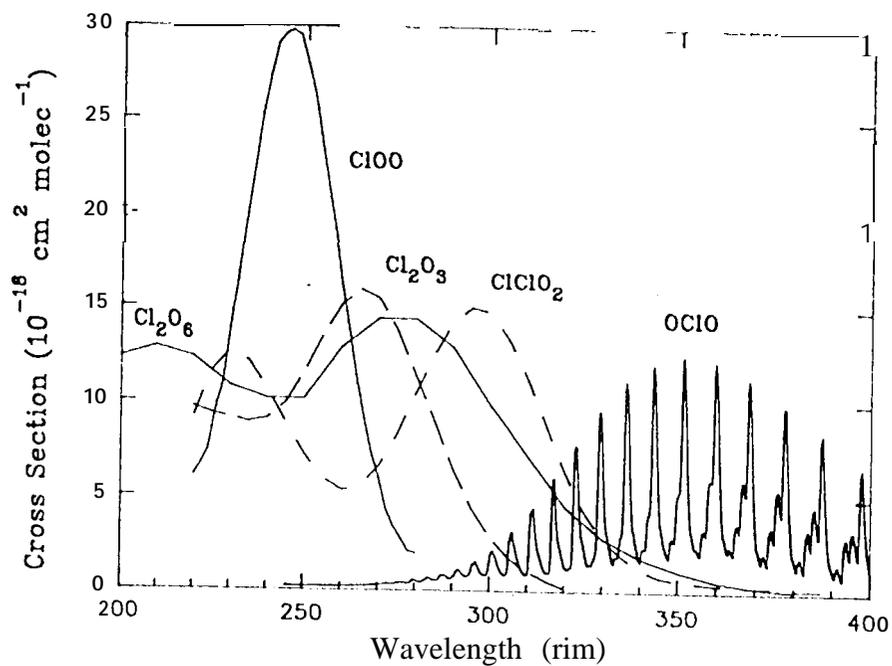
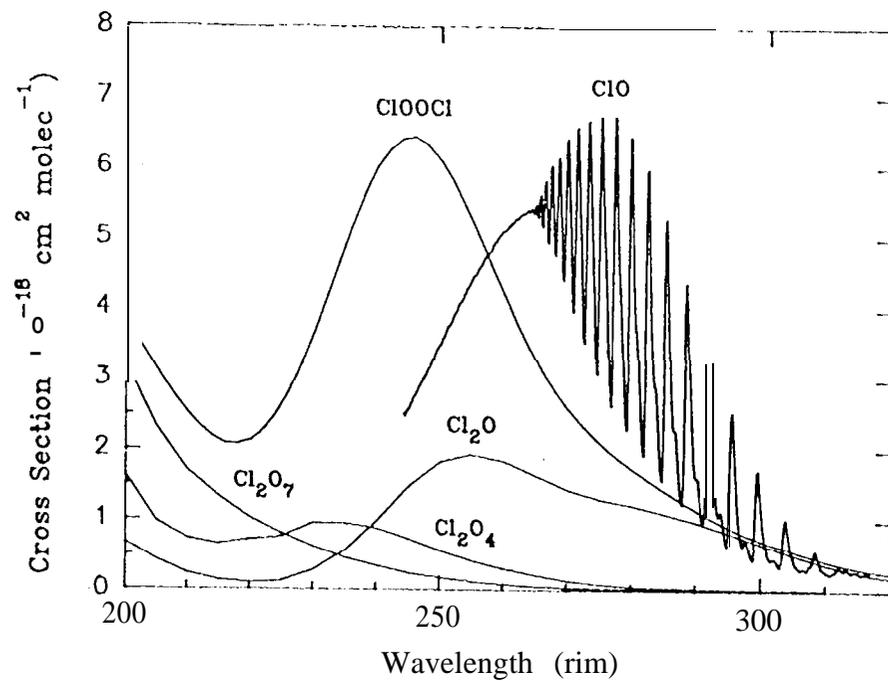
Table 11: (continued)

| Molecule | $\Delta H_f(0\text{ K})$ (kcal/mole) | $\Delta H_f(298\text{ K})$ (kcal/mole) | D_0 (kcal/mole) | Method | Reference |
|----------|---|---|----------------------|----------------------|-----------|
| ClOClO2 | 36.5 | | 11.1 | Expt./Equilibrium | 112 |
| | 33.9 | 32.7 | | Expt./Equilibrium | 111 |
| ClO4 | | 50.0 | | Est./Bond Additivity | 119 |
| Cl2O4 | | 42 | | Expt./Kinetics | 114 |
| | | 37.2 | | Est./Bond Additivity | 119 |
| Cl2O6 | | 52.1 | | Est./Bond Additivity | 119 |
| HOCl | | -17.8 | | Expt./Equilibrium | 126 |
| | | -18.0 | | Expt./Equilibrium | 127 |
| | | -17.9 | | Expt./Equilibrium | 128 |
| | | -18.0 | | Expt./Equilibrium | 129 |
| | | -19.2 | | Ab Initio/MRCDI | 130 |
| | | -22.9 | | Ab Initio/QCISD(T) | 131 |
| | | -19.9 | | Ab Initio/QCISD(T) | 131 |
| HOOC1 | 1.6 | | | Ab Initio/CCSD(T) | 144,145 |
| ClONO2 | | 6.3 | | Expt./Kinetics | |
| | | -4.3 | | Ab Initio/MP2 | 153 |
| ClOONO | | 18.9 | | Ab Initio/RHF | 153 |
| | | 25.7 | | Ab Initio/MP2 | 153 |
| OCINO2 | | 54.4 | | Ab Initio/RHF | 153 |
| OC1ONO2 | | | 18 | Expt./Kinetics | 160 |
| | | | 18.5 | Est./Bond Additivity | 119 |

Table III: Photochemical Data on Selected Chlorine-containing compounds

| Photochemical Reaction | Wavelength (rim) | Yield | | Reference |
|--|---------------------|---------------|--------------|-----------|
| | | Channel(a) | Channel(b) | |
| OCIO → O + ClO (a) | | | | |
| OCIO + Cl + O ₂ (b) | | | | |
| | 308 | 1 | | 58 |
| | 359-368 | 1 | | 59 |
| | 368 | | > 0 | 6,60 |
| | 368 | | 0.15 | 61 |
| | 350-475 | | ≤ 0.04 | 62 |
| Cl ₂ O ₂ → ClO + ClO (a) | | | | |
| Cl ₂ O ₂ → Cl + ClOO (b) | | | | |
| | 254 | | 1 | 89 |
| | 308 | | 0.6 | 90 |
| | 240 | (b) dominates | [prediction] | 92 |
| ClONO ₂ → ClO + NO ₂ (a) | | | | |
| ClONO ₂ → Cl + NO ₃ (b) | | | | |
| | 308 | 0.43 | 0.57 | 7 |
| | 266 | ≤ 0.2 | 0.9 | 155 |
| | 254 | | 1 | 154 |

Figure 1. Ultraviolet absorption cross sections for selected chlorine oxides



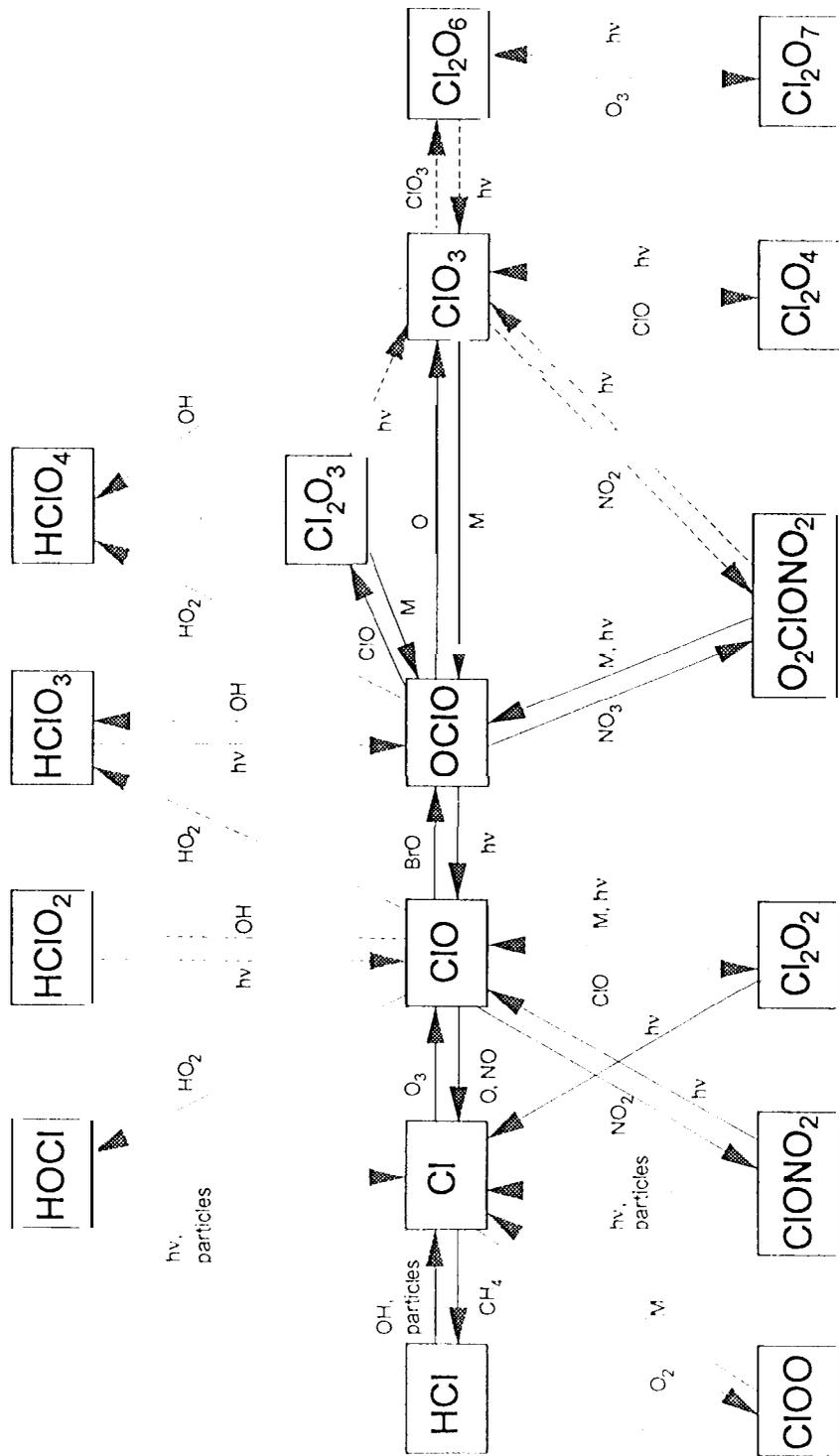


Figure 2. Photochemical pathways of atmospheric inorganic chlorine-containing compounds. Solid and dashed arrows represent major and minor pathways, respectively.