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Chemical Kinetics Data Survey VIII. Rate Constants of ClO_x of Atmospheric Interest

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U. S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary
NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director

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Chemical Kinetics Data Survey

VIII. Rate Constants of $C\ell O_x$ of Atmospheric Interest

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Abstract

The quantitative data on reactions of chlorine atoms and the chlorine oxides are compiled. Preferred values for rate constants are given where possible. Optical absorption cross sections are given for the species that may photolyze in the atmosphere. The experimental techniques used to obtain the rate data are discussed.

Key words: absorption cross sections, atmospheric chemistry, chemical kinetics, chlorine, chlorine dioxide, chlorine monoxide, data evaluation, gas phase, optical, rate constants, stratospheric chemistry.

Introduction

The Chapman mechanism[1] for the production and destruction of ozone has been shown to be inadequate to explain the observed vertical ozone column concentrations in the stratosphere[2]. Catalytic cycles which destroy ozone, based on HO_x and NO_x[3] and more recently ClO_x[4], have been proposed to account for the large discrepancy between the observed and calculated concentrations. Accurate values for the rate constants of reactions involving ground state atomic chlorine ($^2P_{3/2}$) and the oxides of chlorine, (ClO, ClOO and OClO) are required as a function of temperature, in order to perform model calculations which would estimate the perturbation upon the ozone column concentration due to the injection of chlorine containing species into the stratosphere, i.e. Cl_2 HCl, and freons (i.e. $CFCl_3$, CF_2Cl_2).

This compilation of the rate data critically reviews the published data and forwards with a minimum of explanation a set of preferred values for either the rate constant at 298K and/or (whenever possible) the Arrhenius expression. Rate data exists for most of the reactions which are thought to be of importance in the stratosphere, but unfortunately most of it was obtained at 298K, and consequently estimates must be made as to the temperature dependence of the rate constants. Certain reactions are more important in the chemistry of the stratosphere than others, i.e. $Cl + O_3 \rightarrow ClO + O_2$; $O + ClO \rightarrow Cl + O_2$; $NO + ClO \rightarrow NO_2 + Cl$;

$Cl + CH_4 \rightarrow CH_3 + HCl$ and $HO + HCl \rightarrow H_2O + Cl$; and of these, the first three have only been studied at 298K. However, due to the rapidity of these reactions at 298K (all $\geq 1.7 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}) it is unlikely that any of them have an activation energy greater than 2.1 kJ mol^{-1} (0.5 kcal mol^{-1}). Consequently, this means that the rate constants for all three reactions are known to within a factor of 2 at all stratospheric temperatures. The other two reactions have both received recent investigation and their rate constants as a function of temperature are now reasonably well established.

Many of the early published results have recently been shown to be erroneous due to misinterpretation of experimental data indirectly resulting from insufficient sensitivity in the detection apparatus[5]. Thus the modeller must be discriminating in his choice of rate constants and absorption cross-sections, and consequently the writer feels that a brief review of the experimental techniques used to obtain the results reported in this compilation is justified.

Calorimetric Probe

The calorimetric probe method of monitoring chlorine atoms has been used in one study reported[6], and was calibrated to determine absolute atom concentrations by use of the ClNO titration reaction. This technique is both insensitive ($[Cl] \sim 3 \times 10^{14} - 3 \times 10^{15}$ atom cm^{-3}) and non specific and thus of limited use.

Emission Spectroscopy

Several studies of third order reactions have been performed by monitoring the concentration of ground state $^2P_{3/2}$ chlorine atoms via the Cl_2^* ($^3\Pi_{ou^+} \rightarrow {}^1\Sigma_g^+$) afterglow[7-11]. The recombination of $^2P_{3/2}$ chlorine atoms, and the subsequent fate of the $^3\Pi_{ou^+}$ state of molecular chlorine can be written[12]:

$$Cl(^2P_{3/2}) + Cl(^2P_{3/2}) + M \rightarrow Cl_2(^3\Pi_{ou^+}) + M$$

$$Cl_2(^3\Pi_{ou^+}) \rightarrow Cl_2(^1\Sigma_g^+) + h\nu(> 500nm)$$

$$Cl(^2P_{3/2}) + Cl_2(^3\Pi_{ou^+}) \longrightarrow Cl_2(\text{non-radiative})+Cl(^2P_{3/2})$$

It has been shown that $I_\lambda = I_\lambda^\circ[Cl]^{n_\lambda}$, where I_λ represents the emission intensity at wavelength λ[12]. n_λ was shown to vary with λ, (i.e. $n_{520\ nm} = 1.7(M=Ar)$ and $n_{920\ nm} = 1.0(M=Ar)$) and not have a constant value of 2 as had been earlier reported[9]. Therefore, when using this technique to monitor relative Cl atom concentrations, care must be taken to use the correct value for n_λ. Results for some early work which used this method[7] must be slightly modified (the reported rate constants are probably low by ~ $2/n_\lambda \simeq 15\%$) as n_λ was taken to be 2, rather than 1.7 as later determined. This method of monitoring Cl atom concentrations is moderately insensitive, but useful when [Cl] is $10^{14} - 10^{16}$ atom cm^{-3}. Due to the rapidity of the $Cl + ClNO \rightarrow NO + Cl_2$ reaction[13], ClNO can be used to titrate Cl atoms. The critical extinction of the red Cl_2^* afterglow is one method for determining the titration end-point, and this was recently used in a series of Cl + RH reactions[14], where $[Cl]_o \geq 5 \times 10^{12}$ atom cm^{-3}. Under low pressure discharge flow conditions, the extent to which Cl atoms are removed between the ClNO inlet and the observation point at which Cl_2^* is monitored due to the $Cl + Cl + M \rightarrow Cl_2 + M$ and the $Cl + NO + M \rightarrow ClNO + M$ reactions can be calculated, but is normally negligible. The heterogeneous wall removal of atomic chlorine can be inhibited by coating the reactor surfaces with H_3PO_4.

Ultraviolet Spectrophotometry

The technique of monitoring both stable and labile species by UV absorption spectroscopy has been used in conjunction with discharge flow (ClO, OClO, O_3)[15-18]; flash photolysis (ClO, OClO, Cl_2O, ClNO)[19-25] and molecular modulation[26,27] systems. The absolute concentrations of these species can be monitored as a function of reaction time by following the optical absorption of the species and using the experimentally determined values for the absorption cross sections. Although the absorption cross sections are fairly high ($ClO_{277.2\ nm} = 7.2 \times 10^{-18}$ cm^2 $molecule^{-1}$(15); $OClO_{351.5\ nm} = 1.14 \times 10^{-17}$ cm^2 $molecule^{-1}$(15); $O_{3\ 260.4} = 1.10 \times 10^{-17}$ cm^2 $molecule^{-1}$(28); all to base e), this method for following these species is still relatively insensitive compared to molecular beam mass spectrometry. The discharge flow systems used multireflection absorption cells where a typical optical pathlength was 20 cms, resulting in a limit of sensitivity for ClO, OClO and O_3 of $\sim 10^{13}$ molecule cm^{-3}. The molecular modulation technique was two orders of magnitude more sensitive, using an optical pathlength of 400 cm and measuring modulation amplitudes of 10^{-3} -10^{-5}. Thus, concentration modulations of $\sim 10^{11}$ molecules cm^{-3} could be observed for ClO and ClOO.

The first study of reactions (1) ($Cl + O_3 \rightarrow ClO + O_2$)[15] and (2) ($Cl + OClO \rightarrow 2\ ClO$)[15] could only report lower limits for k_1 and k_2 at 300K due to limited detection sensitivity. When studies of the $O + OClO \rightarrow ClO + O_2$[18,19], and $NO + OClO \rightarrow NO_2 + ClO$[16] reactions were performed, several elementary processes were occurring simultaneously, and due to the fact that the rapidity of reaction (2) was not fully realised, its role in the overall mechanism of these reactions was not appreciated. This resulted in the value for k_{31} (O + OClO) being overestimated by two orders of magnitude. Rate constants for reactions 14 ($O + ClO \rightarrow Cl + O_2$) and 15 ($NO + ClO \rightarrow NO_2 + Cl$), which are of utmost importance in the stratosphere, were obtained by indirect methods whereby the $O(^3P)$ and NO (in seperate experiments) competitively reacted with ClO and OClO. The autocatalytic nature of the reaction mechanisms was not known and consequently the published values for k_{14}[18,19] and k_{15}[16] must be rejected. The reaction mechanism for the X + OClO reaction can be written, (X = O, NO)

$$X + OClO \xrightarrow{slow} XO + ClO;\ k \sim 5 \times 10^{-13}\ cm^3\ molecule^{-1}\ s^{-1}$$

$$X + ClO \xrightarrow{fast} XO + Cl\ ;\ k > 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$$

$$Cl + OClO \xrightarrow{fast} ClO + ClO;\ k = 5.9 \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$$

The bimolecular self-disproportionation of ClO radicals has been studied in a wide variety of chemical systems using UV spectrophotometry in conjunction with discharge flow[15,17,56], flash photolysis[19,23,24,25] and molecular modulation[26] experiments, however, the results are at variance with each other. The low pressure discharge flow technique has conclusively shown, both by direct (using atomic resonance absorption)[29] and indirect evidence that, Cl atoms are generated from the decay of ClO radicals, but not 100% efficiently. This technique has been used to show that the reaction is overall 2nd order and has an activation of ~ 10 kJ mol^{-1} (~ 2.4 kcal mol^{-1}). Results using the high pressure flash photolysis method record that there is no generation of Cl atoms, and that the overall decay is strictly 2nd-order (with possibly no activation energy). The third technique, molecular modulation spectroscopy, yielded results that indicated that the ClO radical decayed by both overall 2nd and 3rd order processes, producing atomic chlorine in the former. Thus, any results used to compute the following important equilibrium constants from these results must be used with caution. The discharge flow results indicate the possibility of two primary decay reactions, but the experimental decay data cannot differentiate between the pathways and measures the overall rate of decay. Also, the measured activation energy refers to the overall activation energy for ClO decay.

$$ClO + ClO \underset{k_6}{\overset{k_{24}}{\rightleftarrows}} ClOO + Cl \; ; \; K_1^* = k_{24}/k_6$$

$$Cl + O_2 + M \underset{k_{30}}{\overset{k_3}{\rightleftarrows}} ClOO + M \; ; \; K_2^* = k_3/k_{30}$$

Mass Spectrometry

The discharge flow technique has been used in conjunction with mass spectrometry for several studies reported in this compilation. Many of the preferred rate constants were measured using a system which utilized efficient collision free sampling between the flow tube and the ion source of the mass spectrometer[5,29,30]. The ion currents of both labile and stable species were shown to be linearly proportional to the concentrations of their flow tube precursors and could be calibrated on an absolute basis. Typical limits of sensitivity, with a signal to noise ratio of unity, were, ClO (m/e 51) = 1.5×10^9 molecule cm^{-3}; OClO (m/e 67) = 5.0×10^8 molecule cm^{-3}; O_3(m/e 48) = 2.0×10^9 molecule cm^{-3}. Therefore, it can be seen that this technique is ~ 4 orders of magnitude more sensitive than UV absorption spectrophotometry for monitoring ClO and

OClO and as such is well suited to study the kinetics of fast reactions. The preferred values of the rate constants obtained using this technique used psuedo first order conditions, whereby, complicating 1st and 2nd order secondary reactions were eliminated. Reactions due to trace concentrations of active impurities produced in the microwave discharge (i.e. NO, O, H) were carefully eliminated utilizing the discharge bypass technique and/or by chemical scavenging.

The mass spectrometric study of the Cl + CH_4 reaction used a similar but somewhat less efficient, and less sensitive sampling system than the above[14]. However, the study was performed using pseudo 1st order conditions whereby, if there had been any secondary reaction between the atomic chlorine and the product methyl radicals it would not have affected the reported rate constant.

Time of flight mass spectrometry has been used to determine the overall reaction rate and stoichiometry for the O + Cl_2 reaction[31]. Both atomic oxygen and molecular chlorine were monitored and this technique yielded results in good agreement with those obtained using chemiluminescence[32] to monitor O atoms.

Resonance Fluorescence

The technique of atomic resonance fluorescence is both highly specific and sensitive, and thus, well suited to the study of rapid reactions. Both discharge flow[5,33] and flash photolysis[34] experiments have monitored the fluorescent flux of the Cl $4s^4P_{3/2} - 3\ p^5\ {}^2P_{3/2}$ transition at 138.0 nm. The results of the discharge flow experiments showed that the fluorescent flux was linearly proportional to the concentration of ${}^2P_{3/2}$ chlorine atoms when $[Cl, {}^2P_{3/2}] \leq 10^{12}$ atom cm^{-3}.

This is in slight contrast to the flash photolysis results which show that when the chlorine atom concentration is in the range of 10^{11} - 10^{12} atom cm^{-3}, the fluorescent flux is not linearly proportional to the atom concentration, but obeys the following: $I_F \alpha [Cl]^{0.9}$. The paper did not report the nature of the relationship between I_F and $[Cl, {}^2P_{3/2}]$ when the latter was $\leq 10^{11}$ atom cm^{-3}, but it would be expected that I_F was linearly dependant upon the atom concentration in this region[35]. The lower limit for detection of ${}^2P_{3/2}$ Cl atoms using the discharge flow system was reported to $\geq$ 5 x 10^{10} atom cm^{-3}(13), but later after system modification this value was reduced to $\geq$ 3 x 10^9 atom cm^{-3}(5).

Kinetic studies involving O ${}^3P$ atoms have been performed using the discharge flow technique[5]. The fluorescent emission used to monitor the concentration of O ${}^3P$ atoms was that produced by the O 3s ${}^3S_1$ - $2p^4$ ${}^3P_o$ transition at λ 130.6 nm. The limit of detection was reported to be ~ 4 x 10^9 atom cm^{-3}, and from this value to $\leq 10^{12}$ atom cm^{-3} the intensity of fluorescence was found to be linearly proportional to the atom concentration.

Hydroxyl radicals have been monitored in a discharge flow system using the emission produced at 309 nm, the band head of the A ${}^2\Sigma \rightarrow$ X ${}^2\Pi$ (O-O) transition[36]. Hydroxyl radical concentrations $\leq 10^{10}$ radical cm^{-3} can be detected, thus, allowing reaction conditions to be chosen whereby the problem of the bimolecular disproportionation of HO radicals is eliminated. Under these conditions, where $[HO]_o \leq 10^{12}$ radical cm^{-3}, the only process removing HO radicals, besides its interaction with the added reagent, is the heterogeneous 1st order wall removal. However, if the reaction is performed using pseudo first order conditions and the fixed observation point technique (as was the case) then 1st order reactions such as wall recombination do not need to be considered in the analysis of the decay data[37,38].

It is apparent that the technique of atomic and molecular resonance fluorescence allows even the most rapid reactions to be performed under psuedo first order conditions, whereby, the problem of complicating secondary reactions can be successfully eliminated. The technique becomes insensitive at high absorber concentrations ($> 10^{12}$ particle cm^{-3}), although the lamp design and operating conditions control the range in which the intensity of the fluorescent flux is linear (or nearly) with atom concentration. The technique of atomic resonance fluorescence is powerful in that it can be used to directly observe in a quantative manner trace concentrations of both, (a) impurity atoms produced either photolytically or in a microwave discharge, and (b) atoms produced in the course of a reaction. This can be achieved by alteration of the chemical composition of the discharge lamp.

Calibration of the fluorescent flux intensity is normally achieved by producing known concentrations of atoms, either photolytically or by use of a stoichiometric reaction and observing the fluorescent flux produced. Even though this procedure may/or may not be to within an accuracy of 10%, it introduces no error into the rate constants reported in this compilation as all studies were performed under psuedo first order conditions, whereby, the concentration of the species being monitored was always significantly (a factor of $\geq$ 5) lower than the un-monitored species, therefore, only relative atom concentrations were required.

Resonance Absorption

This technique has been infrequently used in the studies to be reported in this compilation. It is typically about two orders of magnitude less sensitive than resonance fluorescence, and thus of limited use in the study of rapid bimolecular reactions ($k > 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}), where psuedo 1st order conditions are required to eliminate complicating secondary reactions. Hydroxyl radicals have been monitored using this technique in a flash photolysis study of the HO + HCl reaction[39]. The only other studies to use this technique were; (a) an investigation of the stoichiometry of the Cl + ClNO reaction, in which a lower limit was reported for the rate constant[40], and (b) an investigation of the reaction products of the bimolecular disproportionation of ClO radicals at low total pressure (~ 1-5 torr)[29]. Both studies were performed in a discharge flow apparatus and monitored the concentration of $^2P_{3/2}$ chlorine atoms at λ 138.0 nm (Cl 4s $^4P_{3/2}$ - 3 p^5 $^2P_{3/2}$). The lower limit of detection was $\geq 2 \times 10^{12}$ atom cm^{-3}. Nitric oxide was also monitored in the former study[40] at λ 180 nm (1-0 transition of NO, ε - D $^2\Sigma^+$ - X $^2\Pi_{1/2}$), in which the lower limit of sensitivity was reported to be $\geq 2 \times 10^{13}$ molecule cm^{-3}.

Calibration of the emitting lamp, which is normally achieved in a similar manner to that for fluorescent experiments, could be eliminated if the f value of the electronic transition were known, and if the lamp were totally unreversed with pure Doppler broadened lines. However, the latter criterion is difficult to achieve and often the f values are unknown. When kinetic experiments are performed under second order conditions, or the stoichiometry of a reaction is being measured, then the absolute concentration of the species being monitored is required, and any calibration inaccuracies will be reflected in the accuracy of the final result. Absorption experiments suffer to a greater extent than fluorescent experiments to drift in the lamp output, but are able to measure higher concentrations, which in some systems is essential[29].

Electron Paramagnetic Resonance Spectrometry

Two kinetic studies have used e.p.r. in conjunction with the discharge flow technique. The decay of ground state (^3P) oxygen atoms in the presence of excess HCl was monitored by following the intensity of their e.p.r. spectrum[45]. The production of $^2P_{3/2}$ chlorine atoms was observed in a qualitative manner.

In a study of the HO + HCl[46] system, absolute concentrations of both $Cl(^2P_{3/2})$ and $HO(^2\Pi)$ were required in order to analyse the kinetic data. Absolute concentrations were obtained by double integration of their spectra, and by using published e.p.r. transition probabilities[47]. Consequently, an error in the calibration would lead to an error in the value of the calculated rate constant. The lower limit for detection of HO radicals was reported to be $2\text{-}5 \times 10^{11}$ molecule cm^{-3}. The sensitivity of this technique for monitoring atoms is similar to that of atomic resonance absorption.

Infrared Spectroscopy

Infrared spectroscopy has been used with the molecular modulation technique to identify the ClOO free radical as an intermediate in the photolysis of Cl_2/O_2 mixtures, and to obtain a value for a product of rate constants[26]. Kinetic data obtained from this system must be analysed in terms of a large complexity of interacting reactions. Thus, the reported rate constants rely upon the analysis using the correct matrix of reactions, and simplyfying assumptions. However, as I.R. absorption cross sections are normally lower than UV absorption cross-sections the technique is rarely used for kinetic experiments, except with the molecular modulation technique which uses long optical path-lengths and is capable of measuring small modulation amplitudes (10^{-4} - 10^{-5}).

Miscellaneous Techniques

Some early studies were performed whereby reaction mechanisms and rate constants were determined from somewhat limited and indirect experimental data such as: pressure change as a function of extent of reaction[41,42]; the chemical analysis of unreacted reagents[43] or reaction products[44] from a competitive study with a known reference rate constant. These studies involved complex kinetic schemes and the results must be regarded as inferior to the more recent direct determinations.

Errors and Uncertainty Limits

The difficulty in assigning reliability limits to the rate data is that the preferred value is normally a single measurement. Although several reactions have been studied more often, many of the determinations can be eliminated due to their indirectness (subject to an accumulation of errors) or incorrect data analysis. Besides the error limit placed on the reported rate constant by the original workers, it is difficult for the writer to arbitrarily increase this error limit. However, a few comments on systematic errors are included to show that ~ ±25% is probably the upper limit to place on single value determinations. Five recent investigations of the $O(^3P) + NO_2$ reaction have been performed using a wide variety of techniques, and the reported rate constants were all within 10% of each other, which strongly suggests that systematic errors are not normally significant[51-54]. Most of the preferred values which was obtained from single measurements were performed using the discharge flow technique.

a. Errors in discharge flow systems

The fundamental measurements in a discharge flow system are: P_T, total flow tube pressure; T, temperature; A, cross-sectional area of the flow tube; and f_i, the flow rates of both carrier and reagent gases. It is possible that errors in these measurements could accumulate and cause an error of 10% in the measured rate constants. Systematic errors may also arise if, (1) the gas flow profile is laminar, rather then plug, and (2) axial diffusion is significant. As the rate of radial diffusion increases, the flow velocity profile tends towards that of plug flow, but the problem of back diffusion increases. A recent paper[48] has calculated the magnitude of the possible errors introduced into the determination of rate constants if the flow velocity profile is laminar, and plug flow has been assumed. The magnitude of the error is dependant upon the type of observation technique used; flow tube dimensions, total pressure, and the first order rate constant. Calculations were performed to show that the errors caused by this effect were always less than 10%[5,29,30], in agreement with earlier views[49,50] that the errors caused in assuming plug flow were small. In flow systems with numerous inlet jets, the formation of laminar flow is unlikely due to the jets acting as centers of turbulence. The effect of back diffusion is to underestimate the true rate constant, and the following expression shows the relationship between the true (k) and measured (k') rate constants:

$$k = k' \left(1 + \frac{k'D}{U^2}\right)$$

k,k' are 1st order rate constants

U = flow velocity

D = diffusion coefficient

The magnitude of the errors introduced by neglecting back diffusion can be seen to be greatest under slow flow conditions, but are still normally < 10%. The last two effects both underestimate the true rate constant and so it is conceivable, but unlikely that they may add to lead to an error of ~25%.

b. Errors in flash photolysis systems

The fundamental measurements in a flash photolysis system are: t, time; T, temperature; and P_i, the reagent and diluent gas pressures. The largest systematic errors present in early flash photolysis systems stemmed from (1) the pressure measurements, and (2) complicating secondary reactions which limited the accuracy of the data analysis. Since the advent of accurate low pressure capacitance manometers, the accuracy of pressure measurements has improved considerably and the errors are now $\leq$ (1-3)%. Previous discussion has shown that the use of modern detection techniques, such as atomic resonance fluorescence, has minimized the effect of secondary reactions in the systems studied. Diffusion of species out of the reaction zone can be accurately determined and should not lead to an error in the data analysis of > 5%. Consequently, it is felt that systematic errors should not exceed 10% in total.

Units

Rate constants for bimolecular reactions are expressed in units of cm^3 $molecule^{-1}$ s^{-1}, and those for termolecular reactions in cm^6 $molecule^{-2}$

s^{-1}. The expression used for a rate constant as a function of temperature is $k = A \exp(-C/T)$ where $C = E/R$, E being the "activation energy", and R the gas constant. To obtain E in kJ mol^{-1}, multiply C by 0.008314 and to obtain E in kcal mol^{-1}, multiply C by 0.001987. Absorption cross sections are given in units of cm^2 $molecule^{-1}$.

Numbered Reactions

The numbered rate constants referred to in the introduction are keyed to the Table of Contents. Tables I list the reactions studied under the various techniques used. An asterisk denotes a study in which the result is used by the writer to forward a preferred value.

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TABLE I Rate Constant Measurements Categorized by Analytical Technique. The kinetic methods and references are given for each study. An asterisk means that measurement was used in developing a preferred value.

Resonance Fluorescence	Ultraviolet Spectroscopy	Emission Spectroscopy	Mass Spectrometry
k_2(Cl+OClO)*; d.F^{5};	k_1(Cl+O$_3$); d.F^{15};	k_3(Cl+O$_2$+M); d.F^{11};	k_1(Cl+O$_3$)*; d.F^{30};
k_4(Cl+CH$_4$)*; F.p^{34};	k_2(Cl+OClO); F.p^{21};	k_3(Cl+O$_2$+M); d.F^{15};	k_2(Cl+OClO)*; d.F^{5};
k_{10}(Cl+ClNO)*; d.F^{33};	k_2(Cl+OClO); d.F^{15};	k_8(Cl+NO+N$_2$)*; d.F^{7};	k_4(Cl+CH$_4$)*; d.F^{14};
k_{14}(O+ClO)*; d.F^{5};	k_3(Cl+O$_2$+M); F.p^{22};	k_9(Cl+NO+O$_2$)*; d.F^{7};	k_{14}(O+ClO)*; d.F^{5};
k_{31}(O+OClO)*; d.F^{5};	k_5(Cl+ClOO); m.m^{26};	k_{11}(Cl+NO$_2$+M)*; d.F^{10};	k_{14}(O+ClO); d.F^{55};
k_{28}(HO+HCl)*; d.F^{36};	k_6(Cl+ClOO); mm^{26};	k_{12}(Cl+ClNO$_2$); d.F^{10};	k_{15}(NO+ClO)*; d.F^{30};
k_{4A}(Cℓ + H$_2$)*; F.p^{34};	k_5/k_6; F.p^{22};	k_{13}(Cl+Cl+Ar)*; d.F^{8};	k_{16}(ClO+CO); d.F^{17};
Resonance Absorption	k_7(Cl+Cl$_2$O)*; F.p^{20};	k_{13}(Cl+Cl+Ar); d.F^{9};	k_{17}(ClO+O$_3$)*; d.F^{29};
k_{10}(Cl+ClNO); d.F^{40};	k_7(Cl+Cl$_2$O); F.p^{23};	k_{27}(O+Cl$_2$)*; d.F^{32};	k_{18}(ClO+H$_2$); d.F^{17};
k_{28}(HO+HCl)*; F.p^{39};	k_{14}(O+ClO); F.p^{19};	k_{4A}(H + HCℓ); d.F^{87} ,	k_{19}(ClO+CH$_4$); d.F^{17};
	k_{14}(O+ClO); d.F^{18};		k_{20}(ClO+C$_2$H$_4$); d.F^{17};
	k_{15}(NO+ClO); F.p^{16};		k_{21}(ClO+C$_2$H$_2$); d.F^{17};
	k_{16}(ClO+CO); mm^{27};		k_{22}(ClO+N$_2$O); d.F^{17};
	k_{16}(ClO+CO)*; d.F^{17};		k_{23}(ClO+NH$_3$); d.F^{17};
	k_{17}(ClO+O$_3$)*; d.F^{15};		k_{24}(ClO+ClO); d.F^{29};
	k_{18}(ClO+H$_2$); d.F^{17};		k(25+25')(ClO+ClO);d.F^{29};
	k_{19}(ClO+CH$_4$); d.F^{17};		$\frac{k_{26}(\mathrm{ClO+ClO+M})}{k_{25'}(\mathrm{ClO+ClO})}$ m.m^{57};

TABLE I (Continued)

Calorimetric Probe	Ultraviolet Spectroscopy	Ultraviolet Spectroscopy	Mass Spectrometry
$k_{13}(Cl+Cl+Ar);d.F^{6};$	$k_{20}(ClO+C_2H_4);\ d.F^{17};$	$k_{(25+25')}(ClO+ClO)^{**};$ $d.F^{19};$	$k_{27}(O+Cl_2)^{*};\ d.F^{31};$
E.P.R.	$k_{21}(ClO+C_2H_2);\ d.F^{17};$	$k_{(25+25')}(ClO+ClO)^{*};$ $F.p^{56};$	$k_{29}(O+HCl);\ s.r^{58};$
$k_{28}(HO+HCl)^{*};d.F^{46};$	$k_{22}(ClO+N_2O);\ d.F^{17};$	$k_{(25+25')}(ClO+ClO)^{*};$ $d.F^{17};$	$k_{31}(O+OClO)^{*};\ d.F^{5};$
$k_{29}(O+HCl);\ d.F^{45};$	$k_{23}(ClO+NH_3);\ d.F^{17};$	$k_{26}(ClO+ClO+M);m.m^{26};$	$k_{32}(NO+OClO)^{*};\ d.F^{30};$
$k_{4A}(C\ell+H_2);\ d.F^{88};$	$k_{(25^*+25')}(ClO+ClO);$ $F.p^{24};$	$k_{26}(ClO+ClO+M);d.F^{17};$	$k_{33}(N+OClO);\ d.F^{59};$
Miscellaneous	$k_{(25+25')}(ClO+ClO);$ $F.p^{25};$	$k_{31}(O+OClO);\ F.p^{21};$	$k_{34}(H+OClO)^{*};\ d.F^{5};$
$k_4(Cl+CH_4);S.C^{44};$	$k_{(25+25')}(ClO+ClO);$ $F.p^{23};$	$k_{31}(O+OClO);\ d.F^{18};$	$k_{35}(O+Cl_2O)^{*};\ d.F^{55};$
$k_4(Cl+CH_4);\ S.C^{43};$	$k_{(25+25')}(ClO+ClO)^{*};$ $d.F^{18};$	$k_{32}(NO+OClO);\ d.F^{16};$	$k_{28}(HO+HCl);\ F^{60};$
$k_8(Cl+NO+N_2);\ S.C^{41};$	$k_{(25+25')}(ClO+ClO)^{*};$ $d.F^{15};$	$k_{4A}(C\ell+H_2)^{*};\ S.C.^{89};$	
$k_{10}(Cl+ClNO);\ S.C^{42};$	$k_{(25')}(ClO+ClO);mm.^{26};$		
$k_{4A}(C\ell+H_2);\ d.F^{83};$			
$k_{4A}(C\ell+H_2);\ S.C.^{84};$			
$k_{4A}(C\ell+H_2);\ S.C.^{85};$			

Key to Methods

d.F = discharge flow

F.p = flash photolysis

s.r. = stirred reactor

S.C. = static cell

F = flame

Compilation of Rate and Photochemical Data

I. Reactions of Ground State $(^2P_{3/2})$ Chlorine Atoms.

$Cl(^2P_{3/2}$ Reactions:

(1) $Cl(^2P_{3/2}) + O_3 \xrightarrow{k_1} ClO(^2\Pi) + O_2$

*Clyne and Watson, 1974[30].	$(1.8_5 \pm 0.3_6) \times 10^{-11}$	300 K	(a)
Clyne and Coxon[15], 1968.	$> 6.7 \times 10^{-13}$	300 K	

(a) Preferred value. Obtained using psuedo 1st order conditions.

(2) $Cl(^2P_{3/2}) + OClO \xrightarrow{k_2} 2\ ClO(^2\Pi)$

*Bemand, Clyne and Watson[5], 1973.	$(5.9 \pm 0.9) \times 10^{-11} \times \exp(0 \pm 120/T)$	(298-588)K	(b)
Bemand, Clyne and Watson[5], 1973.	$(6.1 \pm 0.9) \times 10^{-11}$	298 K	(b)
Bemand, Clyne and Watson[5], 1973.	$(5.9 \pm 0.9) \times 10^{-11}$	298 K	(b)
Basco and Dogra[19], 1971a.	$(8.5 \pm 1.2) \times 10^{-12}$	300 K	
Clyne and Coxon[15], 1968.	$> 1.0 \times 10^{-12}$	300 K	

(b) The preferred value was obtained by combining the results of three separate sets of experimental determinations, using different techniques.

(3) $Cl + O_2 + M \xrightarrow{k_3} ClOO + M$

Stedman in "Clyne and Coxon[11], 1968.	5.6×10^{-34}	(200-300)K	
Clyne and Coxon[15], 1968.	$< 5.6 \times 10^{-33}$	300 K	
Nicholas and Norrish[22], 1968.	1.7×10^{-33}	300 K	(c)

(c) The authors used several kinetic assumptions in their calculations, which if incorrect would lead to their value for k_3 to have been underestimated.

*Preferred value.

(4) $\underline{Cl(^2P_{3/2}) + CH_4 \xrightarrow{k_4} CH_3 + HCl}$

Clyne and Walker[14], 1973.	$5.1 \times 10^{-11} \times$ $\exp(-1790 \pm 37/T)$	(300-686)K	(d)
	$(1.3 \pm 0.1) \times 10^{-13}$	300 K	
Davis, Braun and Bass[34], 1970.	$(1.5 \pm 0.1) \times 10^{-13}$	298 K	(d)
Knox and Nelson[44], 1959.	$4 \times 10^{-11} \times$ $\exp(-1940/T)$	(193-593)K	(d')
Pritchard, Pyke and Trotman-Dickenson[43], 1954.	$4.6 \times 10^{-11} \times$ $\exp(-1920/T)$	(293-488)K	(d')

(d) The preferred value is based on the average value of k_4 at 298K, and the activation energy reported by Clyne and Walker. Therefore,

$$k_4^* = (5.6 \pm 0.9) \times 10^{-11} \times \exp(-1790 \pm 37/T)$$

$$k_4^*(300) = (1.4 \pm 0.1) \times 10^{-13}$$

(d') These values were not considered as they were determined relative to $k(Cl+H_2)$ and differ by a factor of 2 from the other results at 298K.

(4A) $\underline{Cl(^2P_{3/2}) + H_2 \xrightarrow{k_{4A}} HCl + H}$

Hertel[81], 1931.	$E_a = (24.3 \pm 4.2)$ kJ mol^{-1}	~300 K	
Potts and Rollefson[82], 1935.	$E_a = (18.9 \pm 4.2)$ kJ mol^{-1}	<170 K	
	$= (24.3 \pm 4.2)$ kJ mol^{-1}	>200 K	
Rodebush and Klingelhoefer[83], 1933	1.37×10^{-14}	298 K	(e 1)
	5.5×10^{-15}	273 K	(e 1)
	1.08×10^{-14}	298 K	(e 2)
	4.1×10^{-15}	273 K	(e 2)
Steiner and Rideal[84], 1939.	1.17×10^{-11}	1071 K	(e 3)
	8.67×10^{-12}	1013 K	(e 3)
	7.67×10^{-12}	960 K	(e 3)
	6.00×10^{-12}	901 K	(e 3)
	5.90×10^{-12}	1071 K	(e 4)
	4.57×10^{-12}	1013 K	(e 4)
	4.07×10^{-12}	960 K	(e 4)
	3.27×10^{-12}	901 K	(e 4)

Ashmore and Chanmugam[85],1953.	8.0×10^{-13}	523 K	(e 5)
Fettis and Knox[86],1964.	$(1.38 \pm 0.1) \times 10^{-10} \times \exp(-2750 \pm 70/T)$	(273-1071)K	(e 6)
	$(1.4 \pm 0.1) \times 10^{-14}$	298 K	
Clyne and Stedman[87],1966.	1.47×10^{-13}	373 K	(e 7)
	1.95×10^{-14}	294 K	(e 7)
	1.29×10^{-14}	273 K	(e 7)
	7.0×10^{-16}	195 K	(e 7)
Westenberg and de-Haas[88],1968.	$2.0 \times 10^{-11} \exp(-2160/T)$	(251-456)K	(e 8)
	1.35×10^{-14}	298 K	
*Benson, Cruickshank and Shaw[89], 1969.	$(8.0 \pm 2.0) \times 10^{-11} \times \exp(-2655 \pm 200/T)$	(479-610)K	(e 9)
	$(1.1 \pm 0.2) \times 10^{-14}$	298 K	
*Davis, Bass and Braun[34],1970.	$(1.4 \pm 0.1) \times 10^{-14}$	298 K	(e 10)
Galante and Gislason[90],1973.	REVIEW		(e 11)
Clyne and Walker[14],1973.	$(3.7 \pm 0.6) \times 10^{-11} \times \exp(-2146 \pm 51/T)$	(195-610)K	(e 12)
	2.76×10^{-14}	298 K	
	$(5.6 \pm 1.2) \times 10^{-11} \times \exp(-2254 \pm 69/T)$	(195-496)K	(e 13)
	2.95×10^{-14}	298 K	

(e 1). These results should have low or zero weighting when calculating a best value for k_{4A} due to the inaccurate manner used to determine [Cl], and due to the observed dependence of k_{4A} upon the history of the reactor surfaces. These values were calculated by Fettis and Knox,86 from the reaction probabilities reported in reference 83.

(e 2). Same data as in (e 1). These values were calculated by Benson et al.,89. See remarks in (e 1).

(e 3). These results should have low weighting due to the uncertainty regarding the effect of the presence of molecular O_2 (91). The values of k_{-4A} (H + HCl) reported by Steiner and Rideal[84] have been recalculated using more recent thermodynamic data to yield values for k_{4A}.

(e 4). Same data as in (e 3). These values are those given by Benson et al (89). The values of k_{-4A} reported in (84) were recalculated using more recent thermodynamic data and lowered by a factor of 2 based on the report (91) that the presence of molecular oxygen alters the rate of hydrogen exchange.

(e 5). The chemical system is complex and numerous simplylying assumptions were made. However, recent kinetic measurements justify most of these assumptions. Their value of k_{4A} depends only upon the equilibrium constant for $k(Cl_2 + NO)/k(Cl + ClNO)$, and not upon Burns and Dainton's value of k(Cl + ClNO) which they used, and is not believed (by the writer) to be incorrect. Consequently their value may be approximately (± 20%) correct.

(e 6). A review of references (80, 81, 82). Their interpretation of the published data is shown in the table.

(e 7). Calculated by Benson et. al. (89) using the reported values of k_{-4A} in conjunction with the thermodynamic values of K_{eq}. These values predict that the activation energy increases with temperature, which was not observed over the same temperature range in reference 88. The published values of k_{-4A} are in fair (± 30%) agreement with those published for k_{-4A} in reference 88. No obvious systematic error is noticable but these results are at variance with the direct determinations of k_{4A} (especially reference 34).

(e 8.) The Arrhenius expression is shown for the study which directly measured k_{4A}. k_{-4A} was also reported but the results are not shown. K_{eq} (exp) was found to be a factor of 2-3 lower than that calculated from thermodynamic data. The value at 298 K for k_{4A} is in excellent agreement with reference 34, but this is fortuitous in that their measurement of k_{4A} should be seriously underestimated due to the regeneration of Cl via the rapid $H + Cl_2$ reaction. Consequently this result should not be considered. The back reaction should not suffer from such error and could predict a much higher value (factor of ~2.5) for k_{4A}.

(e 9.) The chemical system was somewhat complex, but the study should not suffer from any serious error. Benson et. al. also reviewed earlier data and concluded that their Arrhenius expression was unchanged when including this data. However, the reliability of the earlier data is questionable.

(e 10). This study performed at 298 K should be the only study free from any complicating secondary reactions. Psuedo 1st order conditions were used, and the absence of complications was well verified.

(e 11). This review judged that the data from the direct studies of k_{4A} were accurate, whilst those (87,88) measured for k_{-4A} were in error by a factor of 2. The explanation forwarded for the factor of 2 is certainly questionable with no direct evidence to support it. However the conclusion that it is inaccurate data which results in K_{eq} (calculated) $\gg k_{4A}/k_{-4A}$ is valid.

(e 12). This rate constant expression includes data from references (87, 88 (k_{-4A}) 89 and 34), but rejects the determination of k_{4A} from reference 88.

(e 13). This rate constant expression is based on data from references (87, 88 (k_{-4A}) and 34). However, the weighting given to reference 34 now seems too low.

The writer feels that only the data in reference 34 are free from error. Several other studies support this room temperature value. However there is disagreement about the temperature dependence of k_{4A} and it is not clear how to resolve the matter. For the present the expression of Benson et. al. (89) should be used when values are needed over a range of temperatures. Reference (34 and 89) are essentially in agreement at room temperature. For model calculations the expressions given by Clyne and Walker (14) may be used to test the sensitivity of the model to the value of k_{4A}.

(5) $\underline{Cl(^2P_{3/2}) + ClOO \xrightarrow{k_5} Cl_2 + O_2}$

Johnston, Morris and Van den Bogaerde[26], 1969.	1.56×10^{-10}	298 K	(f)
Johnston, Morris and Van den Bogaerde[26], 1969.	$k_5/k_6 = 108$	298 K	(g)
Nicholas and Norrish[22], 1968.	$k_5/k_6 = 15$		(g)

(f) This value was obtained from the analysis of a complex reaction system, and is dependent upon the value used for $\Delta H_f ClOO$, which is not well established.

(g) These two values are markedly different. The value of 15 is in agreement with a value that can be derived from a study by Porter and Wright (1953).

(6) $Cl(^2P_{3/2}) + ClOO \xrightarrow{k_6} 2\ ClO$

Johnston, Morris and Van den Bogaerde[26], 1969.	1.44×10^{-12}	298 K	

(h) This value was obtained from the analysis of complex reaction scheme, and was obtained relative to k_5. Therefore, both k_5 and the ratio k_5/k_6 have to be accurately known to obtain a value for k_6. Although the ratio k_5/k_6 was not dependent upon the value of $\Delta H_f ClOO$, the kinetic analysis for k_5 required ΔH_f ClOO to be known.

(7) $Cl(^2P_{3/2}) + Cl_2O \xrightarrow{k_7} Cl_2 + ClO$

*Basco and Dogra[20], 1971b.	6.8×10^{-13}	300 K	
Edgecombe, Norrish and Thrush[23], 1957.	$> 6.7 \times 10^{-13}$	300 K	

(8) $Cl(^2P_{3/2}) + NO + N_2 \xrightarrow{k_8} ClNO + N_2$

Clark, Clyne and Stedman[7], 1966.	$(9.7\pm1.4) \times 10^{-32}$	293 K	(i)
*Clark, Clyne and Stedman[7], 1966.	$E_a(M=Ar) = -(4.6\pm.4)\ kJ\ mol^{-1}$	471 K	
Ashmore and Spencer[41], 1959.	$(2.1\pm0.6) \times 10^{-32}$	471 K	

(i) Clyne and Stedman (1968), reported that this value may be too low due to a systematic error in their method of monitoring [Cl], as it has been shown that the intensity of the chlorine afterglow is not always proportional to $[Cl]^2$. Therefore, k_8 and k_9 have probably been underestimated by ~ 15%, and this leads to a preferred value for k_8^* of $(1.1\pm0.2) \times 10^{-31}$.

(9) $Cl(^2P_{3/2}) + NO + O_2 \xrightarrow{k_9} ClNO + O_2$

Clark, Clyne and Stedman[7], 1966.	$(1.1\pm.1_4) \times 10^{-31}$	293 K	

See note (i) above. The preferred value for k_9^* is $(1.3\pm0.3) \times 10^{-31}$.

(10) $Cl(^2P_{3/2}) + ClNO \xrightarrow{k_{10}} NO + Cl_2$

*Clyne and Cruse[33], 1972.	$(3.0\pm0.5) \times 10^{-11}$	298 K	(j)
Clyne, Cruse and Watson[40], 1972.	$\geq 8 \times 10^{-12}$	298 K	
Burns and Dainton[42], 1952.	$(1.9\pm1.0) \times 10^{-11} \times$ $\exp(-533\pm160/T)$	298-328 K	

(j) This direct determination of k_{10} at 298K is preferred to the study of Burns and Dainton, where several systematic errors were likely.

(11) $Cl(^2P_{3/2}) + NO_2 + M \xrightarrow{k_{11}} ClNO_2 + M$

*Clyne and White[10], 1974.	7.2×10^{-31}	298 K	(k)

(k) Provisional data, subject to revision

(12) $Cl(^2P_{3/2}) + ClNO_2 \xrightarrow{k_{12}} Cl_2 + NO_2$

Clyne and White[10], 1974.	$k_{12}/k'_{11} >> 1$	298 K	(l)

(l) k_{12} is greater than the second order component of k_{11} at low pressure (1 torr). Therefore, $k_{12} >> 3 \times 10^{-14}$.

(13) $Cl(^2P_{3/2}) + Cl(^2P_{3/2}) + Ar \xrightarrow{k_{13}} Cl_2 + Ar$

Clyne and Stedman[8], 1968.	$5.6 \times 10^{-34} \times$ $\exp(910\pm350/T)$	(195-500)K	(m)
	$(1.2\pm0.1_4) \times 10^{-32}$	298 K	
Hutton and Wright[9], 1965.	$(1.2\pm0.2) \times 10^{-32}$	298 K	(m)
Bader and Ogryzlo[6], 1964.	1.1×10^{-32}	313 K	(m)
*Lloyd,[61] review.	$6.0 \times 10^{-34} \times$ $\exp(900\pm250/T)$	(200-500)K	

(m) All three determinations of k_{13} are in agreement (±10%) at 298K. The efficiency of N_2 as a third body should not be too dissimilar from Ar. $-d[Cl]/dt = 2k_{13}[Cl]^2 [Ar]$.

II. Reactions producing ground state ($^2P_{3/2}$) Chlorine atoms, and/or involving ClO radicals.

(14) $O(^3P) + ClO \xrightarrow{k_{14}} Cl(^2P_{3/2}) + O_2^*\ (^1\Delta\ ,^1\Sigma)$

*Bemand, Clyne and Watson,[5] 1973.	$(5.3 \pm 0.8) \times 10^{-11}$	298 K	(n)
Bemand, Clyne and Watson[5], 1973.	$(5.7 \pm 2.3) \times 10^{-11}$	298 K	(o)
Basco and Dogra[19], 1971a.	1.2×10^{-11}	300 K	
Clyne and Coxon[18], 1966a.	$> 1.0 \times 10^{-11}$	300 K	
Freeman and Phillips[55], 1968.	$> 1.3 \times 10^{-11}$	300 K	

(n) This value is preferred due to the direct nature and the high specific sensitivity of the study, which utilized atomic resonance fluorescence to monitor atomic oxygen.

(o) This value was obtained using molecular beam mass spectrometry and is in good agreement with the preferred value.

(15) $NO(^2\Pi) + ClO(^2\Pi) \xrightarrow{k_{15}} NO_2 + Cl(^2P_{3/2})$

*Clyne and Watson[30], 1974.	$(1.7 \pm 0.2) \times 10^{-11}$	298 K	(p)
Coxon[16], 1968.	$> 3 \times 10^{-13}$	300 K	

(p) A direct determination of the rate constant, the value was reported in "Bemand, Clyne and Watson (1973)" - to be published by Clyne and Watson in J.C.S. Faraday I.

(16) $ClO(^2\Pi) + CO \xrightarrow{k_{16}} CO_2 + Cl(^2P_{3/2})$

*Walker[17], 1972.	1.7×10^{-15}	587 K	
Harker[27], 1972.	1.4×10^{-15}	300 K	(q)

(q) This value is rejected due to its indirect determination from a complex reaction scheme.

(17) $ClO + O_3 \begin{array}{l} \xrightarrow{k_{17}} OClO + O_2 \\ \xrightarrow[k_{17}]{} ClOO + O_2 \end{array}$

Clyne and Coxon[15], 1968.	$\leq 5 \times 10^{-15}$	300 K	
Clyne, McKenny, Watson[29], 1974.	$\leq 5 \times 10^{-15}$	298 K	(r)

(r) Provisional data subject to revision. The rate constants reported do not differentiate between the two reaction paths.

(18) $ClO + H_2 \xrightarrow{k_{18}} Products$

Walker[17], 1972.	$\leq 8 \times 10^{-16}$	670 K	(s)
Clyne and Coxon[15], 1968.	$\leq 5 \times 10^{-16}$	300 K	

(19) $ClO + CH_4 \xrightarrow{k_{19}} Products$

Walker[17], 1972.	$\sim 4 \times 10^{-15}$	670 K	(s)

(20) $ClO + C_2H_4 \xrightarrow{k_{20}} Products$

Walker[17], 1972.	$\leq 5 \times 10^{-16}$	670 K	(s)

(21) $ClO + C_2H_2 \xrightarrow{k_{21}} Products$

Walker[17], 1972.	$\leq 5 \times 10^{-16}$	670 K	(s)

(22) $ClO + N_2O \xrightarrow{k_{22}} Products$

Walker[17], 1972.	$\leq 7 \times 10^{-16}$	587 K	(s)

(23) $ClO + NH_3 \xrightarrow{k_{23}} Products$

Walker[17], 1972.	$\leq 5 \times 10^{-16}$	670 K	(s)

(s) These values were directly determined using the discharge flow technique coupled to UV absorption spectrophotometry and/or a line of sight mass spectrometer.

(24) $\underline{ClO + ClO \xrightarrow{k_{24}} Cl(^2P_{3/2}) + OClO}$

Clyne, McKenny and Watson[29], 1974.	$\leq 2.2 \times 10^{-15}$	298 K	(t)

(t) This is a provisional experimental upper limit. Using the thermodynamic values reported by Domalski et.al.[76], 1974 in conjunction with the preferred value for $k_2(Cl + OClO \rightarrow 2\ ClO)$, the following can be calculated. $\log_{10} k_{24} = -15.05 \pm 0.55$. The limits are due to the uncertainty in the value of ΔH_{f298} OClO. $-d[ClO]/dt = k_{24}[ClO]^2$.

(25) $$\underline{ClO + ClO} \begin{array}{l} \xrightarrow{k_{25}'} Cl_2 + O_2{}^{\dagger} \\ \xrightarrow{k_{25}''} Cl + ClOO^{\dagger} \end{array}$$

Porter and Wright[24], 1953.	$1.52 \times 10^{-13} \times \exp(0 \pm 325/T)$	293-433 K	(u)
Lipscomb, Norrish and Thrush[25], 1956.	1.93×10^{-13} 3.39×10^{-13}	300 K 300 K	(u)(v) (u)(w)
Edgecombe, Norrish and Thrush[23], 1957.	6.57×10^{-14}	300 K	(u)
*Clyne and Coxon[18], 1966.	2.33×10^{-14}	300 K	(u)
*Clyne and Coxon[15], 1968.	$(1.2 \pm 0.3) \times 10^{-12} \times \exp(-1260 \pm 150/T)$	(294-495)K	(u)
Clyne and Coxon[15], 1968.	$(1.0 \pm 0.3) \times 10^{-12} \times \exp(-1215 \pm 160/T)$	(294-495)K	(x)
Johnston, Morris and Van den Bogaerde[26], 1969.	2.6×10^{-14}	298 K	(u)(y)
*Clyne and White[56], 1971.	$(1.3 \pm 0.1) \times 10^{-12} \times \exp(-1150 \pm 50/T)$	(273-710)K	(u)(x)
**Basco and Dogra[19,20], 1971a,b.	4.4×10^{-14}	300 K	
*Walker[17], 1972.	$(1.9 \pm 0.6) \times 10^{-12} \times \exp(-1300 \pm 120/T)$		(u)
*Clyne, McKenny and Watson[29], 1974.	2.25×10^{-14}	300 K	(z)

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† The high pressure (> 75 torr) results indicate that all the reaction proceeds via channel 25, whilst the low pressure (1-3 torr) results indicate that the ratio $k_{25}'/k_{25}'' \simeq$ unity.

(u) Clyne and Coxon's (1968)[15] value for the absorption cross section was used to calculate k_{25}.

(v) k_{25} was reported to be flash energy dependent, due to the reaction mechanism being misinterpreted. Low flash energy.

(w) High flash energy.

(x) Clyne and White (1971)[56] reanalysed the data to allow for any third order decay of ClO.

(y) This value derived by combining their value of k_6 with the thermodynamic value of $K_2 = 109 = k_6/0.5\ k_{25}$. Neither k_6 nor K_2 is accurately known. (The value for $K_2 = 227$ in reference 26 was calculated incorrectly). Two likely values for K_2 may be derived: 109 and 661, corresponding, respectively, to $\Delta H_f(\text{C}\ell\text{OO}) = 86$ and 96 kJ mol^{-1}. See also remarks for reaction 30.

(z) This is the only published study not to use an optical spectroscopic method.

The preferred value for k_{25} at 298 K is: $-d[\text{ClO}]/dt = k_{25}[\text{ClO}]^2$.

(a)* $(2.4\pm0.4) \times 10^{-14}$ (low pressure)

(b)** 4.6×10^{-14} (high pressure)

The activation energy (for the overall process, which cannot be described by one simple initial step) is:

(a) (10.3 ± 1.0) kJ mol^{-1} (low pressure)

(26) $\underline{\text{ClO} + \text{ClO} + \text{M} \xrightarrow{k_{26}} \text{Cl}_2 + \text{O}_2 + \text{M}}$

Johnston, Morris and Van den Bogaerde[26], 1969.	1.0×10^{-31} (O_2) 6.6×10^{-32} (Ar)	298 K 298 K	(A) (A)
Wu[57], 1970.	$k_{26}/k_{25} =$ 1.1×10^{-17}		(B)
Walker[17], 1972.	$(2.0\pm2.0) \times 10^{-32}$ (Ar)	298 K	(C)(A)

(A) This value of k_{26} is defined as: $-d[\text{ClO}]/dt = k_{26}[\text{ClO}]^2\ [\text{M}]$.

(B) This value is only accurate to within a factor of two.

(C) This value was derived using data from; Clyne and Coxon (1968); Clyne and White (1971) and Walker (1972). The slope of $-d[\text{ClO}]/dt$ versus [M], was positive but within the error limits of being zero.

(27) $O + Cl_2 \xrightarrow{k_{27}} ClO + Cl(^2P_{3/2})$

Clyne and Coxon[32], 1966b.	$(9.3\pm2.2) \times 10^{-12} \times$ $\exp(-1560\pm50/T)$	(174-396)K	(D)
	5.1×10^{-14}	300 K	
Niki and Weinstock[31], 1967.	$(7.5\pm0.6) \times 10^{-14}$	300 K	(D)

(D) These two studies, both performed using the discharge flow technique, but with different detection techniques, are in fair agreement at 300 K. Therefore, the preferred value would be an average of the two at 300 K, and equal to 6.3×10^{-14}.

(28) $HO + HCl \xrightarrow{k_{28}} H_2O + Cl(^2P_{3/2})$

Takacs and Glass[46], 1973.	$(6.4\pm1.5) \times 10^{-13}$	295 K	(E)
Anderson, Zahniser and Kaufman[36], 1974.	$2.0 \times 10^{-12} \times$ $\exp(-313/T)$	(225-460)K	
	6.9×10^{-13}	295 K	(E)
Smith and Zellner[39], 1974.	$4.1 \times 10^{-12} \times$ $\exp(-500/T)$	(210-460)K	
	7.5×10^{-13}	295 K	(E)
Wilson, O'Donovan, and Fristrom[60], 1969.	1.3×10^{-11}	(1920-1940)K	(E')
Wong and Belles[58], 1972.	Estimated E_a = 21 kJ mol^{-1}		(F)

(E) There is good agreement between these three groups of workers at 295K, and the preferred value at this temperature is an average of the three, and equal to $(6.9\pm0.6) \times 10^{-13}$. The preferred Arrhenius expression for the (220-300)K temperature range is:

$$k_{28}^{*} = 2.8 \times 10^{-12} \exp(-400\pm100/T)$$

This yields values which are the average of references (36) and (39).

(E') This value is greater than would be predicted at 1920 K from the Arrhenius expressions of references (36) and (39).

(F) This value for the activation energy was estimated from the production of H_2O in the O + HCl study.

(29) $O + HCl \xrightarrow{k_{29}} OH + Cl(^2P_{3/2})$

Balakhnin, Egorov and Intezarova[45], 1971.	$(1.75 \pm 0.6) \times 10^{-12} \times \exp(-2260/T)$	(295-371)K	(G)
Wong and Belles[58], 1972.	$(1.9 \pm 0.27) \times 10^{-11} \times \exp(-3584 \pm 70/T)$	(356-628)K	(G)

(G) These two results are at variance with each other and thus no preferred value is given.

(30) $ClOO + M \xrightarrow{k_{30}} Cl(^2P_{3/2}) + O_2 + M$

There is no experimental determination of k_{30}, but a value can be calculated from the thermodynamic value of $K_2^* = k_3/k_{30}$ and from the experimental value of k_3. However, neither K_2^* nor k_3 are particularly well known. The value for ΔH_{f298} ClOO is possibly not better known than (89 ±5)kJ mol^{-1}(80). However, if ΔH_{f298} ClOO is 84.2 kJ mol^{-1}, as has been reported[76], then the following values for K_2^* can be calculated. This does not mean that the writer believes that this is the best value for ΔH_f ClOO, but this value is a lower limit and calculations using this value will predict the maximum possible ratio of [ClOO] to [Cl].

Elevation	T(K)	$K_2^*(atm^{-1})$	k_{30}(a)	k_{30}(b)
0	298	9.3	1.5×10^{-15}	4.5×10^{-15}
18	216.7	3007	6.3×10^{-18}	1.9×10^{-17}
23	219.6	2279	8.2×10^{-18}	2.5×10^{-17}
28	224.5	1439	1.3×10^{-17}	3.9×10^{-17}
33	231.1	823	2.2×10^{-17}	6.6×10^{-17}
38	244.8	279	6.0×10^{-17}	1.8×10^{-16}
43	258.6	105	1.5×10^{-16}	4.6×10^{-16}
48	270.7	49	3.1×10^{-16}	9.5×10^{-16}

(a) k_3 was taken to be temperature independent and equal to 5.6×10^{-34}. Reference 11.

(b) k_3 was taken to be temperature independent and equal to 1.7×10^{-33}. Reference 22.

III. Reactions of OClO and Cl_2O which involve ClO radicals

(31) $O(^3P) + OClO \xrightarrow{k_{31}} ClO + O_2\ (^3\Sigma_g^-)$

*Bemand, Clyne and Watson[5], 1973.	$(5^{+1}_{-2}) \times 10^{-13}$	298 K	(H)
Basco and Dogra[21], 1971	5.0×10^{-11}	300 K	
Clyne and Coxon[18], 1966a.	$> 4.0 \times 10^{-11}$	300 K	

(H) This value was determined from two separate direct studies.

(a) mass spectrometry: $-(4.7 \pm 1.6) \times 10^{-13}$

(b) atomic resonance fluorescence: $-(6.3 \pm 1.9) \times 10^{-13}$

(32) $NO + OClO \xrightarrow{k_{32}} NO_2 + ClO$

*Bemand, Clyne and Watson[5], 1973.	$(3.4 \pm 0.5) \times 10^{-13}$	298 K
Coxon,[16] 1968.	$> 8.5 \times 10^{-13}$	300 K

(33) $N(^4S) + OClO \xrightarrow{k_{33}} NO + ClO$

Watson[59], 1973.	$\leq 6 \times 10^{-13}$	298 K	(I)

(I) A preliminary experimental value, no detailed results.

(34) $H(^2S) + OClO \xrightarrow{k_{34}} OH + ClO$

*Bemand, Clyne and Watson[5], 1973.	$(5.7 \pm 1.2) \times 10^{-11}$	298 K

(35) $O + Cl_2O \xrightarrow{k_{35}} ClO + ClO$

*Freeman and Phillips[55], 1968.	$(1.4 \pm 0.2_3) \times 10^{-11}$	300 K

IV Optical Absorption Cross Sections

(36) $Cl_2 + h\nu \rightarrow 2\ Cl$ (Seery and Britton[62], 1964).

$Cl_2 + h\nu \rightarrow Cl(^2P_{1/2}) + Cl(^2P_{3/2})$; $\lambda < 483.0$ nm

λ(nm)	$10^{21} \times \sigma$ (cm^2 molecule^{-1})	λ(nm)	$10^{21} \times \sigma$ (cm^2 molecule^{-1})
240	0.8	350	189
250	1.2	360	131
260	2.3	370	83
270	8.8	380	49
280	27	390	33
290	65	400	19
300	120	410	13
310	185	420	9.9
320	236	430	7.3
330	256	440	5.3
340	236	450	3.4

(a) The authors[62] reported that each measurement was only accurate to within $\pm 2.0 \times 10^{-21}$ cm^2 molecule^{-1}.

(37) The Absorption Spectrum of HCl

*Romand, J.[74], 1949.

*Romand, J., Vodar, B.[63],
1948.

See figure 1.

$$HCl(^1\Sigma^+) + h\nu \rightarrow H(^2S_{1/2}) + Cl(^2P_{3/2})$$

$$\rightarrow H(^2S_{3/2}) + Cl(^2P_{1/2})$$

λ(nm)	$10^{20} \times \sigma$(cm^2 molecule^{-1})	λ(nm)	$10^{20} \times \sigma$(cm^2 molecule^{-1})
206.8	0.72	172.9	105
203.5	1.6	171.3	129
201.2	1.9	166.9	186
199.0	2.8	163.0	224
195.1	5.5	159.7	269
193.1	7.8	157.9	275
191.3	9.9	155.3	332
189.1	14.1	152.4	334
188.4	21.4	149.5	298
183.0	31.6	146.3	275
181.1	41.7	145.6	224
179.2	57.5	141.3	166
177.4	64.5	139.4	132

Also the spectrum has been reported by Myer and Samson[75], 1970.

(38) The Absorption Spectrum of ClOO

$ClOO + h\nu \rightarrow ClO(^2\Pi_{3/2}) + O(^1D)$

$\lambda < (267.9 \pm 3.0)$ nm

Johnston, Morris and Van den Bogaerde[26], 1969*. See figure 1. (a)

λ(nm)	$10^{18} \times \sigma$(ClOO) cm^2 $molecule^{-1}$	λ(nm)	$10^{18} \times \sigma$(ClOO) cm^2 $molecule^{-1}$
225	2.6	255	12.4
230	4.9	260	10.0
235	7.8	265	7.3
240	10.5	270	5.1
245	12.7	275	3.4
250	13.3	280	2.3

(a) The spectral band width was 1.3 nm.

(39) ## The Absorption Spectrum of ClO

$$ClO(^2\Pi_{3/2,\ 1.2}) + h\nu \rightarrow Cl(^2P_{3/2}) + O(^1D)$$

$\lambda < 263.0$ nm $(ClO(^2\Pi_{3/2}))$

$\lambda < 265.0$ nm $(ClO(^2\Pi_{1/2}))$

$$ClO(^2\Pi) \xrightarrow{h\nu} Cl(^2P_{3/2}) + O(^3P)$$

ClO is known to predissociate to $Cl(^2P_{3/2}) + O(^3P)$ at wavelengths > 280 nm. Durie and Ramsay[65], 1958 reported that the 7.0 band is totally predissociated.

Johnston, Morris and Van den Bogaerde[26], 1969*. See figure 1. (b)

λ(nm)	$10^{18} \times \sigma(ClO)$ cm^2 molecule^{-1}	λ(nm)	$10^{18} \times \sigma(ClO)$ cm^2 molecule^{-1}
225	$.6_4$	255	4.5
230	$.8_5$	260	5.3
235	1.3	265	5.7
240	1.9	270	5.6
245	2.7	275	4.9
250	3.6	280	4.7

(b) The spectral band width was 1.3 nm, and these values were placed on an absolute basis using Clyne and Coxon's[15] 1968 value for (ClO at 255.7 nm.

Porter and Wright[64], 1950.

λnm	10^{18} x σ(ClO) cm^2 molecule^{-1}	λnm	10^{18} x σ(ClO) cm^2 molecule^{-1}
263.63	1.4	274.95	5.8
264.06	1.4	277.16	7.2
264.58	2.2	279.60	5.8
265.25	3.6	282.24	5.8
266.10	3.6	285.18	4.3
267.12	3.6	288.40	3.6
268.25	3.6	291.80	3.6
269.50	4.3	295.43	2.2
271.11	5.0	299.30	1.4
272.94	5.0	303.45	0.7

(c) These values represent the absorption cross sections at the band heads. The value at 277.16 nm was equated to that reported by Clyne and Coxon[15], 1968.

(39a) The vacuum ultra-violet spectrum of ClO has recently been reported by Basco and Morse[78], 1973. Figures of the extinction coefficients for the C←X (160- 175nm), and D←X(~145-160nm) transitions of ClO are shown.

(40) Other Absorption Processes

(i) $OClO + h\nu \xrightarrow{(a)} ClO(^2\Pi) + O(^1D)$

$\xrightarrow{(b)} ClO(^2\Pi) + O(^3P)$

$\lambda_a < 276 \pm 3.nm$ (continuum)

$\lambda_b < 375.3nm$ (predissociation)

Finkelnburg and Schumacher [66], 1931.

Urey and Johnston[67], 1931.

Goodeve and Stein[68], 1929.

Coon and Ortiz[69], 1957.

Coon, DeWames and Loyd[70], 1962.

$\varepsilon(351.5_{nm}) = 1.14 \times 10^{-17}$ cm^2 molecule^{-1}. (Clyne and Coxon[15], 1968.

Basco and Morse[79], 1974, reported the extinction coefficients for the $C \leftarrow X$; $D \leftarrow X$ and $E \leftarrow X$ systems of OClO in the region ~145nm-184nm.

(ii) $ClNO \xrightarrow{h\nu} Cl + NO$

Continuous spectrum from (~630 - < 200)nm

Goodeve and Katz[71], 1939.

(iii) $Cl_2O\ h\nu \rightarrow ClO + Cl$

Continuous absorption from (850-220)nm. See "Photochemistry", Calvert & Pitts, p. 232(72).

(iv) The absorption coefficients for $CFCl_3$ and CF_2Cl_2 (freons) have been measured between 200 nm and 120nm. Doucet, Sauvagea, and Sandorfy, 1973(73). Molina and Rowland [77], 1974 have measured the absorption coefficients between 226nm and 186nm- their data is tabulated below:

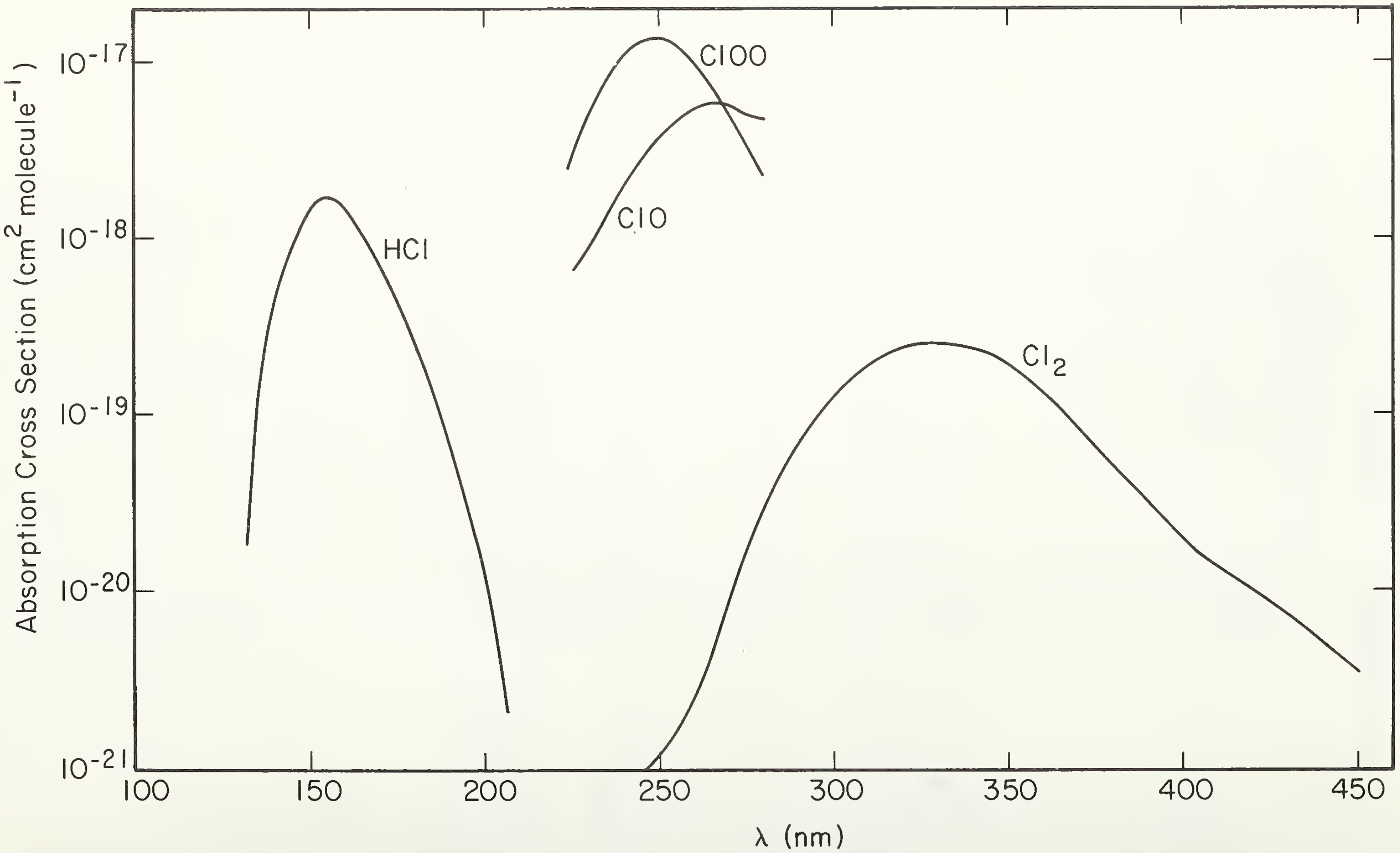
The Absorption Spectra of $CFCl_3$ and CF_2Cl_2.

$CFCl_3 + h\nu \longrightarrow CFCl_2 + Cl$

$CF_2Cl_2 + h\nu \longrightarrow CF_2Cl + Cl$

Molina and Rowland [77] (1974).

λnm	$10^{20} \times \sigma$ cm^2 molecule^{-1}	
	$CFCl_3$	CF_2Cl_2
226.0	0.9	-
223.5	1.3	-
221.0	1.8	-
218.6	3.4	-
216.2	5.1	-
213.9	8.0	0.3
211.6	12.5	0.7
209.4	18.5	1.4
207.3	25.0	1.8
205.1	34.5	3.1
203.0	46	4.9
201.0	59	7.2
199.0	73	11.3
197.0	89	16.4
195.1	113	24.5
193.2	137	34.5
191.4	164	49
189.6	197	66
187.8	227	87
186.0	241	91


Absorption Cross Section (cm^2 molecule^{-1})
10^{-17}
10^{-18}
10^{-19}
10^{-20}
10^{-21}
ClOO
ClO
HCl
Cl_2
100
150
200
250
300
350
400
450
λ (nm)

XBL 744-5990

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CHEMICAL KINETICS DATA SURVEY PUBLICATIONS

Chemical Kinetics Data Survey are listed below. Several of the Survey reports have been superseded by later issues. They are not listed, but are referred to in the citations of the current work.

a. "Photochemical and Rate Data for Twenty-eight Gas Phase Reactions: A Survey of the Data," R. F. Hampson, Ed., J. Phys. Chem. Ref. Data 2, No. 2, 267 (1973); These are slightly revised versions of data sheets originally distributed as NBS Reports 10692 and 10828.

b. "Chemical Kinetics Data Survey III. Selected Rate Constants for Chemical Reactions of Interest in Atmospheric Chemistry," NBS Report No. 10867 (1972), 48 p. D. Garvin and L. H. Gevantman *
Supersedes NBS Report 9884 (1968) which is out of print and out of date

c. "Chemical Kinetics Data Survey V. Sixty-six Contributed Rate and Photochemical Data Evaluations on Ninety-four Reactions," NBSIR 73-206 (1973), 115 p., D. Garvin, Ed., (National Technical Information Service, Springfield, Va. 22151, Order as COM-73-11262 $8.25 hard copy, $1.45 microfiche)

d. "Chemical Kinetics Data Survey VI. Photochemical and Rate Data for Twelve Gas Phase Reactions of Interest for Stratospheric Chemistry," NBSIR 73-207 (1973), 124 p., R. F. Hampson, Ed., (National Technical Information Service, Springfield, Va. 22151, Order as COM-73-11862 $4.50 hard copy, $1.45 microfiche)

e. "Chemical Kinetics Data Survey VII. Tables of Rate and Photochemical Data for Modelling of the Stratosphere (Revised)," NBSIR 74-430 (1974), 101 p., D. Garvin and R. F. Hampson, Ed., (National Technical Information Service, Springfield, Va. 22151, Order as COM-74-10724, $8.25 hard copy, $1.45 microfiche); Supersedes Part IV NBSIR 73-203 (1973)

f. "Chemical Kinetics Data Survey VIII. Rate Constants of ClO_x of Atmospheric Interest," NBSIR 74-516 (1974), 45 p., R. T. Watson

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* Available from: Chemical Kinetics Information Center
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15. SUPPLEMENTARY NOTES

16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

The quantitative data on reactions of chlorine atoms and the chlorine oxides are compiled. Preferred values for rate constants are given where possible. Optical absorption cross sections are given for the species that may photolyze in the atmosphere. The experimental techniques used to obtain the rate data are discussed.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)* Absorption cross sections; atmospheric chemistry; chemical kinetics; chlorine, chlorine dioxide; chlorine monoxide; data evaluation; gas phase; optical; rate constants; stratospheric chemistry

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