Rate Constants for Reactions of ClO_x of Atmospheric Interest

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Chemical kinetics measurements on 82 gas phase reactions of chlorine containing species are reviewed. Recommended rate constants are given. The principal species of interest are Cl, Cl_2, ClO, Cl_2O, ClOO, OClO, ClNO, HCl and halo derivatives of methane and ethane. Absorption spectra are given for 21 species. In addition the chemical kinetics methods used to obtain these data are discussed with regard to their applicability and reliability.

Key words: Absorption spectra; chemical kinetics; chlorine; data compilation and evaluation; chlorocarbon; chlorofluorocarbon; chlorine oxides; nitrosyl chloride; rate constant.

Contents

1. Introduction

The Chapman mechanism [1][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 fully halogenated methanes (i.e. $CFCl_3$, CF_2Cl_2). In addition, it is essential to include rate data for reactions involving chlorinated alkanes and alkenes, which may play an important role in atmospheric chemistry (e.g. CH_3Cl), with electronically excited O (^1D) atoms and HO radicals. 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 298 K and/or (whenever possible) the Arrhenius expression.

Rate data exist for most of the reactions which are thought to be of importance in the stratosphere, but unfortunately some of it was obtained only at 298 K, 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. $Cl + O_3 \rightarrow ClO + O_2$; $O + ClO \rightarrow Cl + O_2$; $NO + ClO \rightarrow NO_2 + Cl$; $Cl + CH_4 \rightarrow CH_3 + HCl$; $HO + HCl \rightarrow H_2O + Cl$ and $ClO + NO_2 + M \rightarrow ClONO_2 + M$. These six reactions have been the subject of numerous recent investigations and their rate constants have been reported as a function of temperature. However, further studies are required before the values can be considered to be well-established. See Addenda for recent results (includes all data on $ClONO_2$ formation).

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[1] Figures in brackets indicate literature references at the end of this paper.

2. Experimental Techniques

Many of the early published results on reactions such as $O + ClO \rightarrow Cl + O_2$; $O + OClO \rightarrow O_2 + ClO$; $Cl + OClO \rightarrow 2ClO$; $NO + OClO \rightarrow NO_2 + ClO$; and $NO + ClO \rightarrow NO_2 + Cl$; 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 modeler 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.

2.1. 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.

2.2. 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]:

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

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

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

It has been shown that $I_\lambda = I^\circ_\lambda[Cl]^n$, where I_λ represents the emission intensity at wavelength λ [12]. n_λ was shown to vary with λ, (i.e. $n_{520\,\text{nm}} = 1.7(M=Ar)$ and $n_{920\,\text{nm}} = 1.0\ (M=Ar)$) 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 of some early work which used this method [7] must be slightly modified (the reported rate constants are probably low by $\sim 2/n_\lambda \simeq 15\%$) as n_λ was taken to be 2, rather than 1.7 as later determined [12]. This method of monitoring Cl atom concentrations is moderately insensitive, but useful when [Cl] is $10^{13} - 10^{16}$ 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 surface with H_3PO_4 [111].

A study [93] of the $O(^3P) + HCl$ reaction used the NO_2^* chemiluminescence produced from the $O + NO + M$ reaction to monitor the decay of the oxygen atom concentration in the presence of a small concentration of NO, and a large excess concentration of HCl:

$$O(^3P) + NO + M \rightarrow NO_2^* + M,$$

$$NO_2^* \rightarrow NO_2 + h\nu\ (\lambda > 400\,\text{nm})\ [131],$$

$$\xrightarrow{M} NO_2 + M\ (\text{non-radiative}).$$

This technique is normally used to monitor fairly high concentrations of $O(^3P)$, (typically greater than 10^{12} atom cm^{-3}), and can only be used when the presence of NO does not adversely perturb the kinetic scheme.

2.3. 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, Cl_2) [19–25, 171], shock tube [175] (ClO, Cl_2) and molecular modulation [26, 27] (ClO, ClOO) 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 nm) $= 1.14 \times 10^{-17}$ cm^2 molecule^{-1} [28; 112]; 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 cm, resulting in a lower 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 300 K due to limited detection sensitivity [2]. When studies of the $O + OClO \rightarrow$

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[2] The numbering of reactions and rate constants in this introductory material matches that used in the tables.

ClO + O_2 [18, 19], and NO + OClO → 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 realized, its role in the overall mechanism of these reactions was not appreciated. This resulted in the value for k_{41} (O + OClO) being overestimated by two orders of magnitude. Rate constants for reactions 21 (O + ClO → Cl + O_2) and 22 (NO + ClO → NO_2 + Cl), which are of utmost importance in the stratosphere, were obtained by indirect methods whereby the O(^{3}P) and NO (in separate experiments) competitively reacted with ClO and OClO. The autocatalytic nature of the reaction mechanisms was not known and consequently the published values for k_{21} [18, 19] and k_{22} [16] must be rejected. The reaction mechanisms for the X + OClO reaction can be written, (X = O, NO)

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

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

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

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 energy of ~10 kJ mol^{-1} (~2.4 kcal mol^{-1}). Results using the high pressure flash photolysis technique 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 of 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 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.

$$\mathrm{ClO + ClO \underset{k_{13}}{\overset{k_{32}}{\rightleftarrows}} ClOO + Cl};\ K_1 = k_{32}/k_{13},$$

$$\mathrm{Cl + O_2 + M \underset{k_{40}}{\overset{k_3}{\rightleftarrows}} ClOO + M};\ K_2 = k_3/k_{40}.$$

Ozone was monitored spectrophotometrically at 253.7 nm in a study [98] of reactions between electronically excited oxygen atoms O (^{1}D), and a series of halogenated methanes (CX_nY_{4-n}; X=Cl, Y=F). The quantum yield for destruction of ozone ($-\Phi[O_3]$) indicated that one of the primary reaction products was ClO. By monitoring the [O_3] decay in the presence of various concentrations of molecular oxygen and halogenated alkanes, the relative rate constants for reaction with O (^{1}D) were obtained [(k(O (^{1}D) + O_2)/k(O (^{1}D) + Alkane)].

2.4. 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, 108]. 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 (the calibration is accurate to within ~10%). Typical lower 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 with 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 by-pass technique and/or by chemical scavenging.

Three mass spectrometric studies of the Cl + CH_4 reaction used similar samplying systems to the above [14, 157, 126]. The studies were 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. Several other reactions have been studied utilizing the mass spectrometric technique, including a series of reactions involving ClO radicals [17, 30, 108, 179] and Cl atoms [14, 126].

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 study yielded results in fair agreement with those obtained using chemiluminescence [32] and resonance flourescence [92] to monitor O atoms.

2.5. Resonance Fluorescence

The technique of atomic resonance fluorescence is both highly specific and sensitive, and thus, well-suited to the study of rapid reactions.

Discharge flow experiments have monitored the wavelength resolved fluorescent flux of the $Cl(3p^4 4s)^4P_{3/2} - (3p^5)^2P_{3/2}$ transition at 138.0 nm [5, 33, 122] and the $Cl(3p^4 4s)^2P_{3/2} - (3p^5)^2P_{3/2}$ transition at 134.7 nm [94, 122, 129, 172]. Wavelength resolution is normally only possible using the discharge flow technique where long time integrations of the signal can be utilized, and where the optical collection efficiency of the fluorescent signal is more easily optimized. This enables monitoring of the individual electronic transitions which suffer least from self-reversal, increasing the range of linearity between I_F (intensity of fluorescence) and atom concentration. Clyne et al. [5, 33, 122] showed that the fluorescent flux at 138.0 nm was linearly proportional to the concentration of $^2P_{3/2}$ chlorine atoms when $[Cl, {}^2P_{3/2}] \leq 10^{12}$ atom cm^{-3}. Their lower limit for detection of $^2P_{3/2}$ Cl atoms was reported to be $\leq 5 \times 10^{10}$ atom cm^{-3} [13], but later after system modification this value was reduced to $> 3 \times 10^9$ atom cm^{-3} [5]. Anderson et al. [94] have shown that the intensity of fluorescence at 134.7 nm is linearly proportional to $[Cl, {}^2P_{3/2}]$ when $[Cl] \leq 10^{11}$ atom cm^{-3}, and that their lower limit for detection of $^2P_{3/2}$ Cl atoms is $\sim 2 \times 10^9$ atom cm^{-3}, whereas Bemand and Clyne [122] observed that I_F was linearly proportional to [Cl] up to $\leq 3 \times 10^{11}$ atom cm^{-3} using the 134.7 nm transition. The oscillator strength of the 134.7 nm transition is significantly higher (factor of $\sim$35) [107], than that of the 138.0 nm transition, but Clyne et al. [5, 13] observed that the latter transition was, under their operating conditions of an optically thick plasma lamp with strongly self-reversed lines, as sensitive. The resonance lamp used by Anderson et al. [94] showed significantly less self-reversal as indicated by the fact that the 134.7 nm line was observed to be more sensitive than the 138.0 nm line.

Flash photolysis kinetic studies have monitored chlorine atom resonance fluorescence without wavelength resolution [34, 95, 113, 116, 173]. The lack of wavelength resolution imposes no serious problems assuming that, (a) the reaction mixture contains no other species (reactants, intermediates or products) which can fluoresce due to excitation by the Cl atom lamp; (b) the equilibrium concentration of low lying metastable $(3p^5)^2P_{1/2}$ Cl atoms (0.8%) do not react at a significantly different rate to the $^2P_{3/2}$ atoms. The early [34] flash photolysis results of Davis et al. show that when the chlorine atom concentration is in the range 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 $[Cl, {}^2P_{3/2,\,1/2}]$ when the latter was $\leq 10^{11}$ atom cm^{-3}, but it would be expected that I_F was linearly dependent when the atom concentration is in this region [35]. The more recent studies [95] indicate that the intensity of fluorescence, I_F, is linearly proportional to the Cl atom concentration under all experimental conditions, where [Cl] was typically $\leq 3 \times 10^{11}$ atom cm^{-3}, but on occasions as high as $\sim 10^{12}$ atom cm^{-3}, indicating the use of an optically thick lamp where the dominant fluorescence is due to the 138.0 nm transition.

Kinetic studies involving O (^3P) atoms have been performed using the discharge flow techniques [5, 92, 147]. The fluorescent emission used to monitor the concentration of O (^3P) atoms was that produced by the O $(2p^3 s)^3S_1 - (2p^4)^3P_0$ transition at 130.6 nm [5]. The lower limit of detection was reported to be $\sim 4 \times 10^9$ atom cm^{-3} and from this value to $\leq 5 \times 10^{12}$ atom cm^{-3} the intensity of fluorescence was found to be linearly proportional to the atom concentration. It has been shown [102] that the transition at 130.6 nm suffers from negligible self-reversal and that the range of linearity between I_F and $[O, {}^3P]$ exceeds that of the transition at 130.2 nm $[(2p^3 3s)^3S_1 - (2p^4)^3P_2]$. The kinetic study of the O + Cl_2 reaction [92] did not use wavelength resolution, but monitored the complete $(2p^3 3s)^3S_1 - (2p^4)^3P_{0,1,2}$ multiplet. $[O, {}^3P]$ was typically $\leq 5 \times 10^{11}$ atom cm^{-3}, and in this concentration range it has been shown [102] that I_F is linearly proportional to $[O, {}^3P]$. A flash photolysis study [168] of the O (^3P) + HCl reaction used resonance fluorescence to monitor O (^3P).

Hydroxyl radicals have been monitored in both discharge flow [36, 96, 130, 170] and static systems [103, 104, 109, 115, 123, 127, 136, 168] using the emission produced at 309 nm, the band head of the $A\,^2\Sigma \rightarrow X\,^2\Pi$ (0–0) transition. 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 $[HO]_0 \leq 10^{12}$ radical cm^{-3}, the only process removing HO radicals in a discharge flow system, 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]. In a flash photolysis system the two processes removing HO radicals are both kinetically first order, (a) reaction with the added reagent, and (b) diffusion out of the reaction zone. However, there is no difficulty involved in allowing exactly for the diffusion process. Both the discharge flow, [36, 96, 130] and the flash photolysis [104, 109, 115, 123, 127, 136] studies used flowing resonance lamps to excite ground state HO radicals. One study [103] used a static cell whereby steady state concentrations of HO radicals were produced, where the exact steady state concentration of HO was governed by the concentration of the reagent which was added to the cell. Thus relative rate constants were obtained by monitoring relative [HO] using laser induced fluorescence. The ground state HO radical was excited from a specific rotational level via the (1,0) Q_1 (2) transition. Fluorescence due to both the (1,1) and (0,0) transitions at (310 ± 10) nm was detected.

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 quantitative 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 resonance discharge lamp.

Calibration of the fluorescent flux intensity is normally achieved by producing known concentrations of atoms, either photolytically (flash photolysis) or by use of a stoichiometric reaction (discharge flow) and observing the fluorescent flux produced. This is much easier using the discharge flow technique where the relationship between the fluorescent flux and the atom or radical concentration can be determined to within an accuracy of ± 10% (dependent upon how well gas flow rates can be calibrated). The flash photolysis technique is difficult to calibrate to better than a factor of 2–3. For an accurate calibration the following are required: (a) the wavelength distribution of the flux from the flash lamp, (b) the absolute extinction coefficient of both the actinic gas, and the gaseous precursor of the atoms or radicals, as a function of wavelength, (c) cell geometry (with respect to irradiation and collection efficiency). Laser flash photolysis has two distinct advantages over conventional flash photolysis, where a N_2 spark discharge lamp is used for the photolytic production of transients; (a) accurate calibration of transients is easier as λ, and therefore σ_λ (absorber), and photolysis flux (laser energy) can be measured accurately, and (b) indiscriminate photolysis of added reagents can be minimised, thus eliminating the complication of secondary kinetic processes induced by photolytically produced radicals.

2.6. 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 normally of limited use in the study of rapid bimolecular reactions ($k > 10^{-12}$ cm^3 molecule^{-1} s^{-1}), where pseudo 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], where typical initial concentrations of HO radicals were $\sim 10^{13}$ radical cm^{-3}. A recent study of the Cl + O_3 reaction [105] monitored the chlorine atom concentration, in a discharge flow system, via the $(3p^4 4s)\,^2P_{3/2} - (3p^5)\,^2P_{3/2}$ transition at 134.7 nm. The minimum detectable concentration of Cl($^2P_{3/2}$) atoms was $\sim 10^{10}$ atom cm^{-3}. This excellent sensitivity was obtained by using an unreversed resonance emission line with a high oscillator strength (0.114). Resonance Absorption has been used to monitor O(^{3}P) atoms in a study of the O + ClO reaction [129]. Absolute concentrations of O(^{3}P) were required in this study where k_{21} (O + ClO) was measured relative to k_1(Cl + O_3). Absolute rate constants for O (^{1}D) atoms have been reported [176] using flash photolysis-resonance absorption. A modified form of the Beer-Lambert law was used, where γ has recently been shown to be questionable [177] on theoretical grounds. In both discharge flow and flash photolysis studies wavelength resolution is highly advantageous and in some cases essential, e.g. to study the individual rate constants for $^2P_{1/2}$ and $^2P_{3/2}$ halogen atom reactions. Quenching reactions of $^2P_{1/2}$ chlorine atoms have been studied [180] utilizing the flash photolysis technique in conjunction with resonance absorption.

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 ($\sim$1–5 torr) [29]. Both studies were performed in a discharge flow apparatus and monitored the concentration of $^2P_{3/2}$ chlorine atoms at $\lambda = 138.0$ nm (Cl$(3p^4 4s)\,^4P_{3/2} - (3p^5)\,^2P_{3/2}$). The lower limit of detection was $\geq 2 \times 10^{12}$ atom cm^{-3}. Nitric oxide was also monitored in the former study [40] $\lambda = 180$ nm (1-0 transition of NO, $\varepsilon - D^2\,\Sigma^+ - X^2\,\Pi_{1/2}$), in which the lower limit of sensitivity was reported to be $\geq 5 \times 10^{13}$ 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 and the source temperature 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].

2.7. Electron Paramagnetic Resonance Spectrometry

Five kinetic studies have used e.p.r. in conjunction with the discharge flow technique. The decay of ground state

(^3P) oxygen atoms was monitored by following the intensity of their e.p.r. spectrum in the presence of excess HCl [45], and Cl_2 [106]. In both of these studies Cl atoms were observed by e.p.r. as a reaction product. The Cl + H_2 reaction was studied [88] by monitoring both the decay of chlorine atoms and the production of hydrogen atoms. In addition, there have been two studies of the H + HCl reaction [88, 128], where the decay of atomic hydrogen has been monitored in the presence of a large excess concentration of HCl. One study, [128] observed that the reaction stoichiometry, $[H]_{\text{removed}}/[Cl]_{\text{produced}}$, was dependent upon how the flow reactor walls had been treated. 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 2–5 × 10^{11} molecule cm^{-3}. The sensitivity of this technique for monitoring atoms is similar to that of atomic resonance absorption, and as such is of limited use for the study of bimolecular reactions whose rate constants are in excess of 10^{-12} cm^3 molecule $^{-1}$ s^{-1}.

2.8. 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 certain 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 IR 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}).

The kinetic behavior of $O(^1D)$ atoms with a series of halogenated compounds was investigated [99] by monitoring the relative consumption of halocarbon, CF_xCl_y, and N_2O ($\Delta[CF_xCl_y]/\Delta[N_2O]$) as a function of $[CF_xCl_y]/[N_2O]$ using IR Spectroscopy. Rate constants for $O(^1D)$ + CF_xCl_y were obtained relative to $O(^1D)$ + N_2O, and were then placed on an absolute basis using a literature value for k ($O(^1D)$ + N_2O).

2.9. Laser Magnetic Resonance

A series of reactions between hydroxyl radicals and hydrogen containing halogenated alkanes and alkenes was studied in a discharge flow system using the technique of laser magnetic resonance to monitor hydroxyl radicals [101, 110, 124]. This technique is extremely sensitive and enables low initial ($<10^{12}$ radical cm^{-3} concentrations of hydroxyl radicals to be used thus eliminating kinetic complications due to the bimolecular disproportionation reaction (HO + HO → H_2O + H). A lower limit of $\sim 10^8$ radical cm^{-3} has been reported. The calibration procedure is both simple and accurate and can be performed in a manner similar to that for resonance fluorescence.

2.10. Miscellaneous Techniques

Some studies have been 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. Some studies [43, 44] involved complex kinetic schemes and the results must be regarded as inferior to the more recent direct determinations.

3. Errors and Uncertainty Limits

The difficulty in assigning reliability limits to the rate data is that the preferred value is often 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 $\sim \pm 25\%$ 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 were obtained from single measurements were performed using the discharge flow technique.

3.1. 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 (5–10%) in the measured rate constants. Systematic errors may also arise if, (1) the concentration profile is parabolic, rather than plug, and (2) axial diffusion is significant. As the rate of radial diffusion increases, the concentration profile of trace reactants becomes more uniform across the cross-section of the flow reactor and therefore tends towards that of plug flow, but the problem of axial diffusion increases. A recent paper [48] has calculated the magnitude of the possible errors introduced into the determination of rate constants if the concentration profile is parabolic and plug flow has been assumed. The magnitude of the error is dependent 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 jets act to disturb laminar flow and break up the parabolic velocity distribution, i.e. the profile tends towards plug flow. 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 produce an error of $\sim 25\%$.

3.2. 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 partial 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 modern detection techniques, such as atomic resonance fluorescence, have led towards the elimination of secondary reactions in most chemical systems. 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. The static cell technique suffers in accuracy if the added reagent is unstable on the reactor walls, i.e. H_2O_2 and O_3. Compounds such as these may decompose, and even with care (by minimizing decomposition, and allowing for it quantitatively) this may provide a source of error. Precautions also have to be taken to minimize photolysis of the reagent which can lead to complicating secondary photolysis reactions.

4. Units and Arrangements of Tables

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

The numbered rate constants referred to in the introduction are keyed to the Summary of Rate and Photochemical Data. This, in turn is an index to the detailed discussions of each process. Table 2, which follows immediately, identifies the processes that have been studied using each technique.

5. Summary of Rate and Photochemical Data

The following table presents a set of preferred rate constants for reactions (1)–(71), however, the more detailed discussion contained in the text should be consulted before using these values, as there often are reservations concerning their reliability. Upper limits are given for information only, but should not be taken as recommended values. The numbering of reactions and rate constants in this list of contents matches that used in the tables. Reactions (72)–(92) are photo-processes. Absorption spectra for them are discussed in the notes. The Addenda contains recent data obtained for reactions (1)–(71), and data for a few reactions not previously discussed (A1)–(A7).

TABLE 1. Summary table of preferred values

	Reaction	Preferred rate constant cm^3 molecule^{-1} s^{-1}	Temperature range (K)
(1)	$Cl + O_3 \rightarrow ClO + O_2$	$(2.7 \pm 1.2) \times 10^{-11} \exp(-(257 \pm 106)/T)$	205–298
(2)	$Cl + OClO \rightarrow 2\ ClO$	$(5.9 \pm 0.9) \times 10^{-11} \exp(-(0 \pm 120)/T)$	298–588
(3)	$Cl + O_2 + M \rightarrow ClOO + M$	no recommendation, see notes	
(4)	$Cl + CH_4 \rightarrow CH_3 + HCl$	$7.29 \times 10^{-12} \exp(-(1260 \pm 55)/T)$	200–299
(5)	$Cl + H_2 \rightarrow H + HCl$	$3.5 \times 10^{-11} \exp(-2290/T)$	200–300
(6)	$Cl + C_2H_6 \rightarrow C_2H_5 + HCl$	$(7.3 \pm 1.2) \times 10^{-11} \exp(-(61 \pm 44)/T)$	222–322
(7)	$Cl + H_2O_2 \rightarrow HO_2 + HCl$	$1.7 \times 10^{-12} \exp(-384/T)$	265–400
(8)	$Cl + HO_2 \rightarrow O_2 + HCl$	3×10^{-11}	298
(9)	$Cl + CH_3Cl \rightarrow CH_2Cl + HCl$	$(3.4 \pm 0.8) \times 10^{-11} \exp(-(1256 \pm 62)/T)$	233–350
(10)	$Cl + CH_2Cl_2 \rightarrow CHCl_2 + HCl$	$(5.2 \pm 2.2) \times 10^{-13}$	298
(11)	$Cl + CHCl_3 \rightarrow CCl_3 + HCl$	$(1.23 \pm 0.34) \times 10^{-13}$	298
(12)	$Cl + ClOO \rightarrow Cl_2 + O_2$	no recommendation, see notes	298
(13)	$Cl + ClOO \rightarrow 2\ ClO$	no recommendation, see notes	298
(14)	$Cl + Cl_2O \rightarrow Cl_2 + ClO$	6.8×10^{-13}	300
(15)	$Cl + NO + N_2 \rightarrow ClNO + N_2$	$(1.1 \pm 0.2) \times 10^{-31}$	293
(16)	$Cl + NO + O_2 \rightarrow ClNO + O_2$	$(1.3 \pm 0.3) \times 10^{-31}$	293
(17)	$Cl + ClNO \rightarrow Cl_2 + NO$	$(3.0 \pm 0.5) \times 10^{-11}$	298
(18)	$Cl + NO_2 + M \rightarrow ClNO_2 + M$	7.2×10^{-31}	298
(19)	$Cl + ClNO_2 \rightarrow Cl_2 + NO_2$	$>>3 \times 10^{-14}$	298
(20)	$Cl + Cl + Ar \rightarrow Cl_2 + Ar$	$6.32 \times 10^{-34} \exp((903 \pm 55)/T)$	195–514
(21)	$O(^3P) + ClO \rightarrow Cl(^2P_{3/2})$ $+ O_2^* (^1\Sigma, ^1\Delta)$	$(1.07 \pm 0.15) \times 10^{-10} \exp(-(224 \pm 38)/T)$	220–425
(22)	$NO(^2\Pi) + ClO \rightarrow NO_2 + Cl(^2P_{3/2})$	$(8.0 \pm 1.5) \times 10^{-12} \exp(+(250 \pm 50)/T)$	220–298
(23)	$ClO + CO \rightarrow CO_2 + Cl(^2P_{3/2})$	$\leq 1.7 \times 10^{-15}$	587
(24)	$ClO + O_3 \rightarrow ClOO + O_2$ $\rightarrow OClO + O_2$	$< 5 \times 10^{-15}$	298
(25)	$ClO + H_2 \rightarrow$ Products	$\leq 8 \times 10^{-16}$	670
(26)	$ClO + CH_4 \rightarrow$ Products	$\sim 4 \times 10^{-15}$	670
(27)	$ClO + C_2H_4 \rightarrow$ Products	$\leq 5 \times 10^{-16}$	670
(28)	$ClO + C_2H_2 \rightarrow$ Products	$\leq 5 \times 10^{-16}$	670
(29)	$ClO + N_2O \rightarrow$ Products	$\leq 7 \times 10^{-16}$	587
(30)	$ClO + NH_3 \rightarrow$ Products	$\leq 5 \times 10^{-16}$	670
(31)	$ClO + ClO \rightarrow Cl + OClO$	$\leq 3.2 \times 10^{-15}$	298
(32)	$ClO + ClO \rightarrow Cl + ClOO$ $\rightarrow Cl_2 + O_2$	$1.53 \times 10^{-12} \exp(-(1238 \pm 120)/T)$	273–710
(33)	$ClO + ClO + M \rightarrow Cl_2 + O_2 + M$	no recommendation, see notes	
(34)	$ClO + BrO \rightarrow Br + Cl + O_2$	$(6.7 \pm 1.0) \times 10^{-12}$	300
(35)	$ClO + BrO \rightarrow OClO + Br$	$(6.7 \pm 1.0) \times 10^{-12}$	300
(36)	$Br + OClO \rightarrow BrO + ClO$	see notes	300
(37)	$O + Cl_2 \rightarrow ClO + Cl$	$(4.2^{-0.4}_{+0.8}) \times 10^{-13}$	174–602
(38)	$OH + HCl \rightarrow H_2O + Cl$	$(4.15 \pm 1.9) \times 10^{-12} \exp(-(1368 \pm 134)/T)$	220–300
(39)	$O + HCl \rightarrow OH + Cl$	$2.96 \times 10^{-12} \exp(-(425 + 50)/T)$	293–718
(40)	$ClOO + M \rightarrow Cl + O_2 + M$	$1.14 \times 10^{-11} \exp(-(3370 \pm 350)/T)$	
(41)	$O + OClO \rightarrow ClO + O_2$	$(5^{+1}_{-2}) \times 10^{-13}$	300
(42)	$NO + OClO \rightarrow NO_2 + ClO$	$(3.4 \pm 0.5) \times 10^{-13}$	300
(43)	$N + OClO \rightarrow NO + ClO$	$\leq 6 \times 10^{-13}$	300
(44)	$H + OClO \rightarrow OH + ClO$	$(5.7 \pm 1.2) \times 10^{-11}$	300
(45)	$O + Cl_2O \rightarrow ClO + ClO$	$(1.4 \pm 0.2) \times 10^{-11}$	300
(46)	$O(^1D) + CCl_4 \rightarrow CCl_3 + ClO$	3.54×10^{-10}	298
(47)	$O(^1D) + CFCl_3 \rightarrow CFCl_2 + ClO$	2.44×10^{-10}	298
(48)	$O(^1D) + CF_2Cl_2 \rightarrow CF_2Cl + ClO$	2.12×10^{-10}	298
(49)	$O(^1D) + CF_3Cl \rightarrow CF_3 + ClO$	0.86×10^{-10}	298
(50)	$O(^1D) + C_2F_4Cl_2 \rightarrow C_2F_4Cl + ClO$	1.36×10^{-10}	296
(51)	$O(^1D) + CHF_2Cl \rightarrow$ Products	1.45×10^{-10}	296
(52)	$O(^1D) + C_2F_3Cl_3 \rightarrow C_2F_3Cl_2 + ClO$	2.26×10^{-10}	296
(53)	$OH + CH_3Cl \rightarrow CH_2Cl + H_2O$	$(2.18 \pm 0.5) \times 10^{-12} \exp(-(1142 \pm 67)/T)$	240–422
(54)	$OH + CH_2Cl_2 \rightarrow CHCl_2 + H_2O$	$(4.3 \pm 0.6) \times 10^{-12} \exp(-(1094 \pm 81)/T)$	245–375
(55)	$OH + CHCl_3 \rightarrow CCl_3 + H_2O$	$(4.69 \pm 0.71) \times 10^{-12} \exp(-(1134 \pm 107)/T)$	245–375
(56)	$OH + CH_2ClF \rightarrow CHClF + H_2O$	$(2.84 \pm 0.3) \times 10^{-12} \exp(-(1259 \pm 50)/T)$	245–375
(57)	$OH + CHF_2Cl \rightarrow CF_2Cl + H_2O$	$(1.21 \pm 0.17) \times 10^{-12} \exp(-(1648 \pm 75)/T)$	250–434
(58)	$OH + CHFCl_2 \rightarrow CFCl_2 + H_2O$	$(1.59 \pm 0.2) \times 10^{-12} \exp(-(1204 \pm 70)/T)$	245–423
(59)	$OH + CFCl_3 \rightarrow$ Products	$< 5 \times 10^{-16}$	294–434
(60)	$OH + CF_2Cl_2 \rightarrow$ Products	$< 5 \times 10^{-16}$	294–434
(61)	$OH + C_2H_5Cl \rightarrow C_2H_4Cl + H_2O$	$(3.9 \pm 0.7) \times 10^{-13}$	298

TABLE 1. Summary table of preferred values—Continued

	Reaction	Preferred rate constant cm^3 $molecule^{-1}$ s^{-1}	Temperature range (K)
(62)	$OH + CH_2ClCH_2Cl \rightarrow CH_2ClCHCl + H_2O$	$(2.2 \pm 0.5) \times 10^{-13}$	298
(63)	$OH + CHCl_2CH_3 \rightarrow C_2H_3Cl_2 + H_2O$	$(2.6 \pm 0.6) \times 10^{-13}$	298
(64)	$OH + CH_3CCl_3 \rightarrow CH_2CCl_3 + H_2O$	$(3.72 \pm 0.4) \times 10^{-12} \exp(-(1627 \pm 50)/T)$	260–375
(65)	$OH + CH_3CF_2Cl \rightarrow CF_2ClCH_2 + H_2O$	$(1.15 \pm 0.15) \times 10^{-12} \exp(-(1748 \pm 30/T)$	273–375
(66)	$OH + CH_2ClCF_3 \rightarrow CHClCF_3 + H_2O$	$(1.05 \pm 0.23) \times 10^{-14}$	298
(67)	$OH + CF_2ClCF_2Cl \rightarrow$ Products	$< 5 \times 10^{-15}$	298
(68)	$OH + CFCl_2CF_2Cl \rightarrow$ Products	$< 3 \times 10^{-16}$	298
(69)	$OH + CH_2CHCl \xrightarrow{M} CH_2CHClOH$	$\sim 5.8 \times 10^{-12}$	298
(70)	$OH + CCl_2CCl_2 \xrightarrow{M} CCl_2CCl_2OH$	1.55×10^{-13}	298
(71)	$OH + CHClCCl_2 \xrightarrow{M} CHClCCl_2OH$	$(5.2 \pm 0.9) \times 10^{-13} \exp(+(450 \pm 50)/T)$	234–357
(72)	$Cl_2 + h\nu \rightarrow 2\ Cl$	absorption spectrum, see notes	
(73)	$HCl + h\nu \rightarrow H + Cl$	absorption spectrum, see notes	
(74)	$ClOO + h\nu \rightarrow ClO + O(^1D, ^3P)$	absorption spectrum, see notes	
(75)	$ClO + h\nu \rightarrow Cl(^2P_{3/2, 1/2}) + O(^1D, ^3P)$	absorption spectrum, see notes	
(76)	$CFCl_3 + h\nu \rightarrow CFCl_2 + Cl$	absorption spectrum, see notes	
(77)	$CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl$	absorption spectrum, see notes	
(78)	$CCl_4 + h\nu \rightarrow CCl_3 + Cl$	absorption spectrum, see notes	
(79)	$CH_3Cl + h\nu \rightarrow CH_3 + Cl$	absorption spectrum, see notes	
(80)	$CHCl_2F + h\nu \rightarrow CHClF + Cl$	absorption spectrum, see notes	
(81)	$CHClF_2 + h\nu \rightarrow CHF_2 + Cl$	absorption spectrum, see notes	
(82)	$CH_2ClF + h\nu \rightarrow CH_2F + Cl$	absorption spectrum, see notes	
(83)	$CH_3CCl_3 + h\nu \rightarrow CH_3CCl_2 + Cl$	absorption spectrum, see notes	
(84)	$C_2F_4Cl_2 + h\nu \rightarrow C_2F_4Cl + Cl$	absorption spectrum, see notes	
(85)	$C_2F_5Cl + h\nu \rightarrow C_2F_5 + Cl$	absorption spectrum, see notes	
(86)	$COFCl + h\nu \rightarrow COF + Cl$	absorption spectrum, see notes	
(87)	$COCl_2 + h\nu \rightarrow COCl + Cl$	absorption spectrum, see notes	
(88)	$ClNO_3 + h\nu \rightarrow$ Products	absorption spectrum, see notes	
(89)	$OClO + h\nu \rightarrow ClO + O(^1D, ^3P)$	absorption spectrum, see notes	
(90)	$ClNO + h\nu \rightarrow Cl + NO$	absorption spectrum, see notes	
(91)	$HOCl + h\nu \rightarrow$ Products	absorption spectrum, see notes	
(92)	$Cl_2O + h\nu \rightarrow Cl + ClO$	absorption spectrum, see notes	
(A1)	$ClO + NO_2 + M \rightarrow ClONO_2 + M$	$5.1 \times 10^{-33} \exp(+1030/T)$; $M = N_2$	250–417
(A2)	$OH + CF_3CHCl_2 \rightarrow CF_3CCl_2 + H_2O$	$1.24 \times 10^{-12} \exp(-1056/T)$	245–375
(A3)	$OH + CHClFCF_3 \rightarrow CFClCF_3 + H_2O$	$5.25 \times 10^{-13} \exp(-1191/T)$	250–375
(A4)	$OH + CH_2ClCF_2Cl \rightarrow CHClCF_2Cl + H_2O$	$1.87 \times 10^{-12} \exp(-1351/T)$	250–350
(A5)	$Cl + HNO_3 \rightarrow HCl + NO_3$	$(6.8 \pm 3.4) \times 10^{-15}$	295
(A6)	$Cl(^2P_{1/2}) + CCl_4 \rightarrow Cl(^2P_{3/2}) + CCl_4$	5×10^{-11}	298
	$+ CF_3Cl \rightarrow Cl(^2P_{3/2}) + CF_3Cl$	2.5×10^{-13}	298
	$+ HCl \rightarrow Cl(^2P_{3/2}) \rightarrow HCl$	$\sim 6 \times 10^{-12}$	298
	$+ H_2 \rightarrow Cl(^2P_{3/2}) + H_2$	7×10^{-12}	298
	$+ H \rightarrow Cl(^2P_{3/2}) + H$	$\sim 7 \times 10^{-10}$	287
(A7)	$H + Cl_2 \rightarrow HCl + Cl$	$1.45 \times 10^{-10} \exp(-590/T)$	250–750

TABLE 2. Rate constant measurements categorized by direct analytical techniques. The kinetic methods and references are given for each study. D.F. = discharge flow, F.P. = flash photolysis, M.M. = molecular modulation, S.T. = shock tube S.R. = static reactor.

Utraviolet spectroscopy

k_1 (Cl + O_3); D.F. [15]
k_2 (Cl + OClO); F.P. [21]
k_2 (Cl + OClO); D.F. [15]
k_3 (Cl + O_2 + M); F.P. [22]
k_{12} (Cl + ClOO); M.M. [26]
k_{13} (Cl + ClOO); M.M. [26]
k_{12}/k_{13}; F.P. [22]
k_{14} (Cl + Cl_2O); F.P. [20]
k_{14} (Cl + Cl_2O); F.P. [23]
k_{20} (Cl + Cl + M); F.P. [171]
k_{21} (O + ClO); S.T. [175]
k_{21} (O + ClO); F.P. [19]
k_{21} (O + ClO); D.F. [18]
k_{22} (NO + ClO); D.F. [16]
k_{23} (ClO + CO); D.F. [17]
k_{23} (ClO + CO); M.M. [27]
k_{24} (ClO + O_3); D.F. [15]
$k_{24'}$ (ClO + O_3); D.F. [15]
k_{24} (ClO + O_3); S.R. [114]
$k_{24'}$ (ClO + O_3); S.R. [114]
k_{25} (ClO + H_2); D.F. [17]
k_{25} (ClO + H_2); D.F. [15]
k_{26} (ClO + CH_4); D.F. [17]
k_{27} (ClO + C_2H_4); D.F. [17]
k_{28} (ClO + C_2H_2); D.F. [17]
k_{29} (ClO + N_2O); D.F. [17]
k_{30} (ClO + NH_3); D.F. [17]
$k_{32,32'}$ (ClO + ClO); F.P. [24]
$k_{32,32'}$ (ClO + ClO), F.P. [25]
$k_{32,32'}$ (ClO + ClO); F.P. [23]
$k_{32,32'}$ (ClO + ClO); D.F. [18]
$k_{32,32'}$ (ClO + ClO); D.F. [15]
$k_{32'}$ (ClO + ClO); M.M. [26]
$k_{32,32'}$ (ClO + ClO); D.F. [56]
$k_{32,32'}$ (ClO + ClO), F.P. [19]
$k_{32,32'}$ (ClO + ClO); F.P. [20]
$k_{32,32'}$ (ClO + ClO); D.F. [17]
k_{33} (ClO+ClO+M); M.M. [26]
k_{33} (ClO + ClO + M); D.F. [17]
k_{34} (ClO + BrO); F.P. [21]
k_{36} (Br + OClO); D.F. [121]
k_{41} (O + OClO); F.P. [21]
k_{41} (O + OClO); D.F. [18]
k_{42} (NO + OClO); D.F. [16]
k_{45} (O + Cl_2O); F.P [19]

Mass spectrometry

k_1 (Cl + O_3); D.F. [126]
k_1 (Cl + O_3); D.F. [30]
k_2 (Cl + OClO); D.F. [5]
k_4 (Cl + CH_4); D.F. [14]
k_4 (Cl + CH_4); D.F. [126]
k_4 (Cl + CH_4); D.F. [131]
k_7 (Cl + H_2O_2); D.F. [126]
k_8 (Cl + HO_2); D.F. [126]
k_9 (Cl + CH_3Cl); D.F. [14]
k_{10} (Cl + CH_2Cl_2); D.F. [14]
k_{11} (Cl + $CHCl_3$); D.F. [14]
k_{21} (O + ClO); D.F. [5]
k_{21} (O + ClO); D.F. [55]
k_{22} (NO + ClO); D.F. [30]
k_{23} (ClO + CO); D.F. [17]
k_{24} (ClO + O_3); D.F. [29]
$k_{24'}$ (ClO + O_3); D.F. [29]
k_{25} (ClO + H_2); D.F. [17]
k_{26} (ClO + CH_4); D.F. [17]
k_{27} (ClO + C_2H_4); D.F. [17]
k_{28} (ClO + C_2H_2); D.F. [17]
k_{29} (ClO + N_2O); D.F. [17]
k_{30} (ClO + NH_3); D.F. [17]
k_{31} (ClO + ClO); D.F. [29]
$k_{32,32'}$ (ClO + ClO); D.F. [29]
$k_{33}/k_{32,32'}$; M.M. [57]
k_{34} (ClO + BrO); D.F. [108]
k_{35} (ClO + BrO); D.F. [108]
k_{36} (Br + OClO); D.F. [108]
k_{37} (O + Cl_2); D.F. [31]
k_{38} (OH + HCl); S.R. [58]
k_{39} (O + HCl); S.R. [58]
k_{41} (O + OClO); D.F. [5]
k_{42} (NO + OClO); D.F. [5]
k_{43} (N + OClO); D.F. [59]
k_{44} (H + OClO); D.F. [5]
k_{45} (O + Cl_2O); O.F. [55]
k_{A1} (ClO+NO_2+M); D.F. [179]
k_{A5} (Cl + HNO_3); D.F. [126]

TABLE 2. Rate constant measurements categorized by direct analytical techniques. The kinetic methods and references are given for each sudy. D.F. = discharge flow, F.P. = flash photolysis, M.M. = molecular modulation, S.T. = shock tube S.R. = static reactor.—Continued

Resonance fluorescence

k_1 (Cl + O_3); F.P. [95]
k_1 (Cl + O_3); D.F. [94]
k_1 (Cl + O_3); F.P. [113]
k_2 (Cl +OClO); D.F. [5]
k_4 (Cl + CH_4); F.P. [95]
k_4 (Cl + CH_4); F.P. [34]
k_4 (Cl + CH_4); F.P. [173]
k_4 (Cl + CH_4); D.F. [172]
k_5 (Cl + H_2); F.P. [34]
k_5 (Cl + H_2); F.P. [116]
k_6 (Cl + C_2H_6); F.P. [34]
k_6 (Cl + C_2H_6); F.P. [116]
k_6 (Cl + C_2H_6); F.P. [173]
k_7 (Cl + H_2O_2); F.P. [95]
k_9 (Cl + CH_3Cl); F.P. [116]
k_9 (Cl + CH_3Cl); F.P. [173]
k_{10} (Cl + CH_2Cl_2); F.P. [116]
k_{10} (Cl + CH_2Cl_2); F.P. [34]
k_{11} (Cl + $CHCl_3$); F.P. [116]
k_{17} (Cl + ClNO); D.F. [33]
k_{21} (O + ClO); D.F. [5]
k_{21} (O + ClO); D.F. [129]
k_{21} (O + ClO); D.F. [147]
k_{22} (NO + ClO); D.F. [129]
k_{37} (O +Cl_2); D.F. [92]
k_{38} (OH + HCl); D.F. [36]
k_{38} (OH + HCl); F.P. [109]
k_{38} (OH + HCl); F.P. [168]
k_{39} (O + HCl); F.P. [168]
k_{41} (O + OClO); D.F. [5]
k_{53} (OH +CH_3Cl); F.P. [104]
k_{53} (OH +CH_3Cl); F.P. [127]
k_{54} (OH + CH_2Cl_2); F.P. [104]
k_{54} (OH + CH_2Cl_2); F.P. [127]
k_{55} (OH + $CHCl_3$); F.P. [104]
k_{56} (OH + CH_2ClF); F.P. [123]
k_{57} (OH + CHF_2Cl); F.P. [123]
k_{57} (OH + CHF_2Cl); F.P. [115]
k_{57} (OH + CHF_2Cl); D.F. [170]
k_{58} (OH +$CHFCl_2$); F.P. [123]
k_{58} (OH +$CHFCl_2$); F.P. [127]
k_{58} (OH +$CHFCl_2$); D.F. [170]
k_{59} (OH + $CFCl_3$); F.P. [115]
k_{60} (OH + CF_2Cl_2); F.P. [115]
k_{64} (OH + CH_3CCl_3); F.P. [123]
k_{64} (OH + CH_3CCl_3); D.F. [170]
k_{65} (OH + CH_3CF_2Cl); F.P. [123]
k_{68} (OH +$CF_2ClCFCl_2$); F.P. [123]
k_{70} (OH + C_2Cl_4); F.P. [136]
k_{71} (OH + C_2HCl_3); F.P. [136]
k_{71} (OH + C_2HCl_3); D.F. [130]
k_{A1} (ClO + NO_2 + M); D.F. [172]
k_{A2} (OH + CF_3CHCl_2); F.P. [169]
k_{A3} (OH + $CHClFCF_3$); F.P. [169]
k_{A4} (OH + CH_2ClCF_2Cl); F.P. [169]

Laser magnetic resonance

k_{53} (OH + CH_3Cl); D.F. [101]
k_{54} (OH + CH_2Cl_2); D.F. [101]
k_{55} (OH + $CHCl_3$); D.F. [101]
k_{56} (OH + CH_2ClF); D.F. [101]
k_{57} (OH + CHF_2Cl); D.F. [101]
k_{58} (OH + $CHFCl_2$); D.F. [101]
k_{61} (OH + C_2H_5Cl); D.F. [124]
k_{62} (OH + CH_2ClCH_2Cl); D.F. [124]
k_{63} (OH + $CHCl_2CH_3$); D.F. [124]
k_{64} (OH + CH_3CCl_3); D.F. [124]
k_{65} (OH + CH_3CF_2Cl); D.F. [124]
k_{66} (OH + CH_2ClCF_3); D.F. [124]
k_{67} (OH +CF_2ClCF_2Cl); D.F. [124]
k_{68} (OH + $CFCl_2CF_2Cl$); D.F. [124]
k_{69} (OH + CH_2CHCl); D.F. [110]
k_{70} (OH + C_2Cl_4); D.F. [110]
k_{A2} (OH + CF_3CHCl_2); D.F. [124]
k_{A3} (OH + $CHClFCF_3$); D.F. [124]

Calorimetric probe

k_{20} (Cl + Cl + Ar); D.F. [6]
k_5 (Cl + H_2); D.F. [88]
k_{-5} (H + HCl); D.F. [88]
k_{-5} (H + HCl); D.F. [128]
k_{37} (O + Cl_2); D.F. [106]
k_{38} (OH + HCl); D.F. [46]
k_{39} (O + HCl); D.F. [45]

Resonance absorption

k_1 (Cl + O_3); D.F. [105]
k_{17} (Cl + ClNO); D.F. [40]
k_{21} (O + ClO); D.F. [129]
$k_{32'}$ (ClO + ClO); D.F. [29]
k_{38} (OH + HCl); F.P. [39]
k_{47} ($O(^1D)$ + $CFCl_3$); F.P. [176]
k_{48} ($O(^1D)$ + CF_2Cl_2); F.P. [176]
k_{A6} (Cl, $^2P_{1/2}$ + M); F.P. [180]

TABLE 2. Rate constant measurements categorized by direct analytical techniques. The kinetic methods and references are given for each study. D.F. = discharge flow, F.P. = flash photolysis, M.M. = molecular modulation, S.T. = shock tube S.R. = static reactor.—Continued

Emission spectroscopy

k_3 ($Cl + O_2 + M$); D.F. [11]
k_3 ($Cl + O_2 + M$); D.F. [15]
k_{-5} ($H + HCl$); D.F. [87]
k_{15} ($Cl + NO + N_2$); D.F. [7]
k_{16} ($Cl + NO + O_2$); D.F. [7]
k_{18} ($Cl + NO_2 + M$); D.F. [10]
k_{19} ($Cl + ClNO_2$); D.F. [10]
k_{20} ($Cl + Cl + Ar$); D.F. [8]
k_{20} ($Cl + Cl + Ar$); D.F. [9]
k_{27} ($O + Cl_2$); D.F. [32]
k_{39} ($O + HCl$); D.F. [93]

6. Compilation and Discussion of Reaction Rate Measurements

6.1. Reactions of Chlorine Atoms

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

Reference	Rate constant/cm³ molecule⁻¹s⁻¹	Temp./K	Note
Watson, Machado, Fischer, and Davis, 1976 [95]	$(3.08 \pm 0.30) \times 10^{-11} \exp(-(290 \pm 25)/T)$	220–350	(a2)
	$(1.20 \pm 0.10) \times 10^{-11}$	298	(a1)
Zahniser, Kaufman and Anderson 1976 [94]	$(2.17 \pm 0.43) \times 10^{-11} \exp(-(170 \pm 30)/T)$	205–366	(a2)[a]
	$(1.23 \pm 0.25) \times 10^{-11}$	295	(a1)[a]
Kurylo and Braun, 1976 [113]	$(2.72 \pm 0.45) \times 10^{-11} \exp(-(298 \pm 39)/T)$	213–298	(a2)[a]
	$(1.02 \pm 0.15) \times 10^{-11}$	298	(a1)[a]
Nip and Clyne, 1976 [105]	$(5.18 \pm 0.5) \times 10^{-11} \exp(-(418 \pm 28)/T)$	221–629	(a2)
	$(1.33 \pm 0.26) \times 10^{-11}$	298	(a1)
Ming-Taun Leu and DeMore 1976 [126]	$(1.3 \pm 0.3) \times 10^{-11}$	295	(a1)
Clyne and Watson, 1974 [30]	$(1.85 \pm 0.36) \times 10^{-11}$	298	
Clyne and Coxon, 1968 [15]	$> 6.7 \times 10^{-13}$	300	
*Preferred value	$(2.7 \pm 1.2) \times 10^{-11} \exp(-(257 \pm 106)/T)$	205–298	(a2)
	$(1.19 \pm 0.13) \times 10^{-11}$	298	
	$(3.34 \pm 1.0) \times 10^{-11} \exp(-(310 \pm 76)/T)$	205–466	(a2)

[a] The pre-exponential A factors shown above are ~8% lower than those reported in the original papers due to a revision in the value used for the ozone absorption cross-section.

* Throughout the tables an asterisk, *, before a reference or a rate constant expression denotes a preferred value.

(a1) The agreement between these workers at 300 K is moderately good and a mean value of: $^*k_1$ (298 K) = $(1.19 \pm 0.13) \times 10^{-11}$ can be obtained. The higher value of Clyne and Watson is just outside the stated experimental uncertainties of the different studies. However, their result is not included in the computed mean value of k_1. Inclusion of their result would yield a value of $(1.32 \pm 0.28) \times 10^{-11}$ for k_1.

(a2) The four Arrhenius expressions are in fair agreement within the temperature range 205–300 K. In this temperature range, the rate constants at any particular temperature agree to within (30–40%) Although the values of the activation energy obtained by Watson et al., and Kurylo and Braun are in excellent agreement, the value of k_1 in the study of Kurylo and Braun is consistently (~ 17%) lower than that of Watson, et al. This may suggest a systematic underestimate of the rate constant, as the value of the other four studies agree so well at 298 K. A more disturbing difference is the scatter in the values reported for the activation energy (338-831 cal mol⁻¹). However, there is no reason to prefer any one set of data to any other, therefore the suggestion of this author is to use the following Arrhenius expression which was obtained by computing the mean of the four results between 205 and 300 K: $^*k_1 = (2.7 \pm 1.2) \times 10^{-11} \exp(-(257 \pm 106)/T)$, (205–298) K. Inclusion of higher temperature ($\leq$ 466 K) experimental data would yield the following Arrhenius expression: $k_1 = (3.34 \pm 1.0) \times 10^{-11} \exp(-(310 \pm 76)/T)$.

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

Reference	Rate constant/cm^3 $molecule^{-1}s^{-1}$	Temp./K	Note
*Bemand, Clyne and Watson, 1973 [5]	$(5.9 \pm 0.9) \times 10^{-11} \exp(-(0 \pm 120)/T)$	298–588	298
Bemand, Clyne and Watson, 1973 [5]	$(6.1 \pm 0.9) \times 10^{-11}$	298	300
Bemand, Clyne and Watson, 1973 [5]	$(5.9 \pm 0.9) \times 10^{-11}$	298	(b1)
Basco and Dogra, 1971 [21]	$(8.5 \pm 1.2) \times 10^{-12}$	300	(b2)
Gritsan, Panfilov, and Sukhanov,	$(3.7 \pm 0.3) \times 10^{-10} \exp(-(3020 \pm 101)/T)$	335–365	(b3)
1975 [183]	1.47×10^{-14}	298	
Clyne and Coxon, 1968 [15]	$>1.0 \times 10^{-12}$	300	

*Preferred value.

(b1) The preferred value was obtained by combining the results of three separate sets of direct experimental determinations, using different techniques.

(b2) Data incorrectly analyzed.

(b3) These results are totally incompatible with those reported in references [5] and [15] and must be rejected. The study was indirect. In addition to the value reported for k_2, it was stated that a second reactive channel formed $Cl_2 + O_2$ with a temperature invariant rate coefficient of 1.51×10^{-14}, this value should also be rejected.

(3) $Cl + O_2 + M \rightarrow ClOO + M$

Reference	Rate constant/cm^6 $molecule^{-2}s^{-1}$	Temp./K	Note
Stedman in "Clyne and Coxon", 1968 [11]	5.6×10^{-34}	200–300	
Clyne and Coxon, 1968 [15]	$\leq 5.6 \times 10^{-33}$	300	
Nicholas and Norrish, 1968 [22]	1.7×10^{-33}	300	(c)

No recommendations.

(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. No value is recommended.

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

Reference	Rate constant/cm^3 $molecule^{-1}s^{-1}$	Temp./K	Note
*Watson, Fischer, Machado,	$(7.44 \pm 0.7) \times 10^{-12} \exp(-(1226 \pm 50)/T)$	218–401	(d2)
and Davis, 1976 [95]	$(1.16 \pm 0.1) \times 10^{-13}$	298	(d1)
Clyne and Walker, 1973 [14]	$5.1 \times 10^{-11} \exp(-(1790 \pm 37)/T)$	300–686	(d2)
	$(1.31 \pm 0.1) \times 10^{-13}$	300	(d1)
Poulet, Le Bras, and Combourieu,	$(1.84 \pm 0.14) \times 10^{-11} \exp(-(1409 \pm 101)/T)$	295–490	(d2)
1974 [157]	$(1.36 \pm 0.1) \times 10^{-13}$	295	(d1)
Manning and Kurylo,	$(7.93 \pm 1.53) \times 10^{-12} (-(1272 \pm 51)/T)$	218–322	(d2)
1977 [173]	$(1.04 \pm 0.1) \times 10^{-13}$	296	(d1)
Zahniser, Berquist, and Kaufman,	$(8.2 \pm 0.6) \times 10^{-12} \exp(-1320 \pm 20/T)$	200–300	(d2) (d3)
1977 [172]	$(0.99 \pm 0.15) \times 10^{-13}$	298	(d1)
	$2.25 \times 10^{-11} \exp(-1623/T)$	300–500	(d3)
Davis, Braun and Bass, 1970 [34]	$(1.35 \pm 0.1) \times 10^{-13}$	298	(d1) (d4)
Ming-Taun Leu, and DeMore,	$(3.99 \pm 1.0) \times 10^{-11} \exp(-(1720 \pm 100)/T)$	295–434	(d1)
1976 [126]	$(1.2 \pm 0.3) \times 10^{-13}$	295	
Fettis and Knox, 1964 [86]	$(4.0 \pm 1.3) \times 10^{-11} \exp(-(1928 \pm 90)/T)$	193–593	(d5)
(Review)	6.2×10^{-14}	298	
Knox and Nelson, 1959 [44]	$(4.0 \pm 0.7) \times 10^{-11} \exp(-(1938 \pm 30)/T)$	193–593	(d5)
	6.0×10^{-14}	298	
Pritchard, Pyke, and Trotman-	$4.27 \times 10^{-11} \exp(-(1938 \pm 75)/T)$	293–484	(d5)
Dickenson, 1954 [43]	6.4×10^{-14}	298	
Goldfinger, Huybrechts and	$8.34 \times 10^{-11} \exp(-1937/T)$	385–475	(d6)
Martens, 1961 [117]	1.26×10^{-13}	298	
*Preferred Value	$(1.2 \pm 0.2) \times 10^{-13}$	298	

(d1) There have been seven direct studies of the kinetic behavior of chlorine atoms with methane at, or near, 298 K. Three studies, [34], [95] and [173], used the flash photolysis-resonance fluorescence technique to monitor the decay of atomic chlorine in the presence of a large excess concentration of methane, reporting values of 1.5, 1.16, and 1.07 (modified from the value reported at 296 K) $\times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}, respectively for k_4 (298) K). However, the value reported in reference [34] was probably overestimated by 10% by taking the relationship between I_f and [Cl] to be: $I_f \propto [Cl]^{0.9}$ (based on theoretical considerations, not experimental). If $I_f \alpha$ [Cl], as found in other studies (for $[Cl] \leq 10^{12}$ cm^{-3}), then the value calculated for k_4 would be 1.35×10^{-13}. Three other studies [14], [126], and [157] used the low pressure discharge flow-mass spectrometric technique to monitor the decay of methane (*m/e* 16) in the presence of an excess concentration of atomic chlorine, reporting values for k_4 (298 K) of 1.26 (modified from the value reported at 300 K), 1.27 (modified from the value reported at 295 K) and 1.48 (deduced by weighting the limited data reported at 295 K with the single determination at 298 K) × 10^{-13} cm^3 molecule^{-1} s^{-1}, respectively. One study [172] used the discharge flow-resonance fluorescence technique to monitor the decay of atomic chlorine in the presence of a large excess concentration of methane, and reported a value of 0.99 × 10^{-13} cm^3 molecule^{-1} s^{-1} for k_4 (298 K). Therefore, the values reported for k_4 (298 K) range from 0.99 to 1.48 × 10^{-13} cm^3 molecule^{-1} s^{-1}, with a mean value of 1.27 × 10^{-13} cm^3 molecule^{-1} s^{-1}. However, based upon the stated confidence limits reported in each study, the range of values far exceed that to be expected. It should be notd that for studies with excess methane it is essential to use methane which is not contaminated with the higher alkanes (i.e., C_2H_6 and C_3H_8), even in the part per million (ppm) range due to their enhanced chemical reactivity toward atomic chlorine ($(k_6(C_2H_6)/k_4(CH_4) \sim 500$ at 298 K). Davis et al. [34] reported the methane used in their study contained 100 ppm of C_2H_6, which means that their value of 1.35×10^{-13} should probably be reduced by $\sim 5\%$ to 1.28×10^{-13}. However, the accuracy of their chemical analysis was not reported, neither was it stated whether C_3H_8 was observed as a contaminant. Consequently, it is likely that this value may still be an overestimate of the true value of k_4. Manning et al. [173] and Watson et al. [95] reported the impurity to be low in the methane used in their studies (C_2H_6 ~ 20–30 ppm, and C_3H_8 non-detectable). At present the writer does not know the purity of the methane used in the study performed by Zahniser et al. [172]. The purity of the methane used in the mass spectrometric studies is not particularly critical; however, the accuracy of their results may be limited due to the following: (a) at low initial stoichiometries ($[Cl]_0/[CH_4]_0$) loss of atomic chlorine should be considered due to the high reaction stoichiometries ($[Cl]_{removed}/[CH_4]_{removed} \sim 6$) observed by Poulet et al. [157]. Failure to allow for this effect would tend to underestimate the rate constant; unfortunately initial reaction conditions were not published by Clyne and Walker [14] or Ming-Taun Leu and DeMore [126], and (b) γ(Cl), the heterogeneous wall removal coefficient of atomic chlorine, was observed to vary [14] upon addition of CH_4 to the flow system. The limited data of Poulet et al. [157] appears to be of poor precision, and is given a low weighting in the evaluation of the preferred rate constant at 298 K. Until all the results are published and can be more critically analyzed a tentative value for k_4(298 K) is: k_4^*(298 K) = (1.20 ± 0.2) × 10^{-13}. Recent data are presented and discussed in the Addenda.

(d2) There have been six direct determinations of the activation energy of reaction (4), of which only three [14], [95] and [157] have yet been published. Of these three it appears that there is better agreement between the studies of Watson et al. [95] and Poulet et al. [157]; however, the data of Poulet et al. [157] is limited and somewhat scattered. The Arrhenius expressions of Watson et al. [95] and Clyne and Walker [14] are in sharp disagreement, with the values obtained for the activation energy being different by a factor of ~ 1.5. Unfortunately, there was only a short (100°) overlap of the temperature ranges, and at present it is difficult to evaluate the cause for the difference between these results. Indeed, most of the probable errors which may have been present in the studies would tend to increase the discrepancy (see note dl). The results of the recent study by Manning et al. [173] are in excellent agreement with those of Watson et al. [95] indicating a lack of serious systematic errors in the two studies. Similarly the provisional results of Ming-Taun Leu and DeMore [126] are in good agreement with those of Clyne and Walker [14] above 298 K, indicating a lack of serious systematic errors in these two studies. The provisional results of Zahniser et al. [172] are quantitatively in good agreement below 300 K with those of the flash photolysis studies [95] and [173] (typically 20% lower) and qualitatively with the study of Clyne and Walker [14] above 300 K (but significantly lower, 30-60%) (see note d3). However, until the data of the recent studies [172], [173] and [126] are examined more closely, the preferred value for k_4 below 300 K is that of Watson et al. [95]. Recent data are presented and discussed in the Addenda.

(d3) The kinetic behavior of reaction 4 has been studied between 200 and 500 K by Zahniser et al. [172], and a strong nonlinear Arrhenius behavior was observed (noted by the two expressions shown for k_4). This behavior may tend to explain variance in the values reported for the activation energy, although the absolute magnitude of the rate constants at any given temperature are outside quoted confidence limits.

(d4) The value quoted in the table is 10% lower than that reported in the original publication—see note (dl) for the explanation.

(d5) These values were not considered as they were determined relative to k_5 ($Cl + H_2 \rightarrow HCl + H$; $k_5 = 1.3 \times 10^{-10} \exp(-(2768/T))$, and differ by a factor of ~ 2 from the other results at 298 K. Using the value of k_5 forwarded in this new review (see later discussion), and the data of references (43, 44) a value of $1.4 \times 10^{-11} \exp(-(1515 \pm 150)/T)$ can be obtained for k_4. This Arrhenius expression yields a value of 8.7×10^{-14} at 298 K, which is still not in particularly good agreement with the preferred value, but probably within the experimental uncertainties of the data. It has been suggested [95] that the activation energy may have been overestimated due to the reverse reaction (−4) being significant, thus leading to an incomplete analysis of the experimental data. The value of k_5 used is that shown in the main table, not that shown in Table I (summary of preferred values) which includes recent data from the Addenda.

(d6) This study was indirect, and used some data of Knox to normalize the temperature dependence of the reaction.

(5) $Cl(^2P_{3/2}) + H_2 \rightarrow HCl + H$

Reference	Rate constant/cm^3 molecule^{-1}s^{-1}	Temp./K	Note
Hertel, 1931 [81]	E_a = (24.3 ± 4.2) kJ mol^{-1}	~300	
Potts and Rollefson, 1935 [82]	E_a = (18.9 ± 4.2) kJ mol^{-1}	<170	
	= (24.3 ± 4.2) kJ mol^{-1}	>200	
Rodebush and Klingelhoefer, 1933 [83]	1.37×10^{-14}	298	(e1)
	5.5×10^{-15}	273	(e1)
	1.08×0.10^{-14}	298	(e2)
	4.1×10^{-15}	273	(e2)
Steiner and Rideal, 1939 [84]	$1{,}17 \times 10^{-11}$	1071	(e3)
	8.67×10^{-12}	1031	(e3)
	7.67×10^{-12}	960	(e3)
	6.00×10^{-12}	901	(e3)
	5.90×10^{-12}	1071	(e4)
	4.57×10^{-12}	1031	(e4)
	4.07×10^{-12}	960	(e4)
	3.27×10^{-12}	901	(e4)

6.1. Reactions of Chlorine Atoms—Continued

Reference	Rate constant/cm^3 molecule^{-1}s^{-1}	Temp./K.	Note
Ashmore and Chanmugam, 1953 [85]	8.0×10^{-13}	523	(e5)
Fettis and Knox, 1964 [86]	$(1.38 \pm 0.1) \times 10^{-10} \exp(-(2750 \pm 70)/T)$	273–1071	(e6)
	$(1.4 \pm 0.1) \times 10^{-14}$	298	
Clyne and Stedman, 1966 [87]	1.48×10^{-13}	373	(e7)
	2.12×10^{-14}	294	(e7)
	1.20×10^{-14}	273	(e7)
	7.76×10^{-16}	195	(e7)
	$3.2 \times 10^{-11} \exp(-(2099 \pm 98)/T)$	195–373	(e7)
Westenberg and deHaas, 1968 [88]	$(2.0 \pm 0.5) \times 10^{-11} \exp(-(2164 \pm 101)/T)$	251–456	(e8)
	$(1.35 \pm 0.07) \times 10^{-14}$	297	
Westenberg and deHaas, 1968 [88]	5.86×10^{-16}	195	(e9)
	2.76×10^{-15}	226	(e9)
	7.29×10^{-15}	250	(e9)
	1.82×10^{-14}	273	(e9)
	3.75×10^{-14}	297	(e9)
	5.13×10^{-14}	314	(e9)
	7.41×10^{-14}	333	(e9)
	2.64×10^{-13}	413	(e9)
	7.21×10^{-13}	497	(e9)
	$7.2 \times 10^{-11} \exp(-(2285 \pm 48)/T)$	195–497	(e9)
Benson, Cruickshank and Shaw, 1969 [89]	$(8.0 \pm 2.0) \times 10^{-11} \exp(-(2655 \pm 200)/T)$	479–610	(e10)
	$(1.1 \pm 0.2) \times 10^{-14}$	298	
Davis, Bass and Braun, 1970 [34]	$(1.25 \pm 0.1) \times 10^{-14}$	298	(e11)
Galante and Gislason, 1973 [90] Review			(e12)
Clyne and Walker, 1973 [14]	$(3.7 \pm 0.6) \times 10^{-11} \exp(-(2146 \pm 51)/T)$	195–610	(e13)
	2.76×10^{-14}	298	
	$(5.6 \pm 1.2) \times 10^{-11} \exp(-(2254 \pm 69)/T)$	195–496	(e14)
	2.95×10^{-14}	298	
Watson, Davis, Machado, Conaway and Oh, 1976 [116]	$(5.5 \pm 0.5) \times 10^{-11} \exp(-(2375 \pm 100)/T)$	213–350	(e15)
	$(1.80 \pm 0.2) \times 10^{-14}$	298	
Spencer and Glass, 1975 [128]	$\sim 1.71 \times 10^{-14}$	295	(e16)
*Preferred value	$4.7 \times 10^{-11} \exp(-(2340 \pm 30)/T)$	213–1071	(e17)

(e1) These results should have low or zero weighting when calculating a best value for k_5 due to the inaccurate manner used to determine [Cl], and due to the observed dependence of k_5 upon the history of the reactor surfaces. These values were calculated by Fettis and Knox [86], from the reaction probabilities reported in reference [83].

(e2) Same data as in (e1). These values were calculated by Benson et al., [89]. See remarks in (e1).

(e3) 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_{-5} (H + HCl) reported by Steiner and Rideal [84], have been recalculated using more recent thermodynamic data to yield values for k_5.

(e4) Same data as in (e3). These values are those given by Benson et al., [89]. The value of k_{-5} 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.

(e5) The chemical system is complex and numerous simplifying assumptions were made. However, recent kinetic measurements justify most of them. Their value of k_5 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, believed (by the writer) to be incorrect. Consequently, their value may be approximately (± 20%) correct.

(e6) A review of references [80, 81, 82]. Their interpretation of the published data is shown in the table.

(e7) Calculated by using the reported values of k_{-5} 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 data can be approximated by the Arrhenius expression shown. The published values of k_{-5} are in fair (± 30%) agreement with those published for k_{-5} in reference [88]. No obvious systematic error is noticeable but these results are at variance with the direct determination of k_5. A possible explanation has been forwarded in reference [128], discussed in note (e16). The thermochemical data is that recommended by CODATA [146] and is shown at the end of this review.

(e8) The Arrhenius expression is shown for the study which directly measured k_5. k_{-5} was also reported, and the results are shown below (e9). K_{eq} (experimental) was found to a factor of 2–3 lower than that calculated from thermodynamic data. The value at 298 K for k_5 is in excellent agreement with reference [34], but the writer feels the measurement of k_5 could be significantly underestimated due to the regeneration of Cl via the rapid H + Cl_2 reaction. This hypothesis would explain why their value is lower than the preferred one of Watson et al., 1975 at 298 K. The back reaction should not suffer from such error and would predict a much higher value (factor of ~2.5) for k_5 if thermodynamic equilibrium can be assumed (discussed in e9).

(e9) As stated in (e8), the value of k_5 obtained from the experimental determination of k_{-5} and the relevant thermochemical data is significantly greater (> factor of 2) than the direct determinations of k_5. Experimental data obtained in reference [128] strongly indicates that the values reported for k_{-5} are overestimated due to a secondary removal process for atomic hydrogen (see note e16).

(e12) 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 these data. However, the reliability of the earlier data is questionable.

(e11) This study, which was performed at 298 K, should be free from any complicating secondary reactions. Pseudo 1st order conditions were used, and the absence of kinetic complications was seemingly well-verified. However, the technique of flash photolysis resonance fluorescence was in its infancy, and as such lacked the sensitivity of "today's" systems. In addition, the value reported may have been overestimated by ~ 10% (note d1, reaction 4), and a revised value has been entered in these tables.

(e12) This review judged that the data from the direct studies of k_5 were accurate, whilst those [87, 88] measured for k_{-5} were in error by a factor of 2. The explanation, that atomic hydrogen recombines heterogenously with atomic chlorine, 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) $>k_5/k_{-5}$ appears to have been validated by the results reported in reference [128].

(e13) This rate constant expression includes data from references [87, 88, (k_{-5}), 89 and 34], but rejects the determination of k_5 from reference [88]. This evaluation should be rejected in favor of the one to be presented in this review.

(e14) This rate constant expression is based on data from references [87, 88, (k_{-5}), and 34]. This evaluation should be rejected in favor of the one to be presented in this review.

(e15) This study measured k_5 in a temperature range which makes its results directly applicable to the model calculations of the stratosphere. The system used for this determination should be free from complicating secondary processes and significant systematic errors (numerous rate constants have been determined in this system which are in excellent agreement with other workers). Consequently, the data obtained in this study is preferred to that of other workers. Therefore, from this study alone the preferred Arrhenius expression would be $5.5 \times 10^{-11} \exp(-(2375/T))$, yielding a value of 1.8×10^{-14} for the rate constant at 298 K.

(e16) This study of reaction (−5) monitored atomic hydrogen, and atomic chlorine by EPR in the presence of an excess concentration of HCl. It was observed that the stoichiometry of the reaction, ($[Cl]_{formed}/[H]_{reacted}$) and the rate of removal of atomic hydrogen were dependent upon the treatment of the reactor surfaces. It was concluded that the results reported in references [87] and [88] for k_{-5} are too high due to secondary removal of H atoms via the following mechanism: $H + HCl \rightarrow H_2 + Cl$; $Cl + HCl \overset{\text{wall}}{\leftrightarrows} HCl_2$; $H + HCl_2 \rightarrow 2HCl$: By extrapolating the stoichiometry to unity (at which point secondary reactions should be negligible), a value of $\sim 4.3 \times 10^{-14}$ was obtained for k_{-5}. However, a more accurate extrapolation would yield a value of $\sim 5.1 \times 10^{-14}$ for k_{-5}. Using the thermochemical equilibrium constant, a value of 1.71×10^{-14} can be calculated for k_5 (295 K) in reasonable agreement with that derived from the preferred Arrhenius expression (1.69×10^{-14}).

(e17) The preferred Arrhenius expression for k_{-5} is obtained by combining the results of Watson et al., 1975; Benson et al., 1969, and Steiner and Rideal, 1939 (as modified by Benson). The resulting Arrhenius expression is:

$$*k_5 = 4.7 \times 10^{-11} \exp(-(2340 \pm 30)/T) \quad (213\text{–}1071\ \mathrm{K}).$$

This expression is almost identical to the expression obtained from the results of Watson et al., 1975 alone. The conclusion of this writer is that the data from (a) reference [83] is in error by less than a factor of 2; (b) reference 85 and 34 are accurate to within ±25%; (c) the value of k_5 determined from k_{-5} [87, 88] is significantly in error and the values must be rejected due to either experimental errors, or "nonequilibrium" conditions (less likely). Recent results are presented and discussed in the Addenda.

(6) $Cl(^2P_{3/2}) + C_2H_6 \rightarrow C_2H_5 + HCl$

Reference	Rate constant/cm^3 molecule^{-1} s^{-1}	Temp./K	Note
Davis, Braun, and Bass, 1970 [34]	$(6.0 \pm 1.5) \times 10^{-11}$	298	(f1)
Watson, Davis, Machado, Conaway and Oh, 1976 [116]	$(5.5 \pm 0.5) \times 10^{-11}$	298	(f1)
*Manning and Kurylo, 1977, [173]	$(7.29 \pm 1.23) \times 10^{-11} \exp(-(61 \pm 44)/T)$	222–322	(f1)
	$(5.93 \pm 0.44) \times 10^{-11}$	296	
Fettis and Knox, 1964 [86] [review]	$(1.5 \pm 0.3) \times 10^{-10} \exp(-(510 \pm 65)/T)$	193–593	(f2)
	2.7×10^{-11}	298	
Knox, 1955 [118]	$(1.5 \pm 0.2) \times 10^{-10} \exp(-(528 \pm 40)/T)$	193–593	
	2.55×10^{-11}	298	
Pritchard, Pyke and Trotman-Dickenson, 1955 [119]	$2 \times 10^{-10} \exp(-(508 \pm 260)/T)$	349–563	
	3.64×10^{-11}	298	
Preferred value	$(5.8 \pm 0.6) \times 10^{-11}$	298	

(f1) These three values are in excellent agreement at ~ 298 K. The value reported in reference [34] was probably overestimated by 10% (see rate d1, reaction 4), therefore the corrected value has been entered in the table above. The preferred rate constant at 298 K is taken to be the mean of the three reported values. $k_6{}^* = (5.8 \pm 0.6) \times 10^{-11}$. The low activation energy reported in reference [173] is more reasonable than the values obtained in the competitive photo-chlorination studies.

(f2) This value was obtained from two competitive chlorination experiments, references [118] and [119], between CH_4 and C_2H_6. In turn, the rate constant for the $Cl + CH_4$ reaction was obtained in a competitive chlorination study with molecular hydrogen. Consequently, several errors can easily accumulate to have a significant adverse affect upon the reliability of the results; (a) an error in the absolute value of k_5 ($Cl + H_2$), and (b) an error in the ratios of k_{CH_4}/k_{H_2} and $k_{C_2H_6}/k_{CH_4}$.

If the new value of $k_5(Cl + H_2)$ forwarded in this review is taken as the reference rate constant in order to be able to calculate a new value for k_4 ($Cl + CH_4$) from the competitive chlorination data (references 118, 119), then the following Arrhenius expression is obtained: k_6 ($Cl + C_2H_6$) $= 5.4 \times 10^{-11} \exp-(108/T)$, yielding a value of 3.75×10^{-11} for k_6 at 298 K. This value is closer to that obtained from the direct studies of Watson et al. Alternatively, if the preferred value for k_4 ($Cl + CH_4$) (from this review) is used to calculate k_6, then we obtain the unlikely expression of $1.95 \times 10^{-11} \exp + (295/T)$, which fortuitously predicts a value of 5.15×10^{-11} for k_6 at 298 K. The values used for k_4 and k_5 are shown in the main tables, not those shown in table I (summary of preferred values) which include recent data from the Addenda.

A general conclusion which can easily be reached is that either all the competitive chlorination results are correct, and this seems unlikely in view of the recent direct studies, or that they contain too many propagated errors for them to be compared usefully to the data collected using the direct techniques (e.g. back reaction in the $Cl + CH_4$ system).

(7, 8) Reactions of chlorine atoms with hydrogen peroxide and hydroperoxyl radicals

Reaction/Reference	Rate constant/cm³ molecule⁻¹ s⁻¹	Temp./K	Note
(7) $Cl(^2P_{3/2}) + H_2O_2 \rightarrow HO_2 + HCl$			
(7)′ $Cl(^2P_{3/2}) + H_2O_2 \rightarrow OH + HOCl$			
(7)″ $Cl(^2P_{3/2}) + H_2O_2 \rightarrow ClO + H_2O$			
Watson, Machado, Fischer and Davis, 1976 [95]	5.2×10^{-13} (range: $(2.6–10) \times 10^{-13}$)	298	(g1) (g2)
Ming-Taun Leu, and DeMore, 1976 [126]	$(6.2 \pm 1.5) \times 10^{-13}$	295	(g1) (g3)
(8) $Cl(^2P_{3/2}) + HO_2 \rightarrow O_2 + HCl$			
(8)′ $Cl(^2P_{3/2}) + HO_2 \rightarrow ClO + HO$			
Ming-Taun-Leu, and DeMore, 1976 [126]	3×10^{-11} (range $(1.2–7.5) \times 10^{-11}$)	295	(h)

(g1) All three reaction pathways are exothermic, and at present there is no experimental data indicating the relative importance of the three routes.

(g2) The wide error limits are due to uncertainties in the extent of decomposition of H_2O_2. The k has a value in the range expected for abstraction reactions, possibly indicating that reaction (7) is the dominant path. This value has been modified from that published [95] due to a printing error.

(g3) This value, obtained from a discharge flow—mass spectrometric study, is in excellent agreement with that obtained from the flash photolysis-resonance fluorescence study [95].

(h) Both processes are exothermic, however, (8) is expected to be dominant. This value is the only experimental data available, and was obtained in a competitive study with reaction (7). The value is in the range expected for an atom-radical reaction ($(1–10) \times 10^{-11}$). The wide confidence limits reflect the large uncertainty present in their calibration of the absolute HO_2 concentration.

(9) $Cl(^2P_{3/2}) + CH_3Cl \rightarrow CH_2Cl + HCl$

Reference	Rate constant/cm³ molecule⁻¹ s⁻¹	Temp./K	Note
Clyne and Walker, 1973 [14]	$(2.1 \pm 0.4) \times 10^{-10} \exp(-(1787 \pm 70)/T)$	300–604	(i1)
	$(4.5 \pm 0.45) \times 10^{-13}$	300	(i1)
Watson, Davis, Machado, Conaway and Oh, 1976 [116]	$(3.7 \pm 0.4) \times 10^{-11} \exp(-(1287 \pm 150)/T)$	245–350	(i1)
	$(4.87 \pm 0.5) \times 10^{-13}$	298	(i1)
Manning and Kurylo, 1977 [173]	$(3.36 \pm 0.71) \times 10^{-11} \exp(-(1250 \pm 57)/T)$	233–322	(i1)
	$(5.1 \pm 0.14) \times 10^{-13}$	296	(i1)
Fettis and Knox, 1964 [86] (Review)	$(5.5 \pm 1.5) \times 10^{-11} \exp(-(1650 \pm 100)/T)$	273–598	(i2)
	$(2.17 \pm 0.6) \times 10^{-13}$	298	
Knox, 1962 [120]	$5.67 \times 10^{-11} \exp(-(1660 \pm 100)/T)$	273–598	(i2)
	2.15×10^{-13}	298	
Pritchard, Pyke and Trotman-Dickenson, 1955 [119]	$9.5 \times 10^{-11} \exp(-(1693 \pm 150)/T)$	298–484	(i2)
	3.24×10^{-13}	298	
Goldfinger, Huybrechts and Martens, 1961 [117]	$5.27 \times 10^{-11} \exp(-(1550)/T)$	385–475	(i2, i3)
	2.90×10^{-13}	298	
* Preferred value	$(3.4 \pm 0.8) \times 10^{-11} \exp(-(1256 \pm 62)/T)$	233–350	(i4)
	$(4.9 \pm 0.5) \times 10^{-13}$	298	

(i1) These studies measured k_9 directly using two different techniques: (a) discharge flow mass spectrometry monitoring CH_3Cl in the presence of excess atomic chlorine [14], and (b) flash photolysis resonance fluorescence where Cl atoms were monitored in the presence of an excess concentration of CH_3Cl [116] and [173]. The results are in good agreement at 298 K. However, the value of the activation energy measured by Watson et al. and Manning et al. is significantly lower than that measured by Clyne and Walker. Both groups of workers measured the rate constant for reaction 4, ($Cl + CH_4$) and similarly the activation energy measured by Watson et al. and Manning et al. was significantly lower than that measured by Clyne and Walker. This suggests that one technique is subject to a systematic discrepancy, and at present it is recommended that the flash photolysis results be used for stratospheric calculations in the 200–300 K temperature range. In the discusion of reaction 4 (notes d2 and d3) it was suggested that some of the apparent discrepancy between the results of Clyne and Walker, and the flash photolysis studies [95] and [173] might be explained by non-linear Arrhenius behavior. However, it is less likely that this can be invoked for this reaction as the pre-exponential A factor (as measured in the flash photolysis studies) is already $\sim 3.5 \times 10^{-11}$ and the significant curvature which would be required in the Arrhenius plot to make the data compatible, would result in an unreasonably high value for A ($> 2 \times 10^{-10}$).

(i2) These indirect measurements are subject to propagated errors causing inaccurate results. Consequently, these determinations are rejected in favor of the more recent direct studies (see earlier discussion on reactions 4 and 6).

(i3) These results were based on a very limited data base, and relied (in part) on data supplied to the authors by Knox (the activation energies) which was subsequently modified.

(i4) A least square fit of the individual data points of Watson et al. [116] and Manning et al. [173] has been used to derive the preferred Arrhenius expression of $3.4 \times 10^{-11} \exp -(1256/T)$ for k_9. This expression should be used with caution outside the stated temperature range. A preferred value of $(4.9 \pm 0.5) \times 10^{-13}$ was derived for k_9 (298 K) from the data of the three direct studies.

(10) $Cl(^2P_{3/2}) + CH_2Cl_2 \rightarrow CHCl_2 + HCl$

Reference	Rate constant/cm^3 molecule^{-1} s^{-1}	Temp./K	Note
Clyne and Walker, 1973 [14]	$(8.3 \pm 1.4) \times 10^{-11} \exp(-(1449 \pm 60)/T)$	298–621	(j1)
	$(7.52 \pm 1.0) \times 10^{-13}$	298	
Watson, Davis, Machado, Conaway, and Oh, 1976 [116]	$(3.1 \pm 0.45) \times 10^{-13}$	298	(j1)
Davis, Bass and Braun, 1970 [34]	$(4.95 \pm 0.5) \times 10^{-13}$	298	(j1)
Fettis and Knox, 1964 [86] (review)	$(4.3 \pm 0.7) \times 10^{-11} \exp(-(1490 \pm 50)/T)$	273–563	(j2)
	2.9×10^{-13}	298	
Knox, 1961 [120]	$4.5 \times 10^{-11} \exp(-1510/T)$	237–563	(j2)
	2.8×10^{-13}	298	
Goldfinger, Huybrechts and Martens, 1961 [117]	$4.2 \times 10^{-11} \exp(-1572/T)$	385–475	(j2) (j3)
	2.15×10^{-13}	298	
* Tentative value	$(5.2 \pm 2.2) \times 10^{-13}$	298	(j1)

(j1) The agreement between these direct studies is very poor, and at present no plausible explanation is evident. The value forwarded in reference [34] has been lowered by 10% (note d1, reaction 4), from a value of 5.5×10^{-13}. However this does not improve the agreement. Tentatively a preferred value of $(5.2 \pm 2.2) \times 10^{-13}$ can be obtained by taking the mean of the three direct studies. No value is recommended for the activation energy; the value forwarded in reference [14] may be in error (note i1, reaction 9, and notes d2 and d3, reaction 4).

(j2), (j3) See notes (i2) and (i3) (reaction 10).

(11) $Cl(^2P_{3/2}) + CHCl_3 \rightarrow CCl_3 + HCl$

Reference	Rate constant/cm^3 molecule^{-1} s^{-1}	Temp./K	Note
Clyne and Walker, 1973 [14]	$(3.3 \pm 0.4) \times 10^{-11} \exp(-(1380 \pm 44)/T)$	297–652	
	$(1.4_7 \pm 0.35) \times 10^{-13}$	297	(k1)
Watson, Davis, Machado, Conaway, and Oh, 1976 [116]	$(9.9 \pm 0.9) \times 10^{-14}$	298	(k1)
Fettis and Knox, 1964 [86] (review)	$(1.15 \pm 0.1) \times 10^{-11} \exp(-(1671 \pm 45)/T)$	286–593	
	4.22×10^{-14}	298	(k2)
Knox, 1961 [120]	$1.15 \times 10^{-11} \exp(-1686/T)$	286–593	
	4.01×10^{-14}	298	(k2)
Goldfinger, Huybrechts, and Martens, 1961 [117]	$2.65 \times 10^{-11} \exp(-1677/T)$	385–475	
	9.53×10^{-14}	298	
* Tentative value	$(1.23 \pm 0.34) \times 10^{-13}$	298	

(k1) The agreement between these results is only fair. Unfortunately, no explanation can be forwarded for the discrepancy (the uncertainty limits just overlap). Tentatively a value of $(1.23 \pm 0.34) \times 10^{-13}$ is suggested. No value is recommended for the activation energy; the value forwarded by reference [14] may be in error (note i1, reaction 9, and notes d2 and d3, reaction 4).

(k2) See notes (i2) and (i3) (reaction 10).

(12, 13, 14) Reactions of chlorine atoms with unsymmetrical chlorine dioxide and with chlorine monoxide

Reaction/Reference	Rate constant/cm^3 molecule^{-1} s^{-1}	Temp./K	Note
(12) $Cl(^2P_{3/2}) + ClOO \rightarrow Cl_2 + O_2$			
Johnston, Morris, and Van den Bogaerde, 1969 [26]	1.56×10^{-10}	298	(l1)
Johnston, Morris, and Van den Bogaerde, 1969 [26]	$k_{12}/k_{13} = 108$	298	(l2)
Nicholas and Norrish, 1968 [22]	$k_{12}/k_{13} = 15$	298	(l2)
(13) $Cl(^2P_{3/2}) + ClOO \rightarrow 2\ ClO$			
Johnston, Morris, and Van den Bogaerde, 1969 [26]	1.44×10^{-12}	298	(m)
(14) $Cl(^2P_{3/2}) + Cl_2O \rightarrow Cl_2 + ClO$			
* Basco and Dogra, 1971b [20]	6.8×10^{-13}	300	
Edgecombe, Norrish, and Thrush, 1957 [23]	$>6.7 \times 10^{-13}$	300	

* Preferred value. No recommendations for reactions 12 and 13.

(l1) 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.

(l2) 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).

(m) This value was obtained from the analysis of complex reaction schemes, and was obtained relative to k_{12}. Therefore, both k_{12} and the ratio k_{12}/k_{13} have to be accurately known to obtain a value for k_{13}. Although the ratio k_{12}/k_{13} was not dependent upon the value of $\Delta H_f(ClOO)$, the kinetic analysis for k_{12} required $\Delta H_f(ClOO)$ to be known.

Although no recommendations are forwarded for reactions (12) and (13), it should be noted that the reported rapidity of reaction (12) is expected for an atom-radical reaction where a weak bond is broken. Therefore, this value is probably correct to within an order of magnitude.

(15, 16) Combination of chlorine atoms with nitric oxide

Reference	Rate constant/cm^6 molecule^{-2} s^{-1}	Temp./K	Note
(15) $Cl(^2P_{3/2}) + NO + N_2 \rightarrow ClNO + N_2$			
Clark, Clyne and Stedman, 1966 [7]	$(9.7 \pm 1.4) \times 10^{-32}$	293	(n)
Clark, Clyne and Stedman, 1966 [7]	$E_a(M = Ar) = -(4.6 \pm 4)$ kJ mol^{-1}	270–620	
Ashmore and Spencer, 1959 [41]	$(2.1 \pm 0.6) \times 10^{-32}$	471	(n)
*Preferred value	$(1.1 \pm 0.2) \times 10^{-31}$	293	
(16) $Cl(^2P_{3/2}) + NO + O_2 \rightarrow ClNO + O_2$			
Clark, Clyne and Stedman, 1966 [7]	$(1.1 \pm 0.14) \times 10^{-31}$	293	(n)
* Preferred value	$(1.3 \pm 0.3) \times 10^{-31}$	293	

(n) 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_{15} and k_{16} have probably been underestimated by ~15%„ and this leads to preferred values: $*k_{15} = (1.1 \pm 0.2) \times 10^{-31}$, and $*k_{16} = (1.3 \pm 0.3) \times 10^{-31}$.

(17) $Cl(^2P_{3/2}) + ClNO \rightarrow NO + Cl_2$

Reference	Rate constant/cm^3 molecule^{-1} s^{-1}	Temp./K	Note
* Clyne and Cruse, 1972 [33]	$(3.0 \pm 0.5) \times 10^{-11}$	298	(o)
Clyne, Cruse and Watson, 1972 [40]	$\geq 8 \times 10^{-12}$	298	
Burns and Dainton, 1952 [42]	$(1.9 \pm 1.0) \times 10^{-11} \exp(-(533 \pm 160)/T)$	298–328	
	3.18×10^{-12}	298	

(o) This direct determination of k_{17} at 298 K is preferred to the study of Burns and Dainton, where several systematic errors were likely, due to the competitive nature of the study.

(18, 19) The interaction of chlorine atoms and nitrogen dioxide

Reaction/Reference	Rate constant	Temp./K	Note
(18) $Cl(^2P_{3/2}) + NO_2 + M \rightarrow ClNO_2 + M$			
Clyne and White, 1974 [10]	7.2×10^{-31} cm^6 molecule^{-2} s^{-1}	298	(p)
(19) $Cl(^2P_{3/2}) + ClNO_2 \rightarrow Cl_2 + NO_2$			
Clyne and White, 1974 [10]	$k_{19} >> 3 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}	298	(p,q)

No preferred value for either reaction.

(p) Provisional data, subject to revision.

(q) k_{19} is greater than the second order component of k_{18} at low pressure (1 torr); $k_{19} >> k_{18}$ [M].

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

Reference	Rate constant/cm^6 molecule^{-2} s^{-1}	Temp./K	Note
Clyne and Stedman, 1968 [8]	$5.6 \times 10^{-34} \exp((910 \pm 350)/T)$; M = Ar	195–514	(r1)
	$(1.2 \pm 0.14) \times 10^{-32}$	298	
Hutton and Wright, 1965 [9]	$(1.2 \pm 0.2) \times 10^{-32}$; M = Ar	298	(r1)
Bader and Ogryzlo, 1964 [6]	1.1×10^{-32}; M = Ar	313	(r1)
Lloyd, 1971 [61] review	$6.0 \times 10^{-34} \exp((900 \pm 250)/T)$; M = Ar	200–500	
Wildman and DeGraff, 1973 [171]	$6.89 \times 10^{-34} \exp((905 \pm 25)/T)$; M = Ar	195–373	(r1)
	$(1.47 \pm 0.18) \times 10^{-32}$	293	
Wildman and DeGraff, 1973 [171]	$1.60 \times 10^{-33} \exp((805 \pm 71)/T)$; M = N_2	293–373	(r2)
	$(2.22 \pm 0.44) \times 10^{-32}$	293	
* Preferred value	$6.32 \times 10^{-34} \exp((903 \pm 55)/T)$; M= Ar	195–514	
	$(1.3 \pm 0.2) \times 10^{-32}$	298	

(r1) For a more critical discussion of the data reported in the references [6], [8] and [9] the reader should consult the review of Lloyd [61]. The results reported near 298 K appear to be in good agreement although some uncertainty exists as to the value reported in reference [6] (consult original paper and reference [61]). k_{20} is defined in this review as: $k_{20} = -0.5\,[M]^{-1}\, d[Cl]^{-1}/dt$. The activation energies reported in references [8] and [117] are in excellent agreement, especially considering the significantly different experimental techniques used (low pressure discharge flow—emission spectroscopy [8], and high pressure flash photolysis—absorption spectroscopy [171]). However, this may be somewhat fortuitous considering the experimental complexities which were associated with the studies (e.g. heterogeneous recombination of atomic chlorine, and thermal effects in the reaction cell due to the exothermicity of the atomic recombination). The preferred value was derived from a least squares treatment of the data reported in references [8] and [171].

(r2) This expression shows that the efficiency of N_2 as the third body is similar in efficiency to Ar. Arrhenius expressions were determined for a wide range of chaperon gases which are not shown in this review (He, Ne, CF_4, SF_6 and CO_2).

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

Reference	Rate constant/cm^3 molecule^{-1} s^{-1}	Temp./K	Note
Bemand, Clyne and Watson, 1973 [5]	$(5.3 \pm 0.8) \times 10^{-11}$	298	(s1)
Bemand, Clyne and Watson, 1973 [5]	$(5.7 \pm 2.3) \times 10^{-11}$	220–295	(s2)
Zahniser and Kaufman, 1977 [129]	$(3.38 \pm 0.5) \times 10^{-11} \exp(+(76 \pm 40)/T)$	295	(s3)
	$(4.4 \pm 0.9) \times 10^{-11}$	220–426	
Clyne and Nip, 1976 [147]	$(1.07 \pm 0.15) \times 10^{-10} \exp(-(224 \pm 38)/T)$	298	(s4)
	$(5.2 \pm 1.6) \times 10^{-11}$	298	
Basco and Dogra, 1971a [19]	1.2×10^{-11}	300	(s5)
Clyne and Coxon, 1966a [18]	$> 1.0 \times 10^{-11}$	300	
Freeman and Phillips, 1968 [55]	$> 1.3 \times 10^{-11}$	300	
Park, 1976 [175]	$(7 \pm 1.5) \times 10^{-11}$	1250	(s6)
* Preferred value	$1.07 \times 10^{-10} \exp(-224/T)$	220–425	(s7)
	$(5.2 \pm 0.5) \times 10^{-11}$	298	

(s1) This value is used in the derivation of the preferred value due to the direct nature and the high specific sensitivity of the study, which utilized atomic resonance fluorescence to monitor atomic oxygen.

(s2) This value was obtained using molecular beam mass spectrometry and is in good agreement with the preferred value. However, the precision of the mass spectrometric technique for this reaction was lower than that of the resonance fluorescence studies.

(s3) This value of k_{21} was obtained relative to k_1 ($Cl + O_3 \rightarrow ClO + O_2$) using a discharge flow tube in conjunction with resonance fluorescence to monitor the ground state $Cl(^2P_{3/2})$ atom concentration, and resonance absorption to monitor the ground state $O(^3P)$ atom concentration, in a chemical system of $O(^3P)$, $Cl(^2P_{3/2})$, ClO ($^2\Pi$) and O_3 which had reached a steady state condition. Due to the competitive nature of the study the uncertainty of k_1 is reflected in the uncertainty limits (+20%) reported for k_{21}. The Arrhenius expression shown in the tables was obtained by combining the experimental ratio of k_{21}/k_1, and the Arrhenius expression reported in reference [94] for k_1. Unfortunately significant discrepancies exist between the various Arrhenius expressions reported for k_1 (see earlier discussion and tables). The measured rate constant ratio, k_{21}/k_1, can be expressed: $k_{21}/k_1 = 1.55 \exp(+(246 \pm 70)/T)$. Although the absolute value of k_{21} is dependent upon the absolute value of k_1 ($Cl + O_3$), the reference reaction, care must be exercised in substituting alternative values for k_1(other than that determined by the same authors [94], in the same apparatus). A measurement of a rate constant ratio should be less susceptible to systematic errors than an individual absolute determination of a rate constant, if the chemistry of the reacting system is fully understood. Consequently, substitution of an alternative Arrhenius expression for k_1 (see discussion on reaction 1) would lead to an expression for k_{22} which may or may not be more accurate. Until the data are published, and studied, this value will not be used to determine the recommended value. The value obtained at 295 K is in good (~20%) agreement with that to be recommended.

(s4) This direct study used a similar chemical system, and similar experimental optical techniques to those reported in reference [5]. The value obtained at 298 K is in excellent agreement with that reported in reference [51]. This Arrhenius expression is recommended for use in model calculations of the stratosphere.

(s5) Data incorrectly analyzed (see reference [51]).

(s6) This value was derived from an experimental determination of k_{21} $(O + ClO)/k_{37}(O + Cl_2)$ at 1250 K. Unfortunately there appears to be great potential for error in this study: (a) the value of k_{37} ($O + Cl_2$) is not well-established at 1250 K (± factor of ~2, see comments concerning reaction 37), indeed Park used a value of 2.7×10^{-12} for k_{37} (1250 K) whereas the "preferred value" given in this review would predict a value of 1.38×10^{-12}, (b) σ_{Cl_2} was determined to be ~ 45% lower than the accepted literature value at 298 K, yet no explanation was forwarded. Consequently, the values reported for σ_{Cl_2} at higher temperatures are questionable; (c) the value of k_{21} is quadratically dependent upon σ_{ClO}, and reported values of σ_{ClO} at high temperatures are possibly questionable. Therefore, the reliability of this determination is no better than a factor of ~ 2–3, and it must be considered fortuitous that the value reported is within 25% of that predicted by Clyne and Nip [147].

(s7) The recommended value at 298 K is based on references [5], [147], and [129]. The Arrhenius expression is that of reference [147], and should be used until new data is published and can be evaluated.

(22) $NO(^2\Pi) + ClO(^2\Pi) \rightarrow NO_2 + Cl(^2P_{3/2})$

Reference	Rate constant/cm^3 molecule^{-1} s^{-1}	Temp./K	Note
Clyne and Watson, 1974 [30]	$(1.7 \pm 0.2) \times 10^{-11}$	298	(t1)
Zahniser and Kaufman, 1977 [129]	$(1.13 \pm 0.14) \times 10^{-11} (+(200 \pm 30)/T)$	230–295	(t2)
	$(2.2 \pm 0.4) \times 10^{-11}$	295	
Coxon, 1968 [16]	$> 3 \times 10^{-13}$	300	
* Preferred value	$(1.9 \pm 0.4) \times 10^{-11}$	298	(t3)

(t1) This is the only direct determination of k_{22}. A study [5] of the NO + OClO reaction yielded an indirect determination of k_{22} which is in good agreement (±25%) with that reported here.

(t2) The value of k_{22} was measured relative to k_1 ($Cl + O_3$) by monitoring steady state concentrations of Cl atoms in the presence of NO and O_3. Consequently, the error limits placed on k_{22} reflect an uncertainty in the value of k_1 ($Cl + O_3$). The actual ratio measured can be expressed:

$$k_{22}/k_1 = 0.52 \exp(+(373 \pm 75)/T)$$

$$k_{22}/k_1 \text{ (298 K)} = 1.85 \pm 0.2.$$

The Arrhenius expression tabulated for k_{22} was obtained using the Arrhenius expression reported in reference [94] for k_1. Read note (s_3), reaction (21), for some relevant comments. The Arrhenius expression reported is unusual for a biomolecular diatomic radical-diatomic radical reaction where a small positive, rather than a small negative value for the activation energy would be expected. Until the results of this study are published and the data examined, the value obtained for k_{22} at 295 K will be used to obtain a preferred value at 298 K but no Arrhenius expression can be recommended.

(t3) A preferred value of $(1.9 \pm 0.4) \times 10^{-11}$ is obtained for k_{22} at 298 K by combining the results in [30] and [129]. The reference rate constant, k_1, is thought to be moderately well established at 298 K, therefore the absolute value forwarded in reference [129] for k_{22} should be reasonably accurate. The agreement between the two results at room temperature is quite good. Recent results are presented and discussed in the Addenda.

(23–24) Reactions of ClO with carbon monoxide and ozone

Reaction/Reference	Rate constant/cm^3 molecule^{-1} s^{-1}	Temp./K	Note
(23) $ClO(^2\Pi) + CO \rightarrow CO_2 + Cl(^2P_{3/2})$			
* Walker, 1972 [17]	$\leq 1.7 \times 10^{-15}$	587	
Harker, 1972 [27]	1.4×10^{-15}	300	(u)
(24) $ClO + O_3 \rightarrow OClO + O_2$			
(24′) $ClO + O_3 \rightarrow ClOO + O_2$			
Clyne and Coxon, 1968 [15]	$\leq 5 \times 10^{-15}$	300	
Clyne, McKenny, Watson, 1974 [24]	$\leq 5 \times 10^{-15}$	298	(v1)
DeMore, Lin and Jaffe, 1975 [114]	$k_{24} \leq 1 \times 10^{-18}$	300	(v2)
	k_{24}' similar to k_{24}	300	(v2)

* Preferred value.

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

(v1) The rate constants reported do not differentiate between the two reaction paths.

(v2) These values were obtained by determining the quantum yield for the removal of ozone in a Cl_2/O_3 reaction mixture.

(25–30) Reaction of ClO with various molecules

Reaction/Reference	Rate constant/cm^3 molecule^{-1} s^{-1}	Temp./K	Note
(25) $ClO + H_2 \rightarrow$ Products			
Walker, 1972 [17]	$\leq 8 \times 10^{-16}$	670	(w)
Clyne and Coxon, 1968 [15]	$\leq 5 \times 10^{-16}$	300	
(26) $ClO + CH_4 \rightarrow$ Products			
Walker, 1972 [17]	$\sim 4 \times 10^{-15}$	670	(w)
(27) $ClO + C_2H_4 \rightarrow$ Products			
Walker, 1972 [17]	$\leq 5 \times 10^{-16}$	670	(w)
(28) $ClO + C_2H_2 \rightarrow$ Products			
Walker, 1972 [17]	$\leq 5 \times 10^{-16}$	670	(w)
(29) $ClO + N_2O \rightarrow$ Products			
Walker, 1972 [17]	$\leq 7 \times 10^{-16}$	587	(w)
(30) $ClO + NH_3 \rightarrow$ Products			
Walker, 1972 [17]	$\leq 5 \times 10^{-16}$	670	(w)

No preferred values for the reactions above.

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

(31–33) Disproportionation reaction of ClO

Reaction/Reference	Rate constant/cm^3 molecule^{-1} s^{-1}.[a]	Temp./K	Note
(31) $ClO + ClO \rightarrow Cl(^2P_{3/2}) + OClO$			
Clyne, McKenny and Watson, 1974 [29]	$\leq 3.2 \times 10^{-15}$	298	(x)
No preferred value			
(32) $ClO + ClO \rightarrow Cl_2 + O_2$			(y1)
(32′) $ClO + ClO \rightarrow Cl + ClOO$			
Porter and Wright, 1953 [24]	$1.52 \times 10^{-13} \exp((0 \pm 325)/T)$	293–433	(y2)
Lipscomb, Norrish and Thrush, 1956 [25]	1.93×10^{-13}	300	(y2,3)
	$3..39 \times 10^{-13}$	300	(y2,4)
Edgecombe, Norrish and Thrush, 1957 [23]	6.57×10^{-14}	300	(y2)
Clyne and Coxon, 1966 [18]	2.33×10^{-14}	300	(y2)
Clyne and Coxon, 1968 [15]	$(1.2 \pm 0.3) \times 10^{-12} \exp(-(1260 \pm 150)/T)$	294–495	(y2)
Clyne and Coxon, 1968 [15]	$(1.0 \pm 0.3) \times 10^{-12} \exp(-(1215 \pm 160)/T)$	294–495	(y5)
Johnston, Morris and Van den Bogaerde, 1969 [26]	1.26×10^{-14}	298	(y2,6)

6.1. Reactions of Chlorine Atoms—Continued

Reaction Reference	Rate constant/cm^3 $molecule^{-1}$ $\cdot s^{-1}$[a]	Temp./K	Note
Clyne and White, 1971 [56]	$(1.3 \pm 0.1) \times 10^{-12} \exp(-(1150 \pm 50)/T)$	237–710	(y2,5)
Basco and Dogra, 1971a,b [19, 20]	4.4×10^{-14}	300	
Walker, 1972 [17]	$(1.9 \pm 0.6) \times 10^{-12} \exp(-(1300 \pm 120)/T)$		(y2)
Clyne, McKenny and Watson, 1974 [29]	$(2.25 \pm 0.3) \times 10^{-14}$	300	(y7)
* Preferred values	$(2.4 \pm 0.4) \times 10^{-14}$ at low pressure	298	(y8)
	4.4×10^{-14} at high pressure ($\geq$ 75 torr)	298	(y8)
	$1.53 \times 10^{-12} \exp(-(1238 \pm 120)/T)$ low pressure	273–170	(y8)
(33) $ClO + ClO + M \rightarrow Cl_2 + O_2 + M$			
Johnston, Morris and Van den Bogaerde, 1969 [26]	1.0×10^{-31} cm^6 $molecule^{-2}$ s^{-1}, $M = O_2$	298	(z1)
	6.6×10^{-32} cm^6 $molecule^{-1}$ s^{-1}, $M = Ar$	298	(z1)
Wu, 1970 [57]	$k_{33}/k_{32} = 1.1 \times 10^{-17}$ cm^3 $molecule^{-1}$	298	(z2)
Walker, 1972 [17]	$(2.0 \pm 2.0) \times 10^{-32}$ cm^6 $molecule^{-2}$ s^{-1}, $M = Ar$	298	(z1,3)
No preferred value			

[a] See definitions of rate constants in notes x, y1, and z1.

(x) This is a provisional experimental upper limit. Using the thermodynamic values reported at the end of this compilation in conjunction with the preferred value for k_2 ($Cl + OClO \rightarrow 2\ ClO$), the following can be calcualted $\log_{10} k_{31} = -15.05 \pm 0.55$. The limits are due to the uncertainty in the value of ΔH_{f298} (OClO). Rate constant is defined for $-d[ClO]/dt = k[ClO]^2$.

(y1) The high pressure ($\geq$ 75 torr) results indicate that all the reaction proceeds via reaction 32, whilst the low pressure (1-3 torr) results indicate that the ratio $k_{32}/k_{32'} \sim$ unity. Rate constants defined for $-d[ClO]/dt = k[ClO]^2$.

(y2) Clyne and Coxon's (1968) [15] value for the absorption cross section was used to calculate k_{32}.

(y3) k_{32} was reported to be flash energy dependent, due to the reaction mechanism being misinterpreted. Low flash energy.

(y4) High flash energy.

(y5) Clyne and White (1971) [56] reanalyzed the data to allow for any third order decay of ClO. Clyne and White used a heated flow reactor in conjunction with the fixed observation point (outside the heated region) technique, to study this bimolecular disproprotionation reaction. Westenberg [97] correctly pointed out that this technique is not strictly valid for studying such reactions. However, the error caused in the measured rate constant should be minimal (<10%) as virtually all the reaction occurred in the high temperature region, and little in the lower (~298 K) observation point region. In addition, it should be mentioned that the results of this study are in good agreement with the earlier (less accurate) results of Clyne and Coxon [15].

(y6) This value was derived by combining their value of k_{13} with the thermodynamic value of $K_2 = 109 = k_{13}/0.5\ k_{32}$. Neither k_{13} 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 ΔH_f (ClOO) = 86 and 96 kJ mol^{-1}. See also remarks for reaction 40.

(y7) This is the only published study not to use an optical spectroscopic method.

(y8) The preferred value for k_{32} at 298 K is: $-d[ClO]/dt = k_{32}[ClO]^2$. (a) $(2.4 \pm 0.4) \times 10^{-14}$ (low pressure)—derived from references [15], [18], [29], and [56]. (b) 4.4×10^{-14} (high pressure)—derived from references [19] and [20]. 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)

(z1) This value of k_{33} is defined as: $-d[ClO]/dt = k_{33}[ClO]^2[M]$. These results disagree completely with those reported by Basco and Dogra [19], where no pressure dependence was observed for the bimolecular disproportionation of ClO.

(z2) This value is only accurate to within a factor of two.

(z3) This value was derived using data from Clyne and Coxon (1968); Clyne and White (1971) and Walker (1972). The slope of $-d[ClO]/dt$ versus [M] was positive but within the error limits of being zero.

(34–35) Reactions of ClO with BrO

Reference	Rate constant/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Note
(34) $ClO\ (^2\Pi) + BrO\ (^2\Pi) \rightarrow Br + Cl + O_2$			
(35) $ClO\ (^2\Pi) + BrO\ (^2\Pi) \rightarrow Br + OClO$			
Basco and Dogra, 1971 [21]	$k_{34} = 2.5 \times 10^{-12}$	300	(A1)
* Clyne and Watson, 1977 [108]	$k_{34} = (6.7 \pm 1.0) \times 10^{-12}$	300	(A2)
	$k_{35} = (6.7 \pm 1.0) \times 10^{-12}$	300	(B)

* Preferred values.

(A1) This value must be rejected due to an erroneous analysis of the kinetic data. In addition, these authors believe the reaction products to be $BrCl + O_2$.

(A2) There is no direct evidence that the reaction products are atomic, but by analogy to $BrO + BrO \rightarrow 2Br + O_2$ [112] ,and $ClO + ClO \rightarrow Cl + 1/2Cl_2 + O_2$ (see earlier) it is quite probable. The reaction system was not as simple as would be ideal, but the concentration profiles of reactants and products were in good agreement when explained by reactions (34), (35), (36) and ($BrO + BrO \rightarrow 2BrO$).

(B) Basco and Dogra [110] did not identify this reaction process, mainly due to the experimental technique used.

(36) $Br(^2P_{3/2}) + OClO \rightarrow BrO + ClO$

Reference	Rate constant/cm^3 molecule^{-1} s^{-1}	Temp./K	Note
* Clyne and Watson, 1975 [108]	$(4.2\,^{+0.8}_{-0.4}) \times 10^{-13}$	300	(C)
Clyne and Coxon, 1967 [121]	$(5.2 \pm 0.5) \times 10^{-14}$	300	

* Preferred value.

(C) This value is preferred as the data were obtained using pseudo first order conditions. The data analysis was not as simple as usual due to the rapid reverse reaction (35). Therefore, reaction 35 had to be suppressed; this was not recognized in the study of Clyne and Coxon who measured k_{36} using high concentrations of Br atoms and OClO under second order kinetic conditions.

(37) $O + Cl_2 \rightarrow ClO + Cl(^2P_{3/2})$

Reference	Rate constant/cm^3 molecule^{-1} s^{-1}	Temp./K	Note
Clyne and Coxon, 1966b [32]	$(9.32 \pm 2.2) \times 10^{-12} \exp(-(1560 \pm 50)/T)$	174–396	(D2)
	5.1×10^{-14}	300	(D1)
Niki and Weinstock, 1967 [31]	$(7.5 \pm 0.6) \times 10^{-14}$	300	(D1)
Bradley, Whytock and Zaleski, 1973 [106]	$1.03 \times 10^{-11} \exp(-1804/T)$	295–461	(D2)
	2.43×10^{-14}	298	(D1)
Clyne, Monkhouse, and Townsend, 1976 [92]	$(2.03 \pm 0.9) \times 10^{-12} \exp(-(1128 \pm 279)/T)$	299–602	(D2)
	$(4.84 \pm 0.53) \times 10^{-14}$	299	(D1)
	$(4.15 \pm 1.9) \times 10^{-12} \exp(-(1368 \pm 134)/T)$	174–602	(D3)
	4.2×10^{-14}	298	(D3)
* Preferred value	$(4.15 \pm 1.9) \times 10^{-12} \exp(-(1368 \pm 134)/T)$	174–602	
	4.2×10^{-14}	298	

(D1) All four studies were performed using discharge flow systems, but with different detection techniques. The agreement is rather poor, except between the two values measured by Clyne et al. At present the cause of this discrepancy is not evident. The mean of the four results yields a value of 5.0×10^{-14}, in agreement with two values of Clyne et al.

(D2) The Arrhenius expressions show considerable variance between the reported activation energies.

(D3) This Arrhenius expression was derived by Clyne et al. [92] using all the published results from the four studies reported in this review. This value should be taken as the preferred one, as the differences between the various results cannot be explained. $k_{37} = (4.15 \pm 1.9) \times 10^{-12} \exp(-(1368 \pm 134/T))$.

(38) $HO + HCl \rightarrow H_2O + Cl\,(^2P_{3/2})$

Reference	Rate constant/cm^3 molecule^{-1} s^{-1}	Temp./K	Note
Takacs and Glass, 1973 [46]	$(6.4 \pm 1.5) \times 10^{-13}$	295	(E1)
Anderson, Zahniser and Kaufman, 1974 [36]	$(2.0 \pm 0.1) \times 10^{-12} \exp(-(312 \pm 10)/T)$	225–460	(E1)
	$(6.7 \pm 0.4) \times 10^{-13}$	297	
Smith and Zellner, 1974 [39]	$(4.1\,^{+2.0}_{-1.4}) \times 10^{-12} \exp(-(528 \pm 25)/T)$	210–460	(E1)
	$(6.9 \pm 1.0) \times 10^{-13}$	298	
Ravishankara, Smith, Watson and Davis, 1977 [168]	$(3.25 \pm 0.3) \times 10^{-12} \exp(-(473 \pm 39)T)$	250–402	(E1)
	$(6.65 \pm 0.39) \times 10^{-13}$	298	
Davis, Schiff and Fischer, 1975 [109]	$(6.5 \pm 0.4) \times 10^{-13}$	300	(E1)
Wilson, O'Donovan, and Fristrom, 1976 [60]	1.3×10^{-11}	1920–1240	(E2)
Wong and Belles, 1972 [58]	Estimated $E_a = 21$ kJ mol^{-1}		(E3)
*Preferred value	$2.96 \times 10^{-12} \exp(-(425 \pm 50)/T)$	220–300	
	$(6.6 \pm 0.6) \times 10^{-13}$	298	

(E1) There is good agreement between these five groups of workers at 298 K, and the preferred value at this temperature is the average of the five and equal to $(6.6 \pm 0.6) \times 10^{-13}$. The preferred Arrhenius expression for the (220–300)K temperature range is: $^*k_{38} = 2.96 \times 10^{-12} \exp(-425 \pm 50/T)$. This Arrhenius expression was derived by giving equal weighting to data reported in reference [36], [39] and [168].

(E2) This value is greater than would be predicted at 1920 K from the Arrhenius expression forwarded in this review.

(E3) This value for the activation energy was estimated from the production of H_2O in the $O + HCl$ study, and must be rejected.

(39) $O + HCl \rightarrow OH + Cl(^2P_{3/2})$

Reference	Rate constant/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Note
Balakhnin, Egorov and	$(1.75 \pm 0.6) \times 10^{-12} \exp(-(2260/T)$	295–371	(F)
Interzarova, 1971 [45]	9.36×10^{-16}	300	
Wong and Belles, 1972 [58]	$(1.9 \pm 0.27) \times 10^{-11} \exp(-(3584 \pm 70)/T)$	356–628	(F)
	1.23×10^{-16}	300	
Brown and Smith, 1975 [93]	$2.5 \times 10^{-12} \exp-(2970/T)$	293–440	(F)
	1.3×10^{-16}	300	
Ravishankara, Smith, Watson and	$(5.2 \pm 0.9) \times 10^{-11} \exp(-(3755 \pm 400)/T)$	350–454	(F)
Davis, 1977 [168]	1.90×10^{-16}	298	

No preferred value (see addenda).

(F) There exists fair agreement between the results of Brown and Smith, Wong and Belles, and Ravishankara et al. at 300 K, but these are a factor of ~ 7 lower than that of Balakhnin et al. Unfortunately all four Arrhenius expressions are in complete disagreement and it is not possible at present to explain this discrepancy. The results of Brown and Smith, Wong and Belles and Ravishankara et al. would predict that this reaction is of little importance to stratospheric chlorine chemistry, whereas if the results of Balakhnin et al. are correct then this reaction must be considered above 40 km. None of the workers measured k_{39} at stratospheric temperatures due to the slow nature of the reaction. Although no preferred value is forwarded it is suggested that this reaction be neglected in stratospheric model calculations.

(40) $ClOO + M \rightarrow Cl(^2P_{3/2}) + O_2 + M$

There is no experimental determination of k_{40}, but a value can be calculated from the thermodynamic value of $K_2^* = k_{40}/k_3$, and the experimental value of k_3. However, neither K_2^* nor k_3 are particularly well-known. The recommended value for ΔH°_{f298} ClOO has been calculated to be 89.2 kJ mol^{-1} [76], however the uncertainty is thought to be ± 5 kJ mol^{-1} [59]. The rate constant for reaction 40, k_{40}, can be represented by the following expressions:

(a) $k_{40} = 1.89 \times 10^{-9} \exp(-(3581 \pm 11)/T)$; K_2^* was calculated using a value of 89.2 kJ mol^{-1} for ΔH°_{f298} ClOO. k_3 was taken to be temperature independent, and equal to 5.6×10^{-34} cm^6 $molecule^{-2}$ s^{-1} (reference [11]). If k_3 is taken to be 1.7×10^{-33} cm^6 $molecule^{-2}$ s^{-1} (reference [22]), then the pre-exponential A factor should be increased by a factor of 3.04.

(b) $k_{40} = 1.95 \times 10^{-9} \exp(-(4191 \pm 35)/T)$; K_2^* was calculated using a value of 84.2 kJ mol^{-1} for ΔH°_{f298} ClOO. k_3 was taken from reference [11]. Multiply the pre-exponential A factor by a factor of 3.04 if k_3 is taken from reference [22].

Whilst expression (a) is thought to be the best estimate of k_{40}, using expression (b) would predict the maximum possible [ClOO]/[Cl] ratio. The following table shows values of K_2^* and k_{40} ($k_3 = 5.6 \times 10^{-34}$ cm^6 $molecule^{-2}$ s^{-1}) that would be calculated (not from the Arrhenius expressions) at various altitudes.

Elevation	Temperature	K_2/atm		k_{40}/cm^3 $molecule^{-1}$ s^{-1}	
km	K	ΔH°_f ClOO = 89.22 kJ mol^{-1}	ΔH°_f ClOO = 84.2 kJ mol^{-1}	ΔH°_f ClOO = 89.22 kJ mol^{-1}	ΔH°_f ClOO = 84.2 kJ mol^{-1}
0	298.15	0.8292	0.1094	1.14×10^{-14}	1.51×10^{-15}
18	216.7	0.00655	0.0004099	1.24×10^{-16}	7.78×10^{-18}
23	219.6	0.00838	0.000536	1.57×10^{-16}	1.00×10^{-17}
28	224.5	0.01224	0.0008309	2.24×10^{-16}	1.52×10^{-17}
33	231.1	0.01988	0.001457	3.54×10^{-16}	2.59×10^{-17}
38	244.8	0.05009	0.004251	8.42×10^{-16}	7.14×10^{-17}
43	258.6	0.1154	0.01171	1.84×10^{-15}	1.86×10^{-16}
48	270.7	0.2239	0.02406	3.40×10^{-15}	3.66×10^{-16}

(41–45) Reactions of OClO and Cl_2O which form ClO Radicals

Reference	Rate constant/cm^3 $molecule^{-1}$ s^{-1}	Temp./K	Note
(41) $O(^3P) + OClO \rightarrow ClO + O_2(^3\Sigma^-_g)$			
* Bemand, Clyne and Watson, 1973 [5]	$(5^{+1}_{-2}) \times 10^{-13}$	298	(H1)
Basco and Dogra, 1971 [21]	5.0×10^{-11}	300	(H2)
Clyne and Coxon, 1966a [18]	$> 4.0 \times 10^{-11}$	300	(H2)
(42) $NO + OClO \rightarrow NO_2 + ClO$			
* Bemand, Clyne and Watson, 1973 [5]	$(3.4 \pm 0.5) \times 10^{-13}$	298	
Coxon, 1968 [16]	$> 8.5 \times 10^{-13}$	300	(I)

6.1. Reactions of Chlorine Atoms—Continued

Reference	Rate constant/cm^3 molecule^{-1} s^{-1}	Temp./K.	Note
(43) $N(^4S) + OClO \rightarrow NO + ClO$			
Watson, 1973 [59]	$\leq 6 \times 10^{-13}$	298	(J)
(44) $H(^2S) + OClO \rightarrow OH + ClO$			
* Bemand, Clyne and Watson, 1973 [5]	$(5.7 \pm 1.2) \times 10^{-11}$	298	
(45) $O + Cl_2O \rightarrow ClO + ClO$			
* Freeman and Phillips 1968 [55]	$(1.4 \pm 0.2_3) \times 10^{-11}$	300	
Basco and Dogra, 1971 [19]	8.67×10^{-12}	300	

* Preferred values

(H1) This value was determined from two separate direct studies. (a) Mass Spectrometry: $(4.7 \pm 1.6) \times 10^{-13}$. (b) Atomic reasonance fluorescence: $(6.3 \pm 1.9) \times 10^{-13}$.

(H2) This value must be rejected due to an error in the data analysis, (see ref [5]).

(I) This value must be rejected due to an error in the data analysis, (see ref [5]).

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

6.3. Reactions of Halogenated Organic Compounds

(46–52) Reactions of $O\ (^1D)$ with halogenated alkanes

Reference	Rate constant/cm^3 molecule^{-1} s^{-1}	Temp./K	Note
(46) $O\ (^1D) + CCl_4 \rightarrow CCl_3 + ClO$			
Jayanty, Simonaitis, and Heicklen, 1975 [98]	2.44×10^{-10} (a)	298	(K1) (K2)
	1.99×10^{-10} (b)	298	(K1) (K2)
* Preferred value	3.54×10^{-10}	298	(K4)
(47) $O\ (^1D) + CFCl_3 \rightarrow CFCl_2 + ClO$			
Jayanty, Simonaitis, and Heicklen, 1975 [98]	1.77×10^{-10} (a)	298	(K1) (K2)
	1.50×10^{-10} (b)	298	(K1) (K2)
Pitts, Sandoval and Atkinson, 1974 [99]	$(3.1 \pm 0.6) \times 10^{-10}$	296	(K1) (K3)
* Preferred value	$(2.44 \pm 0.9) \times 10^{-10}$	298	(K4)
(48) $O\ (^1D) + CF_2Cl_2 \rightarrow CF_2Cl + ClO$			
Jayanty, Simonaitis, and Heicklen, 1975 [98]	1.39×10^{-10} (a)	298	(K1) (K2)
	1.05×10^{-10} (b)	298	(K1) (K2)
Pitts, Sandoval and Atkinson, 1974 [99]	$(2.84 \pm 0.5) \times 10^{-10}$	296	(K1) (K3)
* Preferred value	$(2.12 \pm 1.0) \times 10^{-10}$	298	(K4)
(49) $O\ (^1D) + CF_3Cl \rightarrow CF_3 + ClO$			
Jayanty, Simonaitis and Heicklen, 1975 [98]	0.59×10^{-10}	298	(K1) (K2)
* Preferred value	0.86×10^{-10}	298	(K4)
(50) $O\ (^1D) + CF_2ClCF_2Cl \rightarrow CF_2ClCF_2 + ClO$			
Pitts, Sandoval and Atkinson, 1974 [99]	$(1.77 \pm 0.3) \times 10^{-10}$	296	(K1) (K3)
* Preferred value	1.36×10^{-10}	296	(K4)
(51) $O\ (^1D) + CHF_2Cl \rightarrow CHF_2 + ClO$			
Pitts, Sandoval and Atkinson, 1974 [99]	$(1.88 \pm 0.3) \times 10^{-10}$	296	(K4)
* Preferred value	1.45×10^{-10}	296	(K4)
(52) $O\ (^1D) + CF_2ClCFCl_2 \rightarrow C_2F_3Cl_2 + ClO$			
Pitts, Sandoval and Atkinson, 1974 [99]	$(2.95 \pm 0.5) \times 10^{-10}$	296	(K1) (K3)
* Preferred value	2.26×10^{-10}	296	(K4)

* All preferred values are tentative (see Addenda for reactions (47) and 48)).

(K1) The values shown in the tables have been modified. The authors of the original papers used values of 2.2×10^{-10} for $k\ (O\ (^1D) + N_2O$ [98], [99], and 0.74×10^{-10} for $k\ (O\ (^1D) + O_2)$ [98], (these values were taken from Cvetanovic's evaluations [143], which were heavily weighted towards the absolute rate constant data published by Heidner and Husain [144]), for the primary reference rate constants. However, a recent kinetic investigation of $O\ (^1D)$ reactions reported rate constants of 1.1×10^{-10} and 0.37×10^{-10} for $O\ (^1D) + N_2O$, and $O\ (^1D) + O_2$, respectively [145]. The values tabulated in this review for $O\ (^1D)$ reactions have used recent values of $O\ (^1D) + N_2O$, and $O\ (^1D) + O_2$ as the primary reference standards.

(K2) These rate constants were obtained in a competitive study, where ozone photolysis at ~260 nm was used as the source of $O\ (^1D)$, relative to: (a) k_{N_2O}, by monitoring the production of N_2 as a function of $[CF_xCl_y]/[N_2O]$, and (b) k_{O_2}, by monitoring the decay of ozone as a function of $[CF_xCl_y]/[O_2]$. To show that the data did not contain a systematic error a competitive study between N_2O and CO_2 was performed which yielded results in fair agreement with the literature. By monitoring the quantum yield for the removal of ozone in an O_3/CF_xCl_y mixture it was shown that the dominant primary process was the formation of ClO. The authors claimed that the results were reliable as data sets (a) and (b) agreed to within (10–15)% based on Cvetanovic's evaluations of $k(O\ (^1D) + N_2O)$ and $k(O\ (^1D) + O_2)$. When the reference rate constants used are those reported by Davidson et al. [145], the agreement between the two sets of data ((a) and (b)) remains at (10–15)%.

(K3) These rate constants were obtained relative to k_{N_2O} by measuring $\Delta N_2O/\Delta\ CF_xCl_y$ as a function of $[N_2O]/[CF\ Cl_y]$ using I.R. spectroscopy. The O (^1D) + neopentane reaction was used as the reference standard reaction, but the literature results vary by a factor of 2 which invalidates its usefulness as a method of indicating the system is free from systematic inaccuracies.

(K4) Unfortunately the results of the two groups of workers differ by a factor of 2 which is difficult to explain. Until further results are published (preferably using a direct technique) it is recommended that a mean value of the rate constants reported in references [98] and [99] be used in model calculations. Only data collected relative to $k(O\ (^1D) + N_2O)$ has been considered (data set (a) in reference [98]). The preferred values for reactions (47) and (48), where two separate groups measured the rate constants relative to k_{N_2O}, were obtained by taking a direct average of the two. The preferred values for reactions (46) and (49) were obtained by scaling the rate constant reported in reference [98] by 1.45 (the average ratio of k_{47}/k_{47}^* and k_{48}/k_{48}^*, where k_{47} and k_{48} were the rate constants reported in reference [98], and k_{47}^*, and k_{48}^* were the preferred rate constants. Similarly the preferred values for reactions (50), (51) and (52) were obtained by scaling the rate constants reported in reference [99] by 0.77 (the average ratio of k_{47}/k_{47}^* and k_{48}/k_{48}^*).

(53) $OH + CH_3Cl \rightarrow CH_2Cl + H_2O$

Reference	Rate constant/cm³ molecules⁻¹ s⁻¹	Temp./K	Note
Davis, Hogan and Oh, 1975 [100]	$(4.5 \pm 0.9) \times 10^{-14}$	298	(L1)
Howard and Evenson, 1975 [101]	$(3.6 \pm 0.8) \times 10^{-14}$	298	(L1)
Davis, Machado, Conaway, Oh, and Watson, 1976 [104]	$(1.84 \pm 0.18) \times 10^{-12} \exp(-(1097 \pm 35)/T)$	240–400	(L2)
	$(4.3 \pm 0.2) \times 10^{-14}$	298	(L1)
Perry, Atkinson, and Pitts, Jr. 1976 [127]	$4.1 \times 10^{-12} \exp(-(1359 \pm 150)/T)$	298–422	(L2)
	$(4.4 \pm 0.5) \times 10^{-14}$	298	(L1)
* Preferred value	$(2.18 \pm 0.5) \times 10^{-12} \exp(-(1142 \pm 67)/T)$	240–422	(L3)
	$(4.2 \pm 0.4) \times 10^{-14}$	298	

(L1) These results were obtained using three different experimental techniques, and are in good agreement at 298 K. The preferred value of $(4.2 \pm 0.4) \times 10^{-14}$ is the mean of these studies.

(L2) Within the temperature range covered by both studies (298–400 K) the results agree to within 20%. However, the value of k_{55} obtained by using the Arrhenius expression of reference [127] at 240 K would be ~40% lower than the value obtained directly at that temperature by reference [104].

(L3) The preferred value was obtained from a least squares fit to the data in reference [104] and [127]. Equal weighting was given to each of the bimolecular rate constants (3 from [127] and 5 from [104]).

(54–55) Reactions of hydroxyl with methylene chloride and chloroform

Reaction/Reference	Rate constant/cm³ molecule⁻¹ s⁻¹	Temp./K	Note
(54) $OH + CH_2Cl_2 \rightarrow CHCl_2 + H_2O$			
Davis, Hogan and Oh, 1975 [100]	$(1.5 \pm 0.4) \times 10^{-13}$	298	(M1)
Howard and Evenson, 1976 [101]	$(1.5_5 \pm 0.34) \times 10^{-13}$	298	(M1)
* Davis, Machado, Conaway, Oh, and Watson, 1976 [104]	$(4.3 \pm 0.6) \times 10^{-12} \exp(-(1094 \pm 81)/T)$	245–375	
	$(1.16 \pm 0.05) \times 10^{-13}$	298	(M1)
Perry, Atkinson, and Pitts, Jr. 1976 [127]	$(1.45 \pm 0.2) \times 10^{-13}$	298	
* Preferred value	$(1.4 \pm 0.2) \times 10^{-13}$	298	
(55) $OH + CHCl_3 \rightarrow CCl_3 + H_2O$			
Howard and Evenson, 1976 [101]	$(1.01 \pm 0.15) \times 10^{-13}$	298	(N1)
* Davis, Machado, Conaway, Oh, and Watson, 1976 [104]	$(4.69 \pm 0.7) \times 10^{-12} \exp(-(1134 \pm 107)/T)$	245–375	
	$(1.14 \pm 0.07) \times 10^{-13}$	298	(N1)
* Preferred value	$(1.06 \pm 0.15) \times 10^{-13}$	298	

(M1) The agreement between these results is moderately good, consequently, the preferred rate constant at 298 K is a simple mean of the four values: k_{54} (298 K) = $(1.4 \pm 0.2) \times 10^{-13}$.

(N1) The results of Davis et al. were obtained using two different batches of $CHCl_3$; (a) contained no additive, (b) contained a small quantity of C_2H_5OH (0.75% in the liquid phase). There was no observable dependence upon the rate of decay of hydroxyl radicals with either batch of $CHCl_3$. Consequently, it is felt that the small C_2H_5OH impurity did not adversely affect the interpretation of the kinetic decay data. in addition, the agreement between the results of the two studies is excellent, with a mean value of $(1.0_6 \pm 0.1_5) \times 10^{-13}$ for k_{55} (298 K).

(56–60) Reactions of hydroxyl with fluorochloromethane, difluorochloromethane and fluorodichloromethane, trichlorofluoromethane, dichlorodifluoromethane.

Reaction/Reference	Rate constant/cm³ molecules⁻¹ s⁻¹	Temp./K	Note
(56) $OH + CH_2ClF \rightarrow CHClF + H_2O$			
Howard and Evenson, 1976 [101]	$(3.7 \pm 0.5) \times 10^{-14}$	298	(O)
* Watson, Machado, Conaway, Wagner, and Davis, 1977 [123]	$(2.84 \pm 0.3) \times 10^{-12} \exp(-(1259 \pm 50)/T)$	245–375	
	$(4.42 \pm 0.6) \times 10^{-14}$	298	(O)
* Preferred value	$(4.1 \pm 0.6) \times 10^{-14}$	298	

6.1. Reactions of Chlorine Atoms—Continued

Reaction Reference	Rate constant/cm^3 molecule^{-1} s^{-1}	Temp./K.	Note
(57) OH + $CHF_2Cl \rightarrow CF_2Cl + H_2O$			
Howard and Evenson, 1976 [101]	$(3.4 \pm 0.7) \times 10^{-15}$	298	(P1)
Watson, Machado, Conaway, Wagner, Davis,	$(9.25 \pm 1.0) \times 10^{-13} \exp(-(1575 \pm 71)/T)$	250–350	
1977 [123]	$(4.84 \pm 0.3) \times 10^{-15}$	298	(P1)
Atkinson, Hansen and Pitts, 1975 [115]	$1.21 \times 10^{-12} \exp(-(1636 \pm 151)/T)$	297–434	
	4.75×10^{-15}	297	(P1)
* Preferred value	$(1.21 \pm 0.17) \times 10^{-12} \exp(-(1648 \pm 75)/T)$	250–434	(P2)
	$(4.3 \pm 0.8) \times 10^{-15}$	298	
(58) OH + $CHFCl_2 \rightarrow CFCl_2 + H_2O$			
Howard and Evenson, 1976 [101]	$(2.6 \pm 0.4) \times 10^{-14}$	298	(Q1)
Watson, Machado, Conaway, Wagner and Davis	$(1.87 \pm 0.2) \times 10^{-12} \exp(-(1245 \pm 26)/T)$	245–375	(Q1)
1977 [123]	$(2.88 \pm 0.3) \times 10^{-14}$	298	(Q1)
Perry, Atkinson, and Pitts, Jr. 1976 [127]	$1.75 \times 10^{-12} \exp(-(1253 \pm 150)/T)$	298–423	(Q1)
	$(2.7 \pm 0.3) \times 10^{-14}$	298	
* Preferred value	$(1.59 \pm 0.2) \times 10^{-12} \exp(-(1204 \pm 70)/T)$	245–423	(Q2)
	$(2.8 \pm 0.3) \times 10^{-14}$	298	
(59) OH + $CFCl_3 \rightarrow$ Products			
Atkinson, Hansen and Pitts, 1975 [115]	$< 1 \times 10^{-15}$	297–434	(R)
(60) OH + $CF_2Cl_2 \rightarrow$ Products			
Atkinson, Hansen and Pitts, 1975 [115]	$< 1 \times 10^{-15}$	297–434	(R)

(O) The agreement between these two studies is good, and the preferred value at 298 K was obtained by taking the mean of the two results.

(P1) The results of Watson et al. and Atkinson et al. are in excellent agreement at 298 K, and so are the overall Arrhenius expressions. The value of k_{57} (298 K) from the work of Howard and Evenson is ~25% lower than the other values, but should be considered to be in good agreement. A preferred value of $(4.3 \pm 0.8) \times 10^{-15}$ is obtained for k_{57} (298 K) by taking the mean of the three results.

(P2) A least squares fit of the bimolecular rate constants reported in references [115] and [123] (equal weighting given to all data) was used to obtain the preferred Arrhenius expression.

(Q1) These three studies are in good agreement at 298 K. The preferred value is an average.

(Q2) A least squares fit of the bimolecular rate constants reported in references [123] and [127] (equal weighting given to all data) was used to obtain the preferred Arrhenius expression.

(R) As expected no removal of hydroxyl was observed.

(61–68) Reactions of hydroxyl with saturated C_2 halocarbons

Reaction/Reference	Rate constant/cm^3 molecules^{-1} s^{-1}	Temp./K	Note
(61) OH + $C_2H_5Cl \rightarrow C_2H_4Cl + H_2O$			
Howard and Evenson, 1976 [124]	$(3.9 \pm 0.7) \times 10^{-13}$	298	
(62) OH + $CH_2ClCH_2Cl \rightarrow CHClCH_2Cl + H_2O$			
Howard and Evenson, 1976 [124]	$(2.2 \pm 0.5) \times 10^{-13}$	298	
(63) OH + $CHCl_2CH_3 \rightarrow C_2H_3Cl_2 + H_2O$			
Howard and Evenson, 1976 [124]	$(2.6 \pm 0.6) \times 10^{-13}$	298	
(64) OH + $CH_3CCl_3 \rightarrow CH_2CCl_3 + H_2O$			
Howard and Evenson, 1976 [124]	$(1.5 \pm 0.3) \times 10^{-14}$	298	(S)
* Watson, Machado, Conaway, Wagner and Davis			
1977 [123]	$(3.72 \pm 0.4) \times 10^{-12} \exp(-(1627 \pm 50)/T)$	260–375	(S)
	$(1.59 \pm 0.2) \times 10^{-14}$	298	
(65) OH + $CH_3CF_2Cl \rightarrow CH_2CF_2Cl + H_2O$			
Howard and Evenson, 1976 [124]	$(2.8 \pm 0.4) \times 10^{-15}$	298	(T)
* Watson, Machado, Conaway, Wagner and Davis,	$(1.15 \pm 0.15) \times 10^{-12} \exp(-(1748 \pm 30)/T)$	273–375	
1977 [123]	$(3.11 \pm 0.3) \times 10^{-15}$	298	(T)
(66) OH + $CH_2ClCF_3 \rightarrow CHClCF_3 + H_2O$			
Howard and Evenson, 1976 [124]	$(1.05 \pm 0.23) \times 10^{-14}$	298	
(67) OH + $CF_2ClCF_2Cl \rightarrow$ Products			
Howard and Evenson, 1976 [124]	$< 5 \times 10^{-15}$	298	(U)
(68) OH + $CFCl_2CF_2Cl \rightarrow$ Products			
Howard and Evenson, 1976 [124]	$< 3 \times 10^{-16}$	298	(U)
* Watson, Machado, Conaway, Wagner and Davis,			
1977 [123]	$< 3 \times 10^{-16}$	298	(U)

(S) Excellent agreement. Considerable care must be exercised in order to ensure purity of CH_3CCl_3. All additives must be removed by distillation. A preferred value of 1.55×10^{-14} is obtained for k_{64} (298 K).

(T) Good agreement exists between the results of the two studies. A preferred values of $(2.95 \pm 0.3) \times 10^{-15}$ is obtained from the mean of the results at 298 K. Again it is essential to check gas purity by sensitive analytical techniques.

(U) No observable reaction, as expected.

(69–71) Reactions of hydroxyl with unsaturated C_2 halocarbons

Reference	Rate constant/cm^3 molecule^{-1} s^{-1}	Temp./K	Note
(69) $OH + CH_2{=}CHCl + M \rightarrow CH_2CHClOH + M$			
Howard and Evenson, 1976 [110]	$\sim 5.8 \times 10^{-12}$	298	(V)
(70) $OH + CCl_2{=}CCl_2 + M \rightarrow C_2Cl_4OH + M$			
Howard and Evenson, 1976 [110]	$(1.7 \pm 0.34) \times 10^{-13}$	298	(W1)
Davis, Machado, Smith, Wagner, and Watson, 1977 [136]	$(1.06 \pm 0.5) \times 10^{-11} \exp(-(1295 \pm 150)/T)$	250–375	(W2)
	$(1.55 \pm 0.15) \times 10^{-13}$	298	
(71) $OH + CHCl{=}CCl_2 + M \rightarrow C_2HCl_3OH + M$			
Davis, Machado, Smith, Wagner, and Watson, 1977 [136]	$(2.35 \pm 0.25) \times 10^{-12}$	298	(Y1)
* Chang and Kaufman, 1977 [170)	$(5.2 \pm 0.9) \times 10^{-13} \exp(+(450 \pm 50)/T)$	234–357	(Y2)
	2.37×10^{-12}	296	
* Preferred value	$(2.36 \pm 0.25) \times 10^{-12}$	297	

(V) This study was performed using the low pressure discharge flow technique which is not ideally suited to the study of intermediate 2nd–3rd order reactions (pressure fall-off region). The high pressure limit was reached at ~ 3 torr (He). The rate constant shown represents the bimolecular high pressure limit.

(W1) See note (V). The high pressure limit was reached at ~ 1 toor (He).

(W2) The value at 298 K is in good agreement with that reported by reference [123]. The reaction was studied at total pressures ranging from (10–200) torr with He as the carrier gas. There was no observable dependance of k_{70} upon total pressure, indicating that the high pressure limit is attained at quite low total pressure ($<$ 10 torr). However, this value is still provisional and subject to modification.

(Y1) No observable pressure dependance (40–200) torr with He as the diluent gas.

(Y2) Excellent agreement with the value reported in reference [123]. The rate constant was observed to be independent of total pressure (2–6) torr (high pressure limit).

7. Optical Absorption Cross Sections

The absorption cross sections reported in this review are expressed in units of cm^2 molecule^{-1}, whereby σ is defined in the following Beer's Law expression:

$$\ln_e (I_0/I_t) = \sigma c l,$$

σ: absorption cross section, cm^2 molecule^{-1},

c: concentration, molecule cm^{-3},

l: absorption pathlength, cm.

All spectra discussed are essentially broad band continua, where σ is insensitive to the experimental spectral band width.

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

Seery and Britton, 1964 [62](a).

(a) The authors reported that each measurement was accurate to within $\pm 2.0 \times 10^{-21}$ cm^2 molecule^{-1}. These results are in good agreement with those reported by Gibson and Bayliss [182], and Fergusson, Slotin, and Style [162].

(73) 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}		
	[63,74]	[132] *	[75]		[63,74]	[132] *	[75]
140.0	144	211	~223	175.0	85	109	
2.5	184	251		7.5	65	80.8	
5.0	225	281		180.0	48	58.8	~77
7.5	269	324		2.5	33	43.2	
150.0	308	345	~354	5.0	25	31.3	
2.5	335	372		7.5	17.5	21.5	
5.0	333	382		190.0	12.2	14.5	
7.5	298	347		5.0	5.5	6.18	
160.0	263	332	~320	200.0	2.04	2.56	
2.5	230	297		5.0	1.05	0.983	
5.0	195	248		210.0		.395	
7.5	165	204		5.0		.137	
170.0	133	163	~185	220.0		.048	
2.5	107	131					

Romand and Vodar, 1948, [63] (b1).
Romand, 1949, [74] (b1).
* Inn, 1976, [132] (preferred) (b2).
Myer and Samson, 1790, [75] (b3).

(b1) The absorption cross-sections reported by these workers are in fair agreement (10–40%) with those reported by Inn [132]. These two studies are in agreement at wavelengths of importance (>180 nm) for calculating stratospheric *J* values. The values shown in the tables are deduced by interpolating between the reported experimental data points.

(b2) Preferred value.

(b3) The values shown in the table have been estimated from figure 3 (reference 75), and are in good agreement with those reported by Inn [132] at wavelengths shorter than 180 nm. At wavelengths below 135 nm transitions to the *B* and *C* resonance Rydberg states were observed.

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

λ/nm	$10^{18} \times \sigma$/cm^2 molecule^{-1}	λ/nm	$10^{18} \times \sigma$/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

Johnston, Morris, and Van den Bogaerde, 1968, [26] (c).

(c) A spectral band width of 1.3 nm was used. The absolute cross-sections rely upon the interpretation of a complex kinetic scheme, therefore the reliability of the data must be regarded as suspect. The photolytic processes most likely are:

$$\mathrm{ClOO} + h\nu \rightarrow \mathrm{ClO}\,(^2\Pi_{3/2}) + \mathrm{O}(^1\mathrm{D})\,;\ \lambda < (267.9 \pm 3.0)\ \mathrm{nm},$$

$$\rightarrow \mathrm{ClO}\,(^2\Pi_{3/2}) + \mathrm{O}(^3\mathrm{P})\,;\ \lambda < (267.9 \pm 3.0)\ \mathrm{nm}.$$

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

(75) (a) Absorption coefficients at band heads

λ/nm	Transition v', v''	$10^{18} \times \sigma$/ cm² molecule⁻¹	λ/nm	Transition v', v''	$10^{18} \times \sigma$/ cm² molecule⁻¹
263.63	22,0	1.4	274.95	12,0	5.8
264.06	21,0	1.4	277.16	11,0	7.2
264.58	20,0	2.2	279.60	10,0	5.8
265.25	19,0	3.6	282.24	9,0	5.8
266.10	18,0	3.6	285.18	8,0	4.3
267.12	17,0	3.6	288.40	7,0	3.6
268.25	16,0	3,6	291.80	6,0	3.6
269.50	15,0	4.3	295.43	5,0	2.2
271.11	14,0	5.0	299.30	4,0	1.4
272.94	13,0	5.0	303.45	3,0	0.7

Porter and Wright, 1950, [64] (d1).

(d1) Porter and Wright reported the relative intensities of the absorption cross-sections at the band heads of the strong progression from $v'' = 0$. The absorption cross-sections were placed on an absolute basis by equating the value at 277.16 to that reported by Clyne and Coxon [15]. The vibrational numbering shown above is taken from a recent study by Coxon [133], which led to a downward revision by one of the previous numbering of the $A\ ^2\Pi_i$ state of ClO (Durie and Ramsay, [65]). The experimental band head absorption cross-sections are not particularly sensitive to spectral band width due to the overlapped nature of the spectrum and population distribution, but are temperature dependent due to a redistribution of population. Clyne and Coxon [15] reported a value of 1.53 for $\sigma_{300}/\sigma_{450}$ for the 11,0 band, in agreement with a recent computer simulation (Coxon, [134]). Coxon and Ramsay, [135] reinvestigated the $A\ ^2\Pi_i - X\ ^2\Pi_i$ band system of ClO using high resolution absorption spectroscopy. Rotational bandwith measurements showed that all transitions were subject to extensive predissociation ($\Delta\nu$ varied from 0.3 — 3.1 cm⁻¹, except for the 6,0 transition where no rotational structure could be observed, $\Delta\nu > 5$ cm⁻¹).

The relative populations of the $^2\Pi_{3/2} : {}^2\Pi_{1/2}$ state can be calculated to be 82 : 18 (300 K) and 91 : 9 (200 K), based on a spin orbit coupling constant in the ground state of $A = -318$ cm⁻¹ (Basco and Morse, [78]). The photolytic processes can be written:

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

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

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

$$\text{predissociated band system: } ClO(^2\Pi_{3/2,\ 1/2}) + h\nu \rightarrow Cl(^2P_{3/2}) + O(^3P).$$

(75) (b) Broad band absorption (blended bands) of ClO

λ/nm	$10^{18} \times \sigma$/cm² molecule⁻¹	λ/nm	$10^{18} \times \sigma$/cm² molecule⁻¹
225	0.64	255	4.5
230	.85	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

Johnston, Morris and van den Bogaerde, 1969 [261] (d2).

(d2) The spectral band width was 1.3 nm. These values were placed on an absolute basis using the value of the ClO absorption cross-section at 257.7 nm (in the continuum) reported by Clyne and Coxon, [15].

(d3) The vacuum ultra-violet spectrum of ClO has recently been reported, Basco and Morse, 1973 [78]. The extinction coefficients for the $C \leftarrow X$(160–175 nm), and $D \leftarrow X$(145–160 nm) transitions of ClO were shown graphically, and several spectroscopic constants reported, e.g., $\Delta G_1''(1/2)$, the ground state vibrational interval, $= 845 \pm 4$ cm⁻¹. This value is in good agreement with the more recent determination of Coxon and Ramsay, 1976 [135] of 844.06 ± 0.46 cm⁻¹ (3σ).

(76) $CFCl_3 + h\nu \rightarrow CFCl_2 + Cl$ (e5)

λ/nm	$10^{20} \times \sigma/cm^2$ molecule^{-1}					
	298 K					222 K
	[4a]	[137]	[138]	[73]	Mean*	[138]
174		314			314	
176		320			320	
178		313			313	
180		318			318	
182		298			298	
184		274			274	
186	241	247	225	410	238	233
188	224	212	200	344	212	199
190	190	175	170	288	178	164
192	156	150	142	241	149	134
194	127	122	120	198	123	110
196	101	101	94.4	155	98.6	88.5
198	80.5	78.8	77.0	118	78.8	70.8
200	65.5	65.7	62.6	87.5	64.6	55.6
202	52.5	50.1	48.5	61.0	50.4	44.5
204	40.5	38.4	36.4	44.6	38.4	33.3
206	30.5	28.0	28.7	32.2	29.1	24.3
208	22.5	21.0	20.8	22.7	21.4	17.8
210	16.5	14.7	15.3	16.7	15.5	12.1
212	11.7	10.8	11.1	12.1	11.2	8.0
214	7.9	7.24	7.61	8.7	7.58	5.28
216	5.35	5.17	5.47		5.33	3.44
218	3.75	3.45	3.55		3.58	2.23
220	2.45	2.44	2.45		2.45	1.38
222	1.50	1.51	1.60		1.54	0.92
224	1.10	1.07	1.10		1.09	.58
226	0.90	0.73	0.80		0.81	.40
228			.56		.56	.27
230			.34		.34	.15

Rowland and Molina, 1975 [4a] (el).
Robbins, Rose, and Boykin, 1975 [137] (e2).
Bass, 1976 [138] (e3).
Doucet, Sauvageau, and Sandorfy, 1973 [73] (e4).

* Preferred value: The mean value shown in column 6, is derived from data taken from references [4a], [137] and [138].

(el) The values shown in the table were obtained by graphical interpolation between the reported data points, and are used in the determination of the mean values shown in column 6.

(e2) These values were taken directly from the author's tabulated data, and are used in the determinations of the mean values shown in column 6.

(e3) Although data points were reported at 0.2 nm intervals, only some of the data is shown in this review. Structure ($<5\%$ total absorption) was observed to be superimposed upon the continuum. This data was used in the determination of the mean values shown in column 6. Bass also examined the absorption spectrum at 222 K, and a small but significant decrease in the absolute absorption cross-section were observed, especially at longer wavelengths where the higher vibrational levels were depopulated.

(e4) The results of this study are only in fair agreement with those of other studies, and are not used in the determination of the mean value. However, this spectral region was not of prime interest in their study. The data shown in the table was obtained by graphical interpolation of the data shown in reference [4a], as figure 3 [73] was too small to obtain accurate value directly.

(e5) Several investigators [98, 148, 149] have studied the photochemical decomposition of $CFCl_3$ in the presence of added reagents, C_2H_6 and CH_4 [149]; O_2 [98, 148], and O_3[98]. Analysis of the reaction products, in terms of quantum yield, e.g. $\Phi[Cl_2] \sim 0.5$ [98] at 213.9 nm has led to the conclusion that at wavelengths close to the absorption threshold, the primary process can be written: $CFCl_3 + h\nu \rightarrow CFCl_2 + Cl$ i.e. one chlorine atom liberated per photon absorbed. As λ decreases, the probability of liberating two chlorine atoms is increased [149], i.e. $\phi[Cl] = 1.11$ (213.9), $\phi[Cl] = 1.35$ (184.9), $\phi[Cl] = 1.6$ [163.3 nm): $CFCl_3 + h\nu \rightarrow CFCl + Cl + Cl$.

(77) $CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl$ (f2)

λ/nm	$10^{20} \times \sigma/cm^2$ molecule^{-1}					
	298 K					222 K
	[4a]	[137]	[138]	[73]	Mean *	[138]
174		167			167	
176		176			176	
178		186			186	
180		176			176	
182		159			159	
184		136			136	
186	91	108	103.9	26	101	99.6
188	84	82.8	82.5	22.4	83.1	79.0
190	62.5	59.3	61.3	18.1	61.0	55.0
192	44	42.7	44.0	14.8	43.6	37.7
194	30.4	29.6	30.1	12.2	30.0	24.4
196	20.7	20.0	20.2	9.88	20.3	15.6
198	13.8	13.5	13.5	7.56	13.6	9.64
200	9.1	8.71	8.56	5.75	8.79	5.70
202	5.9	5.37	5.46		5.58	3.38
204	4.0	3.14	3.23		3.57	1.88
206	2.5	1.96	1.99		2.15	1.16
208	1.52	1.18	1.22		1.31	0.656
210	0.98	0.78	0.742		0.834	.383
212	.55	.47	.457		.492	.219
214		.27	.279		.274	.130
216		.17	.165		.168	.072
218			.104		.104	.045
220			.063		.063	.026

Rowland and Molina, 1975 [4a] (f1).

Robbins, Rose and Boykin, 1975 [137] (f1).

Doucet, Sauvageau, and Sandorfy, 1973 [73] (f1).

Bass, 1976 [138] (f1).

* Preferred value. The mean value shown in column (6) is derived from data taken from references [4a], [137], and [138].

(f1) See comments (e1), (e2), (e3) and (e4) (process (76), $CFCl_3 + h\nu \rightarrow CFCl_2 + Cl$).

(f2) The photochemical decomposition of CF_2Cl_2 in the presence of NO [148], O_2 [98, 150], and C_2H_6 and CH_4 [149] has been investigated, and analysis of the reaction products has led to the conclusion that at wavelengths close to the absorption threshold the quantum efficiency for removal of CF_2Cl_2, and for the production of atomic chlorine is close to unity, i.e. $CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl$. At shorter wavelengths it has been shown [149] that the quantum yield for the production of atomic chlorine exceeds unity, i.e. $\Phi[Cl] = 1.41$ (184.9 nm) and that CF_2 radicals are produced [149, 151].

(78) $CCl_4 + h\nu \rightarrow CCl_3 + Cl$ (g2)
$\rightarrow CCl_2 + Cl + Cl$ (g2)

λ/nm	$10^{20} \times \sigma/\text{cm}^2\ \text{molecule}^{-1}$		
	[4]	[137]	Mean *
174		995	995
176		1007	1007
178		976	976
180		772	772
182		589	589
184		450	450
186	336	300	318
188	238	198	218
190	150	134	142
192	101	96.5	98.8
194	68.8	77.8	73.3
196	64.0	71.1	67.6
198	62.8	67.3	65.1
200	62.2	66.1	64.1
202	60.8	62.0	61.4
204	58.9	61.4	60.1
206	56.1	56.8	56.5
208	52.4	53.2	52.8
210	47.5	47.1	47.3
212	39.7	39.6	39.6
214	33.7	33.1	33.4
216	28.0	27.2	27.6
218	22.6	21.6	22.1
220	17.1	16.9	17.0
222	12.7	12.9	12.8
224	9.1	9.88	9.5
226	6.8	7.41	7.1
228		5.60	5.6
230		4.11	4.11
232		3.05	3.05
234		2.24	2.24
236		1.52	1.52
238		1.25	1.25

Rowland and Molina, 1975 [42] (g1).
Robbins, Rose, and Boykin [137] (g1).

(g1) See comments (e1) and (e2) ((process 76), $CFCl_3 + h\nu \rightarrow CFCl_2 + Cl$).

(g2) In addition to the tabulated data, Davis et al. [125] reported the absorption spectrum in graphical form from 120–200 nm. However, this figure is "cosmetic" and data derived from it should not be used (the drifting baseline was not shown). Absorption cross-sections were explicitly reported at four wavelengths including: 6.85×10^{-21} (253.7 nm), and 3.94×10^{-18} (184.9 nm) $\text{cm}^2\ \text{molecule}^{-1}$ (this assumes the reported values of $\varepsilon(\text{cm}^{-1}\ \text{atm}^{-1})$ were to the base 10). This study also demonstrated that close to the absorption threshold the quantum yield for the production of atomic chlorine was unity, whereas at shorter wavelengths it exceeded unity, and CCl_2 radicals were produced in the primary process.

(g3) Russell et al. [152] have reported the extinction coefficients graphically from (110–200) nm. The region of stratospheric importance, $\lambda > 185$ nm, was not of prime interest in their study.

(79) $CH_3Cl + h\nu \rightarrow CH_3 + Cl$

λ/nm	$10^{21} \times \sigma/cm^2$ molecule^{-1}	
	[139] *	[142]
174	1100	800
176	933	670
178	773	535
180	635	410
182	465	302
184	347	210
186	253	142
188	180	83
190	125	43
192	87.6	
194	56.1	
196	38.0	
198	26.0	
200	16.9	
202	10.9	
204	7.18	
206	4.76	
208	3.02	
210	1.91	
212	1.16	
214	0.89	
216	.47	
218	.36	
220	.23	

* Robbins, 1976, [139] (h1).

Herzberg and Scheibe, 1930 [142].

(h1) *Preferred value. This value was obtained in a system which has been used to determine the absorption cross sections of numerous other molecules where the agreement with other studies is excellent.

(h2) Russell et al. [152] have reported the extinction coefficients graphically from (110–200) nm. The region of stratospheric interest, λ > 185 nm, was not of prime importance in their study.

(80) $CHCl_2F + h\nu \rightarrow CHClF + Cl$

λ/nm	$10^{20} \times \sigma/cm^2$ molecule^{-1}		
	[140]	[141]	Mean value *
174	168		168
176	163		163
178	152		152
180	135		135
182	116		116
184	91.7		91.7
186	73.2	50.5	66.4
188	52.9	44.5	48.7
190	40.0	34.5	37.3
192	26.3	25.5	25.9
194	18.0	17.7	17.8_5
196	12.4	11.9	12.2_5
198	8.12	7.5	7.8
200	5.09	4.9	5.0
202	3.34	3.3	3.3
204	2.11	2.3	2.2
206	1.35	1.51	1.4_3
208	0.863	0.95	0.90_6
210	.559	.56	.56
212	.355	.34	$.34_7$
214	.228	.21	$.21_9$
216	.144	.13	$.13_7$
218	.085		$.08_5$
220	.058		$.05_8$
222	.032		$.03_2$

Robbins, 1976, [140].

Chou, Ruiz Vera, Moe, and Rowland, 1976 [141] (i1) (i2).

* Preferred values.

(i1) The preferred values were obtained by taking the mean of the two studies which are in good agreement.

(i2) The values shown in the table were obtained by graphical interpolation between the reported data points, and are used in the determination of the mean value.

(i3) Doucet et al. [73] measured the extinction coefficient between 120–200 nm, however, the data was presented in graphical form and the region of stratospheric interest, λ > 185 nm, was not of prime interest in their study.

(81) $CHClF_2 + h\nu \rightarrow CHF_2 + Cl$

λ/nm	$10^{20} \times \sigma/cm^2$ molecule^{-1}		
	[140]	[141]	Mean value *
174	5.94		5.94
176	4.06		4.06
178	2.85		2.85
180	1.99		1.99
182	1.30		1.30
184	0.825		0.825
186	.525	0.426	.476
188	.353	.325	.339
190	.238	.232	.235
192	.161	.152	.157
194	.102	.099	.100
196	.075	.065	.070
198	.036	.042	.039
200	.027	.025	.026
202	.026	.0172	.0216
204		.0125	.0125

Robbins, 1976, [140] (j1).

Chou, Ruiz Vera, Moe, and Rowland, 1976, [141] (j1).

* Preferred values.

(j1) See comments (i1), (i2) ((process (80), $CHCl_2F + h\nu \rightarrow CHClF + Cl$).

(j2) See note (i3), process (80) ($CHClF_2F + h\nu$).

(82) $CH_2ClF + h\nu \rightarrow CH_2F + Cl$

(83) $CH_3CCl_3 + h\nu \rightarrow CH_3CCl_2 + Cl$

λ/nm	$10^{20} \times \sigma/cm^2\ molecule^{-1}$	
	CH_2ClF	CH_3CCl_3
226.0		3.7
223.5		6.1
221.0		10.7
218.6		15.1
216.2		22.1
213.9		30.9
211.6	0.010	42.3
209.4	.018	54.8
207.3	.036	68.0
205.1	.055	84.2
203.0	.097	101
201.0	.144	117
199.0	.236	134
197.0	.339	155
195.1	.510	174
193.2	.767	195
191.4	1.09	220
189.6	1.54	242
187.8	2.13	285
186.0	2.56	326

Chou, Ruiz Vera, Moe, and Rowland, 1976, [141].

(k1) Doucet et al. [73] also reported extinction coefficients for CH_2ClF, see note (i3), process (80).

(84) $C_2F_4Cl_2 + h\nu \rightarrow C_2F_4Cl + Cl$

(85) $C_2F_5Cl + h\nu \rightarrow C_2F_5 + Cl$

λ/nm	$10^{21} \times \sigma/cm^2\ molecule^{-1}$	
	$C_2F_4Cl_2$	C_2F_5Cl
174	500	39.6
176	409	39.6
176	409	27.8
180	249	14.6
182	196	10.3
184	147	7.73
186	105	5.41
188	80.4	3.83
190	59.7	2.67
192	40.8	1.89
194	25.4	1.28
196	19.5	0.88
198	12.9	.63
200	8.06	
202	5.63	
204	3.76	
206	2.44	
208	1.43	
210	0.87	
212	.47	
214	.41	

Robbins, 1976 [140].

(86) $COFCl + h\nu \rightarrow COF + Cl$

(87) $COCl_2 + h\nu \rightarrow COCl + Cl$

λ/nm	$10^{20} \times \sigma/cm^2\ molecule^{-1}$	
	COFCl	$COCl_2$
226.0	5.9	13.2
223.5	6.6	12.8
221.0	7.0	12.3
218.6	7.9	11.9
216.2	9.0	11.6
213.9	10.0	11.7
211.6	10.3	12.2
209.4	11.2	13.4
207.3	12.1	15.1
205.1	13.0	16.9
203.0	13.7	20.4
201.0	14.3	25.0
199.0	15.1	31.8
197.0	15.9	41.0
195.1	16.9	52.5
193.2	18.2	69.7
191.4	20.1	93.7
189.6	22.5	117
187.8	24.4	137
186.0	26.0	180

Chou, Ruiz Vera, Moe, and Rowland [141].

(88) $ClNO_3 \rightarrow ClO + NO_2$

$\rightarrow Cl + NO_3$
$\rightarrow O + NO_2Cl$

λ/nm	$10^{20} \times \sigma$/cm² molecule⁻¹	λ/nm	$10^{20} \times \sigma$/cm² molecule⁻¹
186	995	300	3.91
190	690	305	2.89
195	502	310	2.04
200	372	315	1.49
205	344	320	1.07
210	348	325	0.79
215	375	330	.61
220	376	335	.48
225	307	340	.38
230	231	345	.34
235	159	350	.29
240	118	360	.23
245	85.4	370	.19
250	65.7	380	.15
255	50.9	390	.11
260	40.7	400	.085
265	32.8	410	.059
270	26.1	420	.042
275	20.2	430	.028
280	14.5	440	.019
285	10.5	450	.013
290	7.34	460	.008
295	5.12		

Rowland, Spencer and Molina, 1976 [164].

At present the photolysis products of $ClNO_3$ are not known. The more limited data of Schmeisser and Brandle [165] is in fair agreement (± 25%) with the data shown. Solar photodissociation rates have been calculated [164] for altitudes between 10 and 50 km, with Solar Zenith Angles from 0°–80°, e.g. the J value at 25 km varies from $(5.7\text{–}9.2) \times 10^{-5}$ s^{-1} as the solar zenith angle decreases from 80° to 0°.

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

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

$\lambda_a < 276 \pm 3$ nm (continuum)
$\lambda_b \sim (276 - 480)$ nm (predissociation)

λ(nm)	Transition	σ(cm² molecule⁻¹)	Reference
475.82	$^2A_2(0,0,0) \leftarrow {^2B_1}(0,0,0)$	9.4×10^{-21}	70
469.35	$^2A_2(0,1,0) \leftarrow {^2B_1}(0,0,0)$	8.0×10^{-21}	70
460.31	$^2A_2(1,0,0) \leftarrow {^2B_1}(0,0,0)$	7.37×10^{-21}	70
454.35	$^2A_2(2,0,0) \leftarrow {^2B_1}(0,0,0)$	5.77×10^{-20}	70
445.92	$^2A_2(2,0,0) \leftarrow {^2B_1}(0,0,0)$	3.40×10^{-19}	70
440.41	$^2A_2(2,1,0) \leftarrow {^2B_1}(0,0,0)$	2.65×10^{-19}	70
351.2	$^2A_2(11,0,0) \leftarrow {^2B_1}(0,0,0)$	1.14×10^{-17}	15
182.91	C – X	3.60×10^{-18}	79
179.50	C – X	2.02×10^{-18}	79
176.40	C – X	4.78×10^{-19}	79
162.79	D – X	1.42×10^{-17}	79
160.10	D – X	1.10×10^{-17}	79
153.19	E – X	1.15×10^{-17}	79
152.04	E – X	1.11×10^{-17}	79
150.91	E – X	1.07×10^{-17}	79
149.82	E – X	6.88×10^{-18}	79
148.66	E – X	4.58×10^{-18}	79

Coon, DeWames and Loyd, 1962 [70].
Clyne and Coxon, 1968 [15].
Basco and Morse, 1974 [79].

The absorption cross-sections were determined at the maxima of the peaks (bands), and may be slightly dependent upon the instrumental spectral bandwidth. Figure 1 illustrates the absorption cross-sections for the $^2A_2 \leftarrow {^2B_2}$ system of OClO [163].

Spectroscopy of OClO

- Finkelnburg and Schumacher, 1931 [66].
- Urey and Johnston, 1931 [67].
- Goodeve and Stein, 1929 [68].
- Coon and Ortiz, 1957 [69].
- Zu, 1933 [153].
- Coon, 1940 [154].
- Sakurai, Clark and Broida, 1971 [155].
- Curl, Abe, Bissinger, Bennett and Tittel, 1973 [156].
- Richardson, Redding, and Brand, 1969 [77].
- Brand, Redding, and Richardson, 1970 [158].

There have been extensive spectroscopic studies of the absorption of the $^2A_2 \leftarrow {}^2B_1$ transition of OClO [66–70, 153–158], which is characterized by a series of well developed progressions of red degraded bands. Vibrational constants for both the ground ($^2B_1$) and excited ($^2A_2$) states have been determined from the high resolution absorption studies [67, 69, 153, 154, 77], and more recently from Laser Induced Fluorescence studies [155, 156]. Although it has been reported [66–68] that the rotational fine structure is sharp and clearly resolved in the visible and near ultraviolet, and that it becomes diffuse at shorter wavelengths, a recent study [158] has shown that the observed rotational linewidths ($\sim$0.1 cm^{-1}) are greater than the calculated Doppler width ($<$0.03 cm^{-1}) for all transitions. The spectroscopic data strongly suggests that the $^2A_2$ state is perturbed by a repulsive predissociative state, even down to the lowest (0,0,0) level. The earlier arguments [66–68] that the onset of predissociation was near 375 nm were erroneously based on the apparent observation that plots of the first differences of the progression $(0, \nu_2') \leftarrow (0,0,0)$ versus ν_2' (vibrational quantum number) showed a sharp discontinuity indicating a gross perturbation to the potential surface of the excited state due to crossing by a repulsive surface. It has been shown more recently that the plots do not exhibit a sharp discontinuity but rather a gradual curvature [153] from which the onset of predissociation cannot be deduced. The conclusion that all the $^2A_2$ state is perturbed by a predissociative state is supported by three observations from laser induced fluorescence studies, (a) the fluorescence yield was low [156]; (b) the major fluorescence decayed rapidly [155] (comparable to the laser pulse of 10 ns; and (c) the OClO photolytically decomposed [155, 156]. Therefore, it appears that the $^2A_2$ state is predissociated to the extent that all bands should be considered for computing atmospheric photolysis rates. Values of 6.9×10^{-2} [163], and 7.6×10^{-2} [174] have been reported for J(OClO). In each case, the value reported by Clyne and Coxon for σ (351.5 nm) was used to deduce the absorption cross-section at other wavelengths. Thermodynamic consideration show that the $^2A_2(0,0,0) \leftarrow {}^2B_2(0,0,0)$ transition is at the energetic threshold for OClO to photodissociate.

$$\nu_{(000) \leftarrow (000)} \begin{array}{l} = 21016.34 \text{ cm}^{-1} \text{ [158]} \\ = 60.09 \text{ kcal} \end{array}$$

$$\begin{array}{lr} \Delta H^\circ_{f0} & \text{OClO} = 24.85 \pm 0.74 \text{ kcal mol}^{-1} \\ \text{"} & \text{ClO}(^2\Pi_{3/2}) = 23.98 \pm 0.19 \text{ kcal mol}^{-1} \\ \text{"} & \text{ClO}(^2\Pi_{1/2}) = 24.89 \pm 0.19 \text{ kcal mol}^{-1} \\ \text{"} & \text{O}(^3\text{P}) = 58.989 \pm 0.024 \text{ kcal mol}^{-1} \end{array}$$

$$\Delta H \text{ (OClO} \rightarrow \text{ClO}(^2\Pi_{3/2}) + \text{O}(^3\text{P})) = 58.12 \pm 0.95 \text{ kcal mol}^{-1}$$

$$\Delta H \text{ (OClO} \rightarrow \text{ClO}(^2\Pi_{1/2}) + \text{O}(^3\text{P})) = 59.03 \pm 0.95 \text{ kcal mol}^{-1}$$

Therefore it can be seen that for OClO to undergo photolytic decomposition via the $^2A_2(0,0,0) \leftarrow {}^2B_1(0,0,0)$ transition, the (0,0,0) level of the $^2A_2$ state must be approximately energetically coincident with the separated products.

The band system observed below 200 nm [79] are assigned to Rydberg transitions.

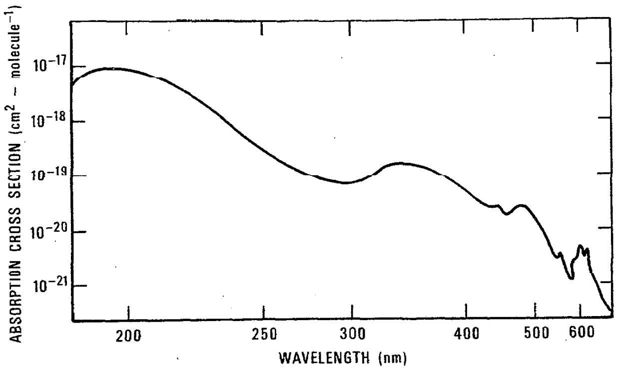

FIGURE 1. The absorption spectrum of OClO

(90) $ClNO + h\nu \longrightarrow Cl + NO$

λ (nm)	$10^{21} \times \sigma/\mathrm{cm^2\ molecule^{-1}}$
197.0	9690
335.0	123
440.0	19.1
475.0	20.2
538.5	27.9
549.5	2.49
561.2	1.41
587.9	2.01
601.7	3.59
615.8	2.64
643.1	0.638

Goodeve and Katz, 1939 [71].

The data shown in the table represent the absorption cross-sections at the maxima of each of the peaks observed between 185 and 675 nm. The complete spectrum is shown in figure 2. The lack of resolved rotational fine structure, and the general appearance of the absorption spectrum indicate that the ClNO photodissociates at all wavelengths between 185 and 675 nm via a series of repulsive surfaces which correlate to NO($^2\Pi$) and Cl (^2P). Photodecomposition studies [159, 160] determined a quantum efficiency of 2, which is explained via the following simple mechanism:

$$ClNO + h\nu \longrightarrow Cl + NO,$$

$$Cl + ClNO \longrightarrow Cl_2 + NO.$$

Absorption cross-section data measured in the visible [161] are in good agreement with that of Goodeve and Katz.

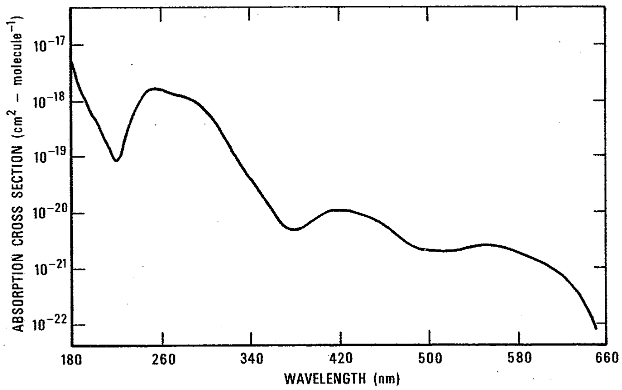

FIGURE 2. The absorption spectrum of ClNO

(91) $HOCl \xrightarrow{a} HO + Cl$

$\xrightarrow{b} HCl + O$

λ (nm)	$10^{21} \times \sigma/\mathrm{cm^2\ molecule^{-1}}$	λ (nm)	$10^{21} \times \sigma/\mathrm{cm^2\ molecule^{-1}}$
230	1800	320	1050
240	1500	330	897
250	991	340	693
260	618	350	457
270	390	360	301
280	382	370	147
290	457	380	53.6
300	693	390	8.45
310	890		

Fergusson, Slotin, and Style, 1936 [162].

The reliability of the data may be questionable due to experimental difficulties which are encountered with HOCl. Although process (a) appears most likely, there is no experimental data. See Addenda for recent results.

(92) $Cl_2O \xrightarrow{\qquad} Cl + ClO$

$\xrightarrow{\qquad} Cl + Cl + O(^3P)$

λ(nm)	$10^{20} \times \sigma/cm^2$ molecule^{-1}		
	[165]	[166]	[167]
180	775		
190	170		
200	66.9		
210	23.3		
220	9.24		11.3
230	28.3	18.5	22.7
240	98.2	57.3	85.2
250	182	85.2	142
260	183	85.2	142
270	142		
280	121	71.1	113
290	97.8		
300	67.2	49.7	71.1
310	38.2		
320	18.5	19.2	28.4
330	8.98		
340	4.13	5.69	3.97
350	2.00		
360	0.997	2.20	0.569
370	.558	1.42	.229
380	.546	0.924	.321
390	.665		
400	.875	1.13	1.78
410	1.08	1.42	2.27
420	1.20	1.63	1.78
430	1.16		
440	1.06	1.28	0.924
450	0.814		
460	.619	0.852	.447
480	.306	.470	.283
500	.206	.214	.229
520	.214	.180	.248
540	.256	.164	.248
560	.222	.157	.157
580	.176	.038	.050
600	.122	.015	.028
620	.069		
640	.015		

Lin, 1976 [165].
Goodeve and Wallace, 1930 [166].
Finkelnburg, Schumacher, and Stieger, 1931 [167].

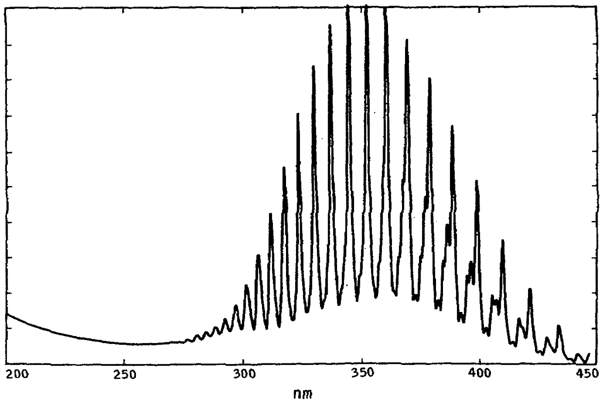

FIGURE 3. The ultraviolet spectrum of Cl_2O

Although the general apperance of the absorption spectrum is similar from different studies, the absolute magnitude of the reported absorption cross-sections vary significantly. Figure 3 shows the complete spectrum.

Addenda

This section contains the results of recent work performed on reactions already mentioned in the tables (the numbering for these reactions remains consistent with the main text), and in addition the results of some studies which have had no prior mention in this review (these reactions are readily identified by the prefix A to their number). A lack of time between receiving some of this data, and the publication deadline of this review has resulted in some of this material being less thoroughly scrutinized than normal: consequently incomplete comments.

(4) $Cl + CH_4 \rightarrow CH_3 + HCl$

Watson, Fischer, Machado, and Davis,
1976 [95].

$(7.94 \pm 0.7) \times 10^{-12} \exp(-(1260 \pm 35)/T)$	218–401	(a)
$(1.13 \pm 0.1) \times 10^{-13}$	298	

Whytock, Michael, Lee, Payne, and Stief,
1976 [189].

$6.78 \times 10^{-12} \exp(-(1242 \pm 45)/T)$	200–299	(b)
$(1.13 \pm 0.08) \times 10^{-13}$	299	
$(2.14 \pm 0.3) \times 10^{-11} \exp(-(1608 \pm 50)/T)$	318–500	

Lin and DeMore, 1977 [190].

$1.75 \times 10^{-11} \exp(-1499/T)$	198–296	(c)
1.12×10^{-13}	296	

Lee and Rowland, 1977 [191].

$(4.1 \pm 0.5) \times 10^{-13}$	361	(d)
$(1.65 \pm 0.2) \times 10^{-13}$	298	
$(3.34 \pm 0.6) \times 10^{-13}$	243	

* Preferred value:

$7.29 \times 10^{-12} \exp(-(1260 \pm 55)/T)$	200–299	(e)
$(1.12 \pm 0.12) \times 10^{-13}$	298	

(a) These values were derived using the original data, but correcting for the presence of C_2H_6.

(b) Data was obtained from 200–500 K, but cannot be fitted by a single Arrhenius expression due to curvature (as previously observed by Zahniser et al. [172]). From 200–299 K the curvature is minimal and the data can be fitted to the Arrhenius expression shown.

(c) Lin and DeMore determined k_4 ($Cl + CH_4$) relative to k_6 ($Cl + C_2H_6$). The experimental ratios were: $k_6/k_4 = (4.16 \pm 0.34) \exp(+(1438 \pm 21)/T)$ from (198–296) K; $k_6/k_4 = 530 \pm 28$ at

296K. These values are in excellent agreement with the earlier competitive chlorination results of Knox and Nelson [44] ($k_6/k_4 = (4.4 \pm 0.1) \exp(+(1444 \pm 65)/T)$) (modified see reference [1901]) and Pritchard et al. [192] ($k_6/k_4 = (4.68 \pm 1.45) \exp(+(1434 \pm 252)/T)$). The values shown for k_4 in the table were obtained by combining the above ratios with the preferred value for k_6. The value of k_4 obtained at 296 K in this study is in excellent agreement with the preferred value forwarded for 298 K in this review. However, whilst the activation energy is in agreement with that reported in references [172] and [189] above 300 K, it is significantly greater than that reported in references [95], [172], [173], and [189] for data below 300 K (from which the preferred value is derived). No explanation can be forwarded for this discrepancy at present.

(d) These data are compatible with an activation energy for reaction 4 of $\geq$ 3750 cal mol^{-1}. However, these results are in rather poor agreement with all the results reported from both direct and indirect (competitive chlorination) studies, e.g., the value of 1.65×10^{-13} for k_4 at 298 K is 50% greater than that forwarded in this review. Therefore, these data were not used in the evaluation of the preferred value. These values were derived using the preferred Arrhenius expression for k_6.

(e) This evaluated expression was obtained from a least squares fit of the data obtained between 200 and 299 K from the studies of Watson et al. [95]; Zahniser et al. [172]; Manning et al. [173] and Whytock et al. [189].

(5) $Cl + H_2 \rightarrow HCl$

Whytock, Lee, Michael, Payne, and Stief, 1977 [198].

$(2.66 \pm 0.42) \times 10^{-11} \exp(-(2230 \pm 60)/T)$	200–500	(a)
$(1.70 \pm 0.13) \times 10^{-14}$	302	

Ambidge, Bradley, and Whytock, 1976 [194].

$(1.55 \pm 0.4) \times 10^{-11} \exp(-(2123 \pm 100)/T)$	298–521	(b)
$(1.25 \pm 0.25) \times 10^{-14}$	298	

* Preferred value:

$3.5 \times 10^{-11} \exp(-2290/T)$	200–300
1.6×10^{-14}	298

(a) These results are in good agreement with those of Watson et al. [116] at and below 300 K, but in rather poor agreement at 350 K.

(b) This value was obtained by combining an experimentally determined value for $k(H + HCl)$ with the best available thermodynamic data (table 3). This value for E/R is in good agreement with the two recent direct determinations [116] and [193] and the values derived from the earlier studies of H + HCl [81, 88]. This paper discusses some of the probable causes for the earlier discrepancy between the thermodynamic value of K_{eq} and the experimental value of k_5/k_{-5}. However, this data is not used to evaluate a preferred value for k_5.

(c) This value is based on the results obtained below 300 K in the recent studies reported by Watson et al. [116] and Whytock et al. [193]. However, if the data of Benson et al. [89] and Westenberg and deHaas [88] are included with all the data from references [116] and [193] the overall expression is almost identical.

(7) $Cl + H_2O_2 \rightarrow HCl + HO_2$

Michael, Whytock, Lee, Payne, and Stief, 1977 [196].

$(1.24 \pm 0.74) \times 10^{-12} \exp(-(384 \pm 168)/T)$	265–400
$(3.64 \pm 0.52) \times 10^{-13}$	299

* Preferred value:

$1.7 \times 10^{-12} \exp(-384/T)$	265–400
$(5.0 \pm 1.3) \times 10^{-13}$	298

The preferred value is based on the activiation energy reported by Michael et al. [196] and a pre-exponential A factor modified to yield the mean of the three values reported for k_7 at 298 K ([95], [126], and [196]).

(8) $Cl + HO_2 \rightarrow HCl + O_2$

Cox and Derwent, 1977 [197].

$(2.5 \pm 1.0) \times 10^{-11}$	306

This value was obtained from the analysis of a complex reaction mechanism and is in good agreement with that reported by Leu and DeMore [126].

(12) $Cl + ClOO \rightarrow Cl_2 + O_2$

Cox and Derwent, 1977 [197].

$(2^{+2}_{-1}) \times 10^{-11}$	306

This value was obtained from the analysis of a complex reaction mechanism.

(22) $NO + ClO \rightarrow NO_2 + Cl$

Leu and DeMore, 1977 [195].

$(6.06 \pm 0.46) \times 10^{-12} \exp(+(298 \pm 21)/T)$	222–400
$(1.65 \pm 0.1) \times 10^{-11}$	298

* Preferred value:

$(8.0 \pm 1.5) \times 10^{-12} \exp(+(250 \pm 50)/T)$	222–298
$(1.85 \pm 0.3) \times 10^{-11}$	298

These data may be subject to minor modification prior to publication. This value of k_{22} (298 K) is in excellent agreement with that reported by Clyne and Watson [30], but poorer agreement with that reported by Zahniser and Kaufman [129]. However, the magnitude of the negative "activation energy" is in very good agreement with that reported by Zahniser and Kaufman [129]. The preferred value at 298 K was obtained by taking the mean of the three reported values. The Arrhenius expression was derived by taking an average of the two values of E/R, and the pre-exponential A-factor was adjusted so that the expression yielded the preferred value at 298 K. These preferred values are provisional and may change after the data from references [129] and [195] have been published and can be critically evaluated.

(39) $O + HCl \rightarrow OH + Cl$

Hack, Mex, and Wagner, 1976 [198].

$(8.5 \pm 1.7) \times 10^{-12} \exp(-(3220 \pm 150)/T)$	293–718
$(1.55 \pm 0.33) \times 10^{-16}$	293

* Preferred value:

$1.14 \times 10^{-11} \exp(-(3370 \pm 350)/T)$	293–718
1.4×10^{-16}	298

The preferred value was based on the results of Wong and Belles [58], Brown and Smith [93], Ravishankara et al. [168], and Hack et al. [198]. The results of Balaknin et al. [45] have not been used.

(47) $O(^1D) + CFCl_3 \longrightarrow CFCl_2 + ClO$

$\longrightarrow CFCl_3 + O(^3P)$

Fletcher and Husain, 1976 [176].

$(2.75 \pm 0.35) \times 10^{-10}$ 300

This value has been modified from that reported by the authors in order to remain consistent with the main text for $O(^1D)$ reaction. The original value of 5.5×10^{-10} has been revised downward by a factor of 2 (see note K1, reactions 46–52) as there are significant discrepancies between the absolute rate data obtained using the flash photolysis-resonance absorption technique, and that obtained using the laser flash photolysis-emission spectroscopy ($O(^1D) \rightarrow O(^3P) + h\nu$) technique [145]. The results obtained by these two direct techniques are normally at variance by a factor of ~2, and may be attributed to an inaccurate determination of the γ-factor (0.41) used in the modified Beer-Lambert Law [177] of the resonance absorption studies. This is the first direct determination of the rate coefficient for reaction 47, and the result (modified) is to be preferred to those obtained from the competitive studies [98] and [99]. However, it should be stated that the direct study could only observe the total loss rate of $O(^1D)$, which may include a contribution due to quenching to $O(^3P)$, whereas the competitive studies would only observe the reactive channel. A recent study [178] directly observed ClO to be a product of the $O(^1D) + CFCl_3$ reaction, and reported that [ClO] produced/[$O(^1D)$] removed $\geq (0.33 \pm 0.13)$. Consequently, the exact branching ratio between quenching of $O(^1D)$ and formation of ClO is not well defined. The data of Fletcher and Hussain [176] are in excellent agreement with those reported by Pitts et al. [99] for both reactions (47) and (48), which may suggest that the data of Jayanty et al. [98] are in error by a ~ factor of 2. Additional data are required.

(48) $O(^1D) + CF_2Cl_2 \longrightarrow CF_2Cl_2 + ClO$

$\longrightarrow CF_2Cl_2 + O(^3P)$

Fletcher and Husain, 1976 [176].

$(2.40 \pm 0.25) \times 10^{-10}$ 300

The original value of 4.8×10^{-10} has been revised downward by a factor of 2 (see all prior comments on reaction 47). A recent study [178] directly observed that ClO was a product of the $O(^1D) + CF_2Cl_2$ reaction, and reported that [ClO] produced/[$O(^1D)$] removed $\geq (0.4 \pm 0.16)$.

(57) $OH + CHF_2Cl \longrightarrow CF_2Cl + H_2O$

Chang and Kaufman, 1977 [170].

$(1.20 \pm 0.16) \times 10^{-12} \exp(-(1657 \pm 39)/T)$	253–427
$(4.3 \pm 0.6) \times 10^{-15}$	298

This reaction was studied using the low pressure discharge flow-resonance fluorescence technique, and the results obtained are in excellent agreement with those reported from the high pressure flash photolysis studies [115] and [123]. The preferred value presented in the main text should still be used.

(58) $OH + CHFCl_2 \longrightarrow CFCl_2 + H_2O$

Chang and Kaufman, 1977 [170].

$(1.16 \pm 0.17) \times 10^{-12} \exp(-(1073 \pm 40)/T)$	242–396
$(3.04 \pm 0.45) \times 10^{-14}$	298

The result at 298 K is in excellent agreement with the values reported in references [101], [123] and [127], and that recommended in this review. However, this value for the activation energy is ~20% lower than those reported in the flash photolysis studies [123], and [127]. At present it is difficult to account for this small but significant discrepancy which results in a spread of ~30% for k_{58} at 230 K.

(59) $OH + CFCl_3 \rightarrow$ Products

Howard and Evenson, 1976 [101]

$< 5 \times 10^{-16}$	296

(60) $OH + CF_2Cl_2 \rightarrow$ Products

Howard and Evenson, 1976 [101].

$< 4 \times 10^{-16}$	296

(64) $OH + CH_3CCl_3 \longrightarrow CH_2CCl_3 + H_2O$

Chang and Kaufman, 1977 [170].

$(1.9 \pm 0.24) \times 10^{-12} \exp(-(1331 \pm 37)/T)$	275–405
$(2.2 \pm 0.3) \times 10^{-14}$	298

This value at 298 K is ~40% higher than the preferred value reported in the text, possibly indicating the presence of a small amount of reactive impurity. However, discounting this possibility would result in a mean value from the three studies of $(1.76 \pm 0.4) \times 10^{-14}$ for k_{64} (298 K). The activation energy measured in this study is ~20% lower than that reported in the flash photolysis study [124] (similar to reaction (58)), and at present there is no obvious reason for the difference.

(70) $OH + CCl_2 = CCl_2 \rightarrow C_2Cl_4OH$

Chang and Kaufman, 1977 [170].

$(9.44 \pm 1.34) \times 10^{-12} \exp(+(1199 \pm 55)/T)$	250–400
1.69×10^{-13}	298

These results are in excellent agreement with the provisional data of Watson et al. [136].

(A1) $ClO + NO_2 + M \longrightarrow ClONO_2 + M$

Leu, Lin, and DeMore, 1976 [179].

$(1.2 \pm 0.05) \times 10^{-31}$; M = He	299
$(2.66 \pm 0.35) \times 10^{-33} \exp(+(1140 \pm 40)/T)$	248–417
$(1.15 \pm 0.1) \times 10^{-31}$; M = Ar	298
$(1.76 \pm 0.12) \times 10^{-31}$; M = N_2	299
$(3.69 \pm 0.24) \times 10^{-33} \exp(+(1150 \pm 20)/T)$	298–417

Zahniser and Kaufman, 1977 [103].

$(3.54 \pm 0.1) \times 10^{-33} \exp((+950 \pm 10)/T)$;	
M = He	250–365
$(0.83 \pm 0.03) \times 10^{-31}$; M = He	300
$(1.52 \pm 0.08) \times 10^{-31}$; M = N_2.	300

Birks, Shoemaker, Leck, Borders, Hart, 1976 [130].

$(0.96 \pm .03) \times 10^{-31}$; M = He	297
$(1.85 \pm 0.05) \times 10^{-31}$; M = N_2	297
$(4.4 \pm 0.66) \times 10^{-33} \exp(+(1087 \pm 70)/T)$;	
M = N_2	250–356

* Preferred value:

$5.1 \times 10^{-33} \exp(+1030/T)$; M = N_2	250–417

The preferred value was derived from a least squares fit to all the data—allowing for the differing 3rd-body efficiencies of N_2 and He. All three groups reported that the reaction was strictly third-order within the limited pressure ranges studied (typically 1–6 torr). To date there are no experimental data in the pressure range relevant to the stratosphere at 20–25 km (~ 50 torr). A slight fall-off behavior (≤ 30% at 50 torr) cannot be ruled out from theoretical considerations (RRKM).

(A2) $OH + CF_3CHCl_2 \longrightarrow CF_3CCl_2 + H_2O$

Watson, Machado, Wagner, Ravishankara, and Davis, 1976 [169].

$(1.24 \pm 0.3) \times 10^{-12} \exp(-(1056 \pm 70)/T)$	245–375
$(3.6 \pm 0.4) \times 10^{-14}$	298

Howard and Evenson, 1976 [124]

$(2.84 \pm 0.43) \times 10^{-14}$	296

Unfortunately the agreement between these two sets of data is not particularly good, a mean of the two results at 298 K of $(3.2 \pm 0.6) \times 10^{-14}$ is forwarded as the preferred value.

(A3) $OH + CHClFCF_3 \longrightarrow CFClF_3 + H_2O$

Watson, Machado, Wagner, Ravishankara and Davis, 1976 [169].

$(6.13 \pm 0.4) \times 10^{-13} \exp(-(1244 \pm 90)/T)$	250–375
$(9.4 \pm 0.3) \times 10^{-15}$	301

Howard and Evenson, 1976 [124]

$(1.24 \pm 0.19) \times 10^{-14}$	296

These results are in fair agreement at ~298 K. A preferred value of $(1.10 \pm 0.16) \times 10^{-14}$ should be used for k_{A3} (298 K).

(A4) $OH + CH_2ClCF_2Cl \longrightarrow CHClCF_2Cl + H_2O$

Watson, Machado, Wagner, Ravishankara and Davis, 1976 [169].

$(1.87 \pm 0.27) \times 10^{-12} \exp(-(1351 \pm 78)/T)$	250–350
$(1.9 \pm 0.2) \times 10^{-14}$	298

(A5) $Cl + HNO_3 \longrightarrow HCl \rightarrow NO_3$

Ming-Taun Leu and DeMore, 1976 [126].

$(6.8 \pm 3.4) \times 10^{-15}$	295

(A6) Reactions of $Cl(^2P_{1/2})$ atoms

Donovan, Husain, Bass, Braun and Davis, 1969 [180].

5×10^{-11}	(CCl_4)	298
2.5×10^{-13}	(CF_3Cl)	
$\sim 6 \times 10^{-12}$	(HCl)	
7×10^{-12}	(H_2)	
$\sim 7 \times 10^{-10}$	(H)	

In addition to the above rate coefficients, it was reported that quenching of $Cl(^2P_{1/2})$ by Ar was negligible for pressures up to 1 atm. It was assumed that the sole process occurring was quenching, however, only the decay of $Cl(^2P_{1/2})$ was monitored, not the production of $Cl(^2P_{3/2})$.

(A7) $H + Cl_2 \xrightarrow{\hspace{2em}} HCl + Cl$

Ambidge, Bradley, and Whytock, 1976 [181].

$(7.64 \pm 2.16) \times 10^{-11} \exp(-(714 \pm 101)/T)$ 292–434

$(7.74 \pm 2.54) \times 10^{-12}$ 298

Albright, Dodonov, Lavrovskaya, Morosov, and Tal'Roze, 1969 [184].

$6.2 \times 10^{-10} \exp(-(901 \pm 150)/T)$ 294–565

3.1×10^{-11} 300

Stedman, Steffenson and Niki, 1970 [185]

$(3.5 \pm 1.2) \times 10^{-11}$ 300

Bemand and Clyne, 1977 [186].

$(1.41 \pm 0.26) \times 10^{-10} \exp(-(578 \pm 64)/T)$ 300–750

$(2.19 \pm 0.32) \times 10^{-11}$ 300

Klein and Wolfsberg, 1961 [187]

$1.71 \times 10^{-10} \exp(-(1049 \pm 150)/T)$ 298

5.06×10^{-12}

Wagner, Welzbacher, and Zellner, 1976 [200].

$(1.4 \pm 0.3) \times 10^{-10} \exp(-(601 \pm 72)/T)$ 252–458

1.92×10^{-11} 298

* Preferred value:

$1.45 \times 10^{-10} \exp(-590/T)$ 250–750

The value of Ambidge et al. [181] is significantly lower than the other values which were determined using direct experimental techniques [184], [185], and [186]. Surface reactions appear to have played a significant role in their study as atomic chlorine was not observed, however, it is not clear as to the effect that this should have had upon k_{A7}. The pre-exponential A factor reported by Albright et al. [184] appears to be too large, even though their activation energy is in good agreement with other workers [181, 187] and with a value of E/R of 950 obtained in a molecular beam study [188]. The expression reported for Klein and Wolfsberg [187] was derived from their value for $k(H + HCl)/k(H + Cl_2)$ of $(0.143 \pm 0.033) \exp(-(744 \pm 66)/T)$, and the value of $k(H + HCl)$ which can be obtained from the preferred value of $k_5(Cl + H_2)$ reported in this review and thermodynamic data. Alternate expressions can be obtained with different choices of $k(H + HCl)$. Provisionally, the preferred value should be derived from the data reported in references [186] and [200].

(91) $HOCl + h\nu \rightarrow OH + Cl$

$\rightarrow HCl + O$

λ (nm)	$10^{20} \times \sigma/cm^2$ molecule^{-1}
290	6.3
300	9.5
310	11.5
320	13.5
330	11.9
340	9.5
350	7.9
360	4.8
370	2.8
380	2.4
390	1.6
400	0.8
410	.6
420	.5
430	.4
440	.3
450	.2

Jaffe and DeMore, 1977 [199].

These values are to be preferred to those of Fergusson et al. [162].

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TABLE 3. Chemical thermodynamic properties of selected molecular species

Enthalpy and Gibbs energy of formation; entropy and heat capacity

Substance			ΔHf°_0	ΔHf°	ΔGf°	$H^\circ_{298} - H^\circ_0$	S°	C°_p	Notes
Formula and description	State	Formula weight	0 K	298.15 K (25°C)					
			kcal/mol					cal/deg mol	
Cl chlorine, atomic	g	35.453	28.59	28.992	25.173	1.499	39.454	5.220	(16)
Cl_2 chlorine, molecular	g	70.906	0	0	0	2.193	53.288	8.104	
ClO chlorine monoxide	g	51.4524	24.33	24.47	23.68	2.278	53.78	8.23	(8,20)
ClO_2 chlorine dioxide (sym.)	g	67.4518	25.09	24.5	28.7	2.581	61.38	10.03	(21)
ClO_2 chlorine dioxide (unsym.)	g	67.4518	21.7	21.3	25.1	2.78	63.0	11.0	(9,21)
ClO_3 chlorine trioxide	g	83.4512		37					
HCl hydrogen chloride	g	36.4610	−22.020	−22.062	−22.777	2.066	44.646	6.96	
HOCl hypochlorous acid	g	52.4604	−18.5	−18.7	−15.7	2.440	56.54	8.88	(18)
NOCl nitrosyl chloride	g	65.4591	12.81	12.36	15.77	2.716	62.52	10.68	
NO_2Cl nitryl chloride	g	81.4585	4.29	3.0	13.0	2.915	65.02	12.71	
NO_3Cl chlorine nitrate	g	97.458		6.28					(19)
Cl_2O dichlorine monoxide	g	86.9054	19.62	19.2	23.3	2.806	64.07	11.48	(10)
Cl_2O_4 chlorine perchlorate	g	134.9036				4.16	78.21	20.56	(11)
O oxygen, atomic	g	15.9994	58.983	59.553	55.389	1.607	38.467	5.237	
$O(^1D)$	g	15.9994	104.34	104.78		1.481			(1)
$O(^1S)$	g	15.9994	155.60	156.04		1.481			(1)
O_2 oxygen, molecular, $(^3\Sigma_g^-)$	g	31.9988	0	0	0	2.0746	49.003	7.016	(2)
$O_2(^1\Delta)$	g	31.9988	22.54	22.54					(1)
$O_2(^1\Sigma)$	g	31.9988	37.51	37.51					(1)
O_3 ozone	g	47.9982	34.74	34.1	39.0	2.4736	57.08	9.37	
H hydrogen, atomic	g	1.0080	51.626	52.095	48.581	1.481	27.391	4.9679	
H_2 hydrogen, molecular	g	2.0159	0	0	0	2.0238	31.208	6.889	
OH hydroxyl	g	17.0074	9.25	9.31	8.18	2.1070	43.890	7.143	
HO_2 hydroperoxyl	g	33.0068	6.	5.		2.39	54.38	8.34	(3)
H_2O water	g	18.0153	−57.102	−57.796	−54.634	2.3667	45.104	8.025	
H_2O_2 hydrogen peroxide	g	34.0147	−31.08	−32.58	−25.24	2.594	55.6	10.3	
N nitrogen, atomic	g	14.0067	112.534	112.979	108.883	1.481	36.622	4.968	
N_2 nitrogen, molecular	g	28.0134	0	0	0	2.072	45.77	6.961	
NO nitric oxide	g	30.0061	21.45	21.57	20.69	2.197	50.347	7.133	
NO_2 nitrogen dioxide	g	46.0055	8.60	7.93	12.26	2.438	57.35	8.89	
NO_3 nitrogen trioxide	g	62.008	18.5	17.0	27.7	2.62	60.4	11.2	(3)
N_2O nitrous oxide	g	44.0128	20.435	19.61	24.90	2.284	52.52	9.19	
CO carbon monoxide	g	28.0106	−27.199	−26.416	−32.780	2.0716	47.219	6.959	
CH_3 methyl	g	15.0351	35.6	34.8	35.3	2.49	46.38	9.25	(3)
CH_4 methane	g	16.0430	−15.970	−17.88	−12.13	2.388	44.492	8.439	
C_2H_2 acetylene	g	26.0382	54.324	54.19	50.00	2.392	48.00	10.50	
C_2H_4 ethylene	g	28.0542	14.515	12.49	16.28	2.525	52.45	10.41	
C_2H_5 ethyl	g	29.0627		25.7	32.0		59.6	10.9	(5)
C_2H_6 ethane	g	30.0701	−16.323	−20.04	−7.66	2.856	54.85	12.58	(6,7)
$COCl_2$ phosgene	g	98.9166	−52.195	−52.61	−49.20	3.067	67.74	13.78	(4)
CH_3Cl methyl chloride	g	50.4881	−17.69	−19.59	−13.98	2.489	55.99	9.73	(3,14)
CH_2Cl_2 methylene dichloride	g	84.9331	−21.19	−22.83	−16.49	2.830	64.57	12.16	(3,12)
$CHCl_3$ chloroform	g	119.3781	−23.49	−24.66	−16.83	3.383	70.63	15.63	(3,12)
CF_3 trifluoromethyl radical	g	69.0064	111.7	112.4	109.21	2.754	63.33	11.90	(3)
CCl_3 trichloromethyl radical	g	118.3702	19.15	19.	22.09	3.392	70.92	15.21	(3)
CCl_4 carbon tetrachloride	g	153.8232	−22.42	−22.94	−12.83	4.120	74.02	19.93	(3,12,13)
C_2Cl_4 tetrachloroethylene	g	165.8343	−2.83	−2.97	5.15	4.759	82.05	22.84	(3)
C_2HCl_3 trichloroethylene	g	131.3893	−1.032	−1.86	4.31	3.975	77.6	19.18	
CH_3CCl_3 1,1,1-trichloroethane	g	133.4052	−34.65	−34.01	−18.21	4.30	76.49	22.07	(15)
$CClF_3$ chlorotrifluoromethane	g	104.4594	−168.0	−169.2	−159.5	3.294	68.17	15.99	(3)
CF_2Cl_2 dichlorodifluoromethane	g	120.9140	−116.5	−117.5	−108.2	3.553	71.91	17.31	(3)
CCl_3F trichlorofluoromethane	g	137.3686	−68.24	−69.0	−59.6	3.838	74.00	18.65	(3)

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21. Values of ΔHf° and ΔGf° for ClO_2 (sym.) and (unsym.) are dependent upon similar values for ClO, but have not been changed because the corresponding experimental errors are between 1 and 2 kcal mol^{-1}.

Acknowledgements

The author is greatly indebted to those scientists who have allowed their unpublished data to be used in this review and who have participated in discussions with him related to chlorine kinetics and photochemistry. He is grateful to Drs. D. Garvin and R. Hampson, of the National Bureau of Standards, for their excellent editorial work and constant encouragement. In addition, a special thank-you must be extended to Mrs. S. Webber for her patience and good cheer in typing the numerous draft and final versions of this paper.