



Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies Evaluation Number 16 Supplement to Evaluation 15: Update of Key Reactions

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Table 1-1. Rate Constants for Second-Order Reactions

O(¹D) Reactions	A-Factor ^a	E/R	k(298 K) ^a	f(298 K) ^b	g	Note
O(¹ D) + H ₂ O → OH + OH	1.63x10 ⁻¹⁰	-60	2.0 x10 ⁻¹⁰	1.08	45	A6
O(¹ D) + N ₂ O → Overall	1.19x10 ⁻¹⁰	-20	1.27x10 ⁻¹⁰	1.1	25	A8
→ N ₂ + O ₂	4.63x10 ⁻¹¹	-20	4.95x10 ⁻¹¹	1.1	25	
→ NO + NO	7.25x10 ⁻¹¹	-20	7.75x10 ⁻¹¹	1.1	25	
O(¹ D) + CH ₄ → Overall	1.75x10 ⁻¹⁰	0	1.75x10 ⁻¹⁰	1.15	25	A11
→ CH ₃ + OH	1.31x10 ⁻¹⁰	0	1.31x10 ⁻¹⁰	1.15	25	
→ CH ₃ O or CH ₂ OH + H	0.35x10 ⁻¹⁰	0	0.35x10 ⁻¹⁰	1.15	25	
→ CH ₂ O + H ₂	0.09x10 ⁻¹⁰	0	0.09x10 ⁻¹⁰	1.15	25	

ClO_x Reactions	A-Factor	E/R	k(298 K)	f(298 K)	g	Note
OH + ClO → Cl + HO ₂	7.4x10 ⁻¹²	-270	1.8x10 ⁻¹¹	1.2	50	F10
→ HCl + O ₂	6.0x10 ⁻¹³	-230	1.3x10 ⁻¹²	1.7	100	
OH + HCl → H ₂ O + Cl	1.8x10 ⁻¹²	250	7.8x10 ⁻¹³	1.1	50	F12
HO ₂ + Cl → HCl + O ₂	1.4x10 ⁻¹¹	-269	3.5x10 ⁻¹¹	1.2	100	F45
→ OH + ClO	3.6x10 ⁻¹¹	375	1.0x10 ⁻¹¹	1.4	150	
HO ₂ + ClO → HOCl + O ₂	2.6x10 ⁻¹²	-290	6.9x10 ⁻¹²	1.2	150	F46

BrO_x Reactions	A-Factor	E/R	k(298 K)	f(298 K)	g	Note
Br + O ₃ → BrO + O ₂	1.6x10 ⁻¹¹	780	1.2x10 ⁻¹²	1.15	100	G31
Br + H ₂ CO → HBr + HCO	1.7x10 ⁻¹¹	800	1.1x10 ⁻¹²	1.2	125	G34
BrO + ClO → Br + OClO	9.5x10 ⁻¹³	-550	6.0x10 ⁻¹²	1.2	100	G41
→ Br + ClOO	2.3x10 ⁻¹²	-260	5.5x10 ⁻¹²	1.2	100	
→ BrCl + O ₂	4.1x10 ⁻¹³	-290	1.1x10 ⁻¹²	1.2	100	

$$k(T) = A \exp(-E/R/T)$$

^a Units are cm³ molecule⁻¹ s⁻¹.

^b $f(298\text{ K})$ is the uncertainty factor at 298 K. To calculate the uncertainty at other temperatures, use the expression: $f(T) = f(298\text{ K}) \exp\left[g\left(\frac{1}{T} - \frac{1}{298}\right)\right]$ Note that the exponent is the absolute value.

$f(T)$ represents approximately one standard deviation. The 95% confidence limit is obtained by squaring $f(T)$. Shaded areas indicate changes or additions since JPL 06-2.

A6. The recommended $k(298\text{ K})$ is based on the results of Davidson et al. [31], Amimoto et al. [1], Wine and Ravishankara [143-144], Gericke and Comes [41], Dunlea and Ravishankara [37], Carl [20], and Takahashi et al. [125], but is weighted towards the study of Dunlea and Ravishankara because the latter study used several different methods to quantify the water vapor concentration. The results of Lee and Slanger [65] and Dillon et al. [34] are consistent with the recommended value. The temperature dependence of this rate coefficient is derived from the data of Streit et al. [123] and Dunlea and Ravishankara, after normalizing the results from the two studies to the $k(298\text{ K})$ value recommended here. The $\text{O}_2 + \text{H}_2$ product yield was measured by Zellner et al. [147] to be $(1 + 0.5/-1)\%$ and Glinski and Birks [42] to be $(0.6 + 0.7/-0.6)\%$. The yield of $\text{O}(^3\text{P})$ from $\text{O}(^1\text{D}) + \text{H}_2\text{O}$ is reported to be less than $(4.9 \pm 3.2)\%$ by Wine and Ravishankara [144], $(2 \pm 1)\%$ by Takahashi et al. [126], and $<0.3\%$ by Carl [20]. The recommended yield of OH in this reaction is 2.0. To calculate the rates of OH production via $\text{O}(^1\text{D})$ reactions in the atmosphere, the quantities of interest are the ratios of the rate coefficients for the reaction of $\text{O}(^1\text{D})$ with H_2O to those with N_2 and O_2 . Ratio data are given in the original references for this reaction. (Table 09-X, Note: 09-X)

A8. $\text{O}(^1\text{D}) + \text{N}_2\text{O}$. This reaction has two channels, one producing 2NO and the other producing $\text{N}_2 + \text{O}_2$. For atmospheric calculations of NO_x production, the rate coefficient for the channel that produces NO is critical, while the overall rate coefficient is important for deriving the loss rate of N_2O . The recommendation for the overall room temperature rate coefficient for the removal of $\text{O}(^1\text{D})$ by N_2O was derived from a weighted average of the results from Davidson et al. [30], Amimoto et al. [1], Wine and Ravishankara [144], Blitz et al. [8], Dunlea and Ravishankara [36], Carl [20], Takahashi et al. [125], Dillon et al. [34], and Vranckx et al. [139]. The temperature dependence of the rate coefficient was derived from the results of Davidson et al. (204 – 359 K), Dunlea and Ravishankara (220 – 370 K), and Vranckx et al. (227 – 715 K); only data at $<400\text{ K}$ were considered in the evaluation, after normalization to the $k(298\text{ K})$ value recommended here for the overall rate coefficient. The recommended rate coefficients for the $\text{N}_2 + \text{O}_2$ and 2NO product channels were evaluated for 298 K, the only temperature at which such data are available. The branching ratio, R , $k(\text{NO} + \text{NO})/k(\text{Total})$ is taken from Cantrell et al. [19] who reported $R = 0.57$ as well as an analysis of all measurements from 1957–1994 that led them to recommend $R = 0.61 \pm 0.06$, where the uncertainty is the 95% confidence interval. Their recommended branching ratio agrees well with earlier measurements of the quantum yield from N_2O photolysis (Calvert and Pitts [17]). Dependencies of the branching ratio on $\text{O}(^1\text{D})$ translational energy and temperature are at present not clearly resolved. The recommended rate coefficients for the two channels as a function of temperature were derived assuming that the branching ratio for the two channels is invariant with temperature.

The yield of $\text{O}(^3\text{P})$ from $\text{O}(^1\text{D}) + \text{N}_2\text{O}$ (physical quenching or chemical deactivation) has been determined to be <0.04 , 0.04 ± 0.02 , 0.056 ± 0.009 , and 0.005 ± 0.002 by Wine and Ravishankara [144], Nishida et al. [92], Carl [20] and Vranckx et al. [139] at 298 K, respectively. Vranckx et al. report a slight increase in the $\text{O}(^3\text{P})$ yield with increasing temperature (248 – 600 K) and their reported yield supercedes the anomalously high value reported by Carl [20] from the same laboratory. A recommended $\text{O}(^3\text{P})$ yield of <0.01 is based on the Vranckx et al. study. A direct measurement of the NO yield from the $\text{O}(^1\text{D}) + \text{N}_2\text{O}$ reaction in synthetic air by Greenblatt and Ravishankara [44] and the re-analysis by Dunlea and Ravishankara [36] agrees very well with the value predicted using the recommended $\text{O}(^1\text{D})$ rate coefficients for N_2 , O_2 , and N_2O and the $\text{O}(^1\text{D}) + \text{N}_2\text{O}$ product branching ratio to give $\text{NO} + \text{NO}$. Better reactive channel branching ratio measurements at stratospheric temperatures and/or measurements of the NO yield in this reaction as a function of temperature below 298 K would be useful. The uncertainty for this reaction includes factors for both the overall rate coefficient and the branching ratio. (Table 09-X, Note: 09-X)

A11. $O(^1D) + CH_4$. The recommended overall rate coefficient for the removal of $O(^1D)$ by CH_4 at room temperature is a weighted average of the results from Davidson et al. [31], Blitz et al. [8], Dillon et al. [33], and Vranckx et al. [138]. The temperature dependence of the rate coefficient was derived from the results of Davidson et al. (198 – 357 K), Dillon et al. (223 – 297 K), and Vranckx et al. (227 – 450 K). The recommended rate coefficients for the product channels (a) $CH_3 + OH$, (b) CH_3O or $CH_2OH + H$ and (c) $CH_2O + H_2$ were evaluated for 298 K, the only temperature at which such data are available. Lin and DeMore [72] analyzed the final products of N_2O/CH_4 photolysis mixtures and concluded that (a) accounted for about 90% and CH_2O and H_2 (c) accounted for about 9%. Casavecchia et al. [21] used a molecular beam experiment to observe H and CH_3O (or CH_2OH) products. They reported that the yield of H_2 was <25% of the yield of H from channel (b). Satyapal et al. [114] observed the production of H atoms in a pulsed laser experiment and reported an H atom yield of $25 \pm 8\%$. Matsumi et al. [77] reported the H atom yield in low pressure gas mixtures to be $(15 \pm 3)\%$. Chen et al. [24] used laser infrared kinetic spectroscopy to study product formation and report yields of $67 \pm 5\%$, $30 \pm 10\%$, and 5% for channels a, b, and c, respectively. The yield of $O(^3P)$ via the physical quenching of $O(^1D)$ by CH_4 has been reported by several groups. Wine and Ravishankara [144], Matsumi et al. [76], and Takahashi et al. [126] reported $O(^3P)$ yields of <4.3%, <5%, and <1%, respectively. Vranckx et al. [138] reported the most sensitive $O(^3P)$ yield measurement to date and obtained a yield of 0.002 ± 0.003 . We recommend the following branching ratios (a) $(75 \pm 15)\%$, (b) $(20 \pm 10)\%$, (c) $(5 \pm 5)\%$ and it is assumed that the branching ratio for the three channels is invariant with temperature. The uncertainties are based on the evaluation of the overall rate coefficient. (Table 09-X, Note: 09-X)

F10. $OH + ClO$. The reaction has two known product channels under atmospheric conditions: $OH + ClO \rightarrow Cl + HO_2$ and $OH + ClO \rightarrow HCl + O_2$. Most studies measure the rate coefficients for the overall reaction ($OH + ClO \rightarrow$ products) that is presumably the sum of the two channels. The recommendation for the $Cl + HO_2$ channel is obtained from the equilibrium constant for this channel combined with the recommended value for the reverse reaction in entry F45. The difference between a critical assessment of the measurements of the overall reaction and the recommendation for the $HCl + O_2$ channel as discussed below is in reasonable accord.

The assessment of the overall reaction ($OH + ClO \rightarrow$ products) is based on a fit to the 219–373 K data of Hills and Howard [51], the 208–298 K data of Lipson et al. [74], the 234–356 K data of Kegley-Owen et al. [59], the 298 K data of Poulet et al. [102], measurements by Wang and Keyser (218–298 K) [141], and measurements by Bedjanian et al. (230–360 K) [6]. Data reported in the studies of Burrows et al. [16], Ravishankara et al. [105], and Leu and Lin [70] were not used in deriving the recommended value because ClO was not measured directly in these studies and the concentration of ClO was determined by an indirect method.

The minor reaction channel forming HCl poses significant experimental difficulties due to the complications associated with the measurement of the HCl reaction product. Early studies inferred the HCl branching ratio without measuring HCl. These included the 298 K measurements of the yield of the $Cl + HO_2$ channel by Leu and Lin [70] (>0.65); Burrows et al. [16] (0.85 ± 0.2) and Hills and Howard [51] (0.86 ± 0.14). Poulet et al. [102] measured the $Cl + HO_2$ product yield to be 0.98 ± 0.12 using mass spectroscopy but their HCl sensitivity was marginal. These studies were not considered in the evaluation. Later studies of Lipson et al. using mass spectroscopy [74] and diode laser spectroscopy by Wang and Keyser [142] improved the precision of the HCl product channel measurements. Lipson et al. [73] measured rate constants for the HCl channel over the temperature range 207–298 K and report a branching ratio of $(7 \pm 3)\%$, while Wang and Keyser [142] measured the HCl yield between 218–298 K, obtaining $(9.0 \pm 4.8)\%$, independent of temperature. Their rate constant was computed from this yield and their overall rate constant [141]. Measurements by Tyndall et al. [134] and Bedjanian et al. [6] were also considered. (It was noted that although the values for this channel obtained by Lipson et al. by combining the values obtained in [74] and [73] and Bedjanian et al. [6] are in agreement, their values for the overall reaction differ by 40-70%.) The recommendation for the HCl channel is unchanged from JPL 06-2 and the error limits have been reduced.

F12. $OH + HCl$. The recommended value is based on a least squares fit to the data over the temperature range 204–300 K reported in the studies of Molina et al. [85], Keyser [60], Ravishankara et al. [107], Battin-Leclerc et al. [5] and Bryukov et

al. [12]. In these studies particular attention was paid to the determination of the absolute concentration of HCl by UV and IR spectrophotometry. Earlier studies by Takacs and Glass [124], Zahniser et al. [146], Smith and Zellner [118], Ravishankara et al. [106], Hack et al. [45], Husain et al. [54], Cannon et al. [18], Husain et al. [55], and Smith and Williams [117] had reported somewhat lower room temperature values. The data of Sharkey and Smith [115] over the temperature range 138–216 K, Battin-Leclerc et al. [5] below 240 K Bryukov et al over the temperature range 298 – 1015 K, depart from normal Arrhenius behavior. Quantum chemical and transition state calculations performed by Battin-Leclerc et al. [5], Bryukov et al. [12] and Steckler et al. [120] generally support the existence of a weakly bound complex, however, a large tunneling effect is required to explain the low temperature data. Additional work at low temperature is needed to confirm the strong non-Arrhenius behavior. (Table 09-X, Note: 09-X)

F45. HO₂ + Cl. The recommendations for the two reaction channels are based upon the results of Hickson and Keyser [48], who measured both channels using the discharge flow-resonance fluorescence technique coupled with infrared diode laser spectroscopy, detecting HO, HO₂, Cl and HCl, by Lee and Howard [67] who measured the total rate constant and the OH + ClO channel, using a discharge flow system with laser magnetic resonance detection of HO₂, OH, and ClO, and by Riffault et al. [109] who measured the total rate constant and the OH + ClO channel using the discharge flow mass spectrometric technique. The latter two studies suggest that the total rate constant is temperature independent with a value of $(4.2 \pm 0.7) \times 10^{-11}$ and $(4.4 \pm 0.6) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ over the temperature range 250–420 K and 230–360 K respectively. The Hickson and Keyser study concludes that the HCl channel may be represented as $(1.4 \pm 0.3) \times 10^{-11} \exp[(269 \pm 58)/T]$ for temperatures from 256 to 296 K, while the OH channel is given by $(12.7 \pm 4.1) \times 10^{-11} \exp[-(801 \pm 94)/T]$ for temperatures of 226–336 K, the sum of which yields 4.3×10^{-11} cm³ molecule⁻¹ s⁻¹ at 298 K with a small temperature dependence.. These values for the total rate constant are in agreement with the results of indirect studies relative to Cl + H₂O₂ (Leu and DeMore [68], Poulet et al. [103], Burrows et al. [14]) or to Cl + H₂ (Cox [27]). The contribution of the reaction channel producing OH + ClO (22% at room temperature) is much higher than the upper limit reported by Burrows et al. (1% of total reaction). Cattell and Cox [22], using a molecular modulation-UV absorption technique over the pressure range 50–760 Torr, report results in good agreement with those of Lee and Howard both for the overall rate constant and for the relative contribution of the two reaction channels. A study by Dobis and Benson [35] reports a total rate constant in good agreement with this recommendation but a much lower contribution (5±3%) of the channel producing OH + ClO. The equilibrium constant for the channel producing ClO + OH can be calculated with excellent accuracy. The recommended value for this channel comes from the combination of this equilibrium constant and the rate constant for the reverse reaction found in entry F10.

F46. HO₂ + ClO. The recommended value is based on studies by Hickson et al. [49], Nikolaisen et al. [89], Knight et al. [61], and Stimpfle et al. [121] that studied the reaction as a function of temperature. Earlier room temperature studies by Reimann and Kaufman [108]; Leck et al. [64], Burrows and Cox [15], and Cattell and Cox [22] are slightly lower than the current recommendation. The studies of Cattell and Cox and Nikolaisen et al. were performed over extended pressure ranges and did not observe a pressure dependence. The most recent studies find the T-dependence to be characterized by linear Arrhenius behavior over the entire temperature range and do not support the finding of Stimpfle et al. of non-Arrhenius behavior. The recommended value for E/R is based on an average of individual E/R values for each of the four studies over their entire temperature ranges. The two most probable pairs of reaction products are, (1) HOCl + O₂ and (2) HCl + O₃. Finkbeiner et al. [39], using matrix isolation/ FTIR spectroscopy, studied product formation between 210 and 300 K at 700 Torr. HOCl was observed to be the dominant product (> 95% at all temperatures). Upper limits ranging from 0.3% to 2% have been determined for the channel (2) room temperature branching ratio by Leu [71], Leck et al., Knight et al., and Finkbeiner et al. Slightly larger branching ratio (<5%) upper limit values for k₂/k were determined at temperatures below 250 K by Finkbeiner et al. and Leck et al. However, no direct evidence of product channels other than channel (1) was found. Theoretical calculations by Nikolaisen et al. suggest that the reaction to channel (1) proceeds mainly through a ClO-HO₂ complex on the triplet potential surface. However, these calculations also suggest that collisionally stabilized HOOCl formed on the singlet surface will possess an appreciable lifetime. Zhu et al. [145], using ab initio molecular orbital methods, hypothesize that stabilization of the HOOCl complex should increasingly occur as temperature is decreased below 298 K for pressures above 1 Torr. Further studies of the possible formation of HOOCl are warranted. (Table 09-X, Note: 09-X)

G31. $\text{Br} + \text{O}_3$. The results reported for $k(298 \text{ K})$ by Clyne and Watson [25], Leu and DeMore [69], Michael et al. [82], Michael and Payne [83], Toohey et al. [130], Nicovich et al. [90] and Ninomiya et al. [91] are in excellent agreement. The preferred value at 298 K is derived by taking the mean of these seven values. There is less agreement among reported temperature dependences, with E/R values ranging from ~ 900 (Leu and DeMore and Toohey et al.) to ~ 600 (Michael et al. and Michael and Payne). The preferred value of E/R represents an average of the E/R 's from the five studies carried out as a function of temperature (not including Clyne and Watson and Ninomiya et al. which were room temperature only). (Table 09-X, Note: 09-X)

G34. $\text{Br} + \text{H}_2\text{CO}$. There have been two direct studies of this rate constant as a function of temperature: Nava et al. [87], using the flash photolysis–resonance fluorescence technique, and Poulet et al. [101], using the discharge flow–mass spectrometric technique. These results are in reasonably good agreement. The Arrhenius expression was derived from a least squares fit to the data reported in these two studies. The higher room temperature value of Le Bras et al. [63], using the discharge flow–EPR technique, has been shown to be in error due to secondary chemistry (Poulet et al.). The relative rate study of Ramacher et al. [104] is in good agreement with the recommendation. (Table 09-X, Note: 09-X)

G41. $\text{BrO} + \text{ClO}$. Friedl and Sander [40], using DF/MS techniques, measured the overall rate constant over the temperature range 220–400 K and also over this temperature range determined directly branching ratios for the reaction channels producing BrCl and OCIO . The same authors in a separate study using flash photolysis–ultraviolet absorption techniques (Sander and Friedl [113]) determined the overall rate constant over the temperature range 220–400 K and pressure range 50–750 Torr and also determined at 220 K and 298 K the branching ratio for OCIO production. The results by these two independent techniques are in excellent agreement, with the overall rate constant showing a negative temperature dependence. Toohey and Anderson [129], using DF/RF/LMR techniques, reported room temperature values of the overall rate constant and the branching ratio for OCIO production. They also found evidence for the direct production of BrCl in a vibrationally excited Π state. Poulet et al. [100], using DF/MS techniques, reported room temperature values of the overall rate constant and branching ratios for OCIO and BrCl production. Overall room temperature rate constant values reported also include those from the DF/MS study of Clyne and Watson [26] and the very low value derived in the flash photolysis study of Basco and Dogra [3]. The recommended Arrhenius expressions for the individual reaction channels are taken from the study of Friedl and Sander [40] and Turnipseed et al. [133]. These studies contain the most comprehensive sets of rate constant and branching ratio data. The overall rate constants reported in these two studies are in good agreement (20%) at room temperature and in excellent agreement at stratospheric temperatures. Both studies report that OCIO production by channel (1) accounts for 60% of the overall reaction at 200 K. Both studies report a BrCl yield by channel (3) of about 8%, relatively independent of temperature. The recommended expressions are consistent with the body of data from all studies except those of Hills et al. [50] and Basco and Dogra [3]. (Table 09-X, Note: 09-X)

Table 2-1. Rate Constants for Termolecular Reactions

Reaction	Low-Pressure Limit ^a $k_0(T) = k_0^{300} (T/300)^{-n}$		High-Pressure Limit ^b $k_\infty(T) = k_\infty^{300} (T/300)^{-m}$		f(298 K)	g
	k_0^{300}	n	k_∞^{300}	m		
ClO_x Reactions						
$\text{ClO} + \text{ClO} \xrightarrow{\text{M}} \text{Cl}_2\text{O}_2$	1.6×10^{-32}	4.5	3.0×10^{-12}	2.0	1.15	0

$$k(M, T) = \left(\frac{k_0(T)[M]}{1 + (k_0(T)[M]/k_\infty(T))} \right) 0.6^{\left\{1 + [\log(k_0(T)[M]/k_\infty(T))]^2\right\}^{-1}}$$

The values quoted are suitable for air as the third body, M.

^a Units are $\text{cm}^6 \text{molecule}^{-2} \text{s}^{-1}$.

^b Units are $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$.

f(298 K) is the uncertainty factor at 298 K. To calculate the uncertainty at other temperatures, use the expression:

$$f(T) = f(298 \text{ K}) \exp \left[g \left(\frac{1}{T} - \frac{1}{298} \right) \right]$$

Note that the exponent is the absolute value

Shaded areas indicate changes or additions since JPL 06-2.

ClO + ClO. The recommendation is based on a fit to data from Sander et al. (195–247 K) [112] as quoted by Nickolaissen et al. (260–390 K) [88], Bloss et al. (183–245 K) [9], Trolrier et al. (200–263 K) [132] and Boakes et al. [10]. The Trolrier et al. data have been corrected for values at the zero pressure intercept as suggested in the Trolrier et al. paper. With this adjustment all the data except the Boakes et al. values are in reasonable agreement. Boakes et al. [10] report higher values. They found a zero pressure intercept as well, but they suggest disregarding their data at less than 100 Torr and report preferred parameters of 2.79×10^{-32} ; 3.78; 3.44×10^{-12} ; 1.73. The Boakes et al [10] values are accommodated in this evaluation by the change in the values of the high pressure limiting rate constant compared with the evaluation in JPL 06-2 [111]. Error limits represent an attempt to include all the data within the 95% uncertainty. Golden [43] has performed RRKM and master equation calculations using the potential energy surface in Zhu and Lin [148] and concluded that while a channel to form ClOClO might exist, the best representation of the data remains that only a single channel exists. The value of $m = 2$ is somewhat high, but attempts to statistically model any and all of the data sets yield even higher values. The k_0 value for N_2 is not in accord with a simple theory as explained in Patrick and Golden [94] and in some detail in Golden [230]. It has been suggested [131] that the “radical-complex” mechanism may apply here, although a study by Liu and Barker [75] suggests otherwise. Other previous rate constant measurements, such as those of Hayman et al. [47], Cox and Derwent [28], Basco and Hunt [4], Walker [140], and Johnston et al. [57], range from $(1-5) \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$, with N_2 or O_2 as third bodies. The major dimerization product is chlorine peroxide (Birk et al. [7], DeMore and Tschuikow-Roux [32], Slanina and Uhlik [116], Stanton et al. [119] and Lee et al. [66]). (Table 09-X, Note: 09-X)

Table 3-1. Equilibrium Constants

Reaction	A/cm ³ molecule ⁻¹	B/°K	K _{eq} (298 K)	f(298 K) ^a	g
ClO + ClO → Cl ₂ O ₂	1.72×10 ⁻²⁷	8649	6.9×10 ⁻¹⁵	1.25	200

$\text{K/cm}^3 \text{ molecule}^{-1} = A \exp(B/T) [200 < T/K < 300]$

Shaded areas indicate changes or additions since JPL06-2.

^a f(298 K) is the uncertainty factor at 298 K, and g is a measure of the uncertainty in the quantity B. To calculate the uncertainty at temperatures other than 298 K, use the expression:

$$f(T) = f(298 \text{ K}) \exp \left[g \left(\frac{1}{T} - \frac{1}{298} \right) \right]$$

ClO + ClO. The values of the equilibrium constant and the thermochemical parameters are from a third-law calculation based on the data from Cox and Hayman [29] and Nickolaisen et al.[88]. The 95% error limits were chosen to incorporate all the data points in these two studies. The entropy of ClOOC1, the value of which is 72.0 cal mol⁻¹ K⁻¹ (301.1 J mol⁻¹ K⁻¹) at 300 K, can be calculated from structures and frequencies calculated by Zhu and Lin [148] (symmetry number corrected by Golden [43] to account for optical isomers) or by treatment of the torsion as a hindered rotor [62], in which case the symmetry number correction is not required. The latter has been adopted here, but there is very little difference between the results. The heat of formation at 0 K is $\Delta H_{f,0}^\circ = 31.6 \pm 0.5 \text{ kcal mol}^{-1}$ (132.4±2 kJ mol⁻¹) and at 300 K is $\Delta H_{f,300}^\circ = 30.8 \pm 0.5 \text{ kcal mol}^{-1}$ (129.0±2 kJ mol⁻¹). A study of branching ratios of ClO + ClO channels in Cl₂/O₂/O₃ mixtures by Horowitz et al. [52] also finds the equilibrium constant in O₂ at 285 K to be in agreement with the recommendation. Values at single temperatures are available from Ellermann et al. [38] and Boakes et al. [10], the former agreeing with this recommendation, while the latter is a bit outside the 95% confidence limit. Broske and Zabel [11] measured the reverse reaction at four temperatures between 245 and 260 K. They used the parameters for the forward reaction recommended in JPL 02-25 to suggest van't Hoff parameters of 5.09×10⁻²⁶ and 7584. Van't Hoff parameters suggested by Plenge et al. [98], who measured $\Delta H_{f,0}(\text{ClOOC1}) = 134.0 \pm 2.80 \text{ kJ mol}^{-1}$ by photoionization mass spectrometry and computed the entropy change for the reaction, are 1.92×10⁻²⁷ and 8430.

Several studies have derived values of K_{eq} using atmospheric measurements in the nighttime polar stratosphere under conditions where ClO and ClOOC1 should be in equilibrium. These are summarized here but are not used in the derivation of the recommended equilibrium constants. Avallone and Toohey [2] used $K_{eq} = 1.99 \times 10^{-30} \times T \times \exp(8854/T)$ derived from *in situ* aircraft experiments. The Avallone and Toohey [2] expression yields values that are quite close to those from the recommended expression. Atmospheric measurements from an airborne platform have also been used by von Hobe et al. [137] to deduce K_{eq} parameters of 3.61×10⁻²⁷ and 8167, resulting in values which lie outside the 95% confidence limits. A reanalysis by Salawitch and Canty [110] of ER-2 data between 185 and 200 K, from Stimpfle et al. [122] results in an expression for K_{eq} which lies within the uncertainty bounds and is quite close to the Avallone and Toohey [2] expression. (Table 09-X, Note: 09-X)

Table 4-1. Photochemical Reactions

CIOOCl. The recommendation for the cross-sections is unchanged from JPL 06-2. However, changes in the recommended uncertainties have been made. The new note discusses these changes and other recent activities.

F7.	CIOOCl + hv	→ ClO + ClO	17.7 kcal mol ⁻¹	1614 nm(1)
		→ Cl + ClOO	21.6 kcal mol ⁻¹	1323 nm(2)

Absorption Cross Sections: The gas-phase UV absorption spectrum of ClOOCl is continuous with a maximum at 245 nm, a minimum near 218 nm, and a weak diffuse shoulder in the wavelength region 280 – 300 nm. There are a number of studies that have reported UV absorption data for ClOOCl over a range of wavelengths or at specific wavelengths. Table 1 summarizes the currently available studies. The ClOOCl UV absorption spectrum reported by Basco and Hunt [4] and Molina and Molina [84] have been shown to contain systematic errors and are not considered further in this evaluation. In laboratory studies, ClOOCl has been produced in the gas-phase at low temperature as a product of the termolecular ClO radical self-reaction, ClO + ClO + M. Studies, to date, indicate that only one stable isomer of Cl₂O₂ is produced in the ClO self-reaction and that this species is dichlorine peroxide, ClOOCl, rather than ClOCIO or ClClO₂. Using sub-millimeter wave spectroscopy, Birk et al. [7] have further established the structure of the reaction product to be ClOOCl. This is in general agreement with the quantum mechanical calculations of McGrath et al. [79-80], Jensen and Odersheide [56], and Stanton et al. [119] although the recent theoretical study by Matus et al. [78] found the ClClO₂ isomer to be more stable than ClOOCl by 3.1 kcal mol⁻¹ at 298 K.

Cox and Hayman [29], Burkholder et al. [13], DeMore and Tschuikow-Roux [32], and Bloss et al. [9] report absolute ClOOCl cross section, $\sigma(\lambda)$, values. The studies of Permien et al. [95], Vogt and Schindler [135], Huder and DeMore [53], McKeachie et al. [81] and Pope et al. [99] report absorption spectra normalized to 245 nm. von Hobe et al. [136] report a solid-phase ClOOCl UV absorption spectrum measured in a Ne matrix at ~10 K with reported cross sections obtained by normalization using the cross section value recommended in JPL-2006 for the gas-phase spectrum.

Discrepancies in the wavelength dependence of the ClOOCl absorption spectrum at wavelengths >300 nm, the region that is most critical for atmospheric photolysis rate calculations, exist and most likely originate from uncertainties in corrections for spectral interferences by reactant precursors (O₃, Cl₂O, and Cl₂) and impurities (OCIO, Cl₂, and Cl₂O₃) formed in the ClOOCl source chemistry. Near the peak, the reported spectra are in reasonable agreement. The studies of Cox and Hayman, Burkholder et al., DeMore and Tschuikow-Roux, Vogt and Schindler, and McKeachie et al. show systematic deviations that are possibly consistent with spectral interference due to minor absorption by Cl₂O and in the case of Cox and Hayman, Burkholder et al., and McKeachie et al. possibly Cl₂O₃. At $\lambda > 300$ nm, the ClOOCl spectrum is weaker and more sensitive to spectral interferences from impurities, in particular Cl₂. The studies of Burkholder et al. and DeMore and Tschuikow-Roux are the only gas-phase studies to date that report cross section data at $\lambda > 360$ nm. Pope et al. recently developed a method to isolate bulk samples of ClOOCl in which ClOOCl is produced in the gas-phase and condensed at low temperatures. Pope et al. measured gas-phase UV spectra that are due mostly to Cl₂ and ClOOCl absorption following the warming of the condensate. The spectra were analyzed using a Gaussian fitting procedure and they report a ClOOCl absorption spectrum that decreases rapidly at $\lambda > 320$ nm with a cross section at 350 nm that is a factor of 6 lower than recommended in JPL-2006. The von Hobe et al. matrix study used the Pope et al. method to prepare their ClOOCl samples and Raman spectroscopy to evaluate the spectral contribution from Cl₂ impurities. They report a ClOOCl spectrum with significant absorption at wavelengths out to 400 nm.

The recommended ClOOCl absorption cross sections for the temperature range 190 – 250 K are listed in Table 4-85 and are unchanged from JPL-2006. The peak absorption cross section was obtained from the studies given in Table 1. Cross sections at other wavelengths are based on the data of DeMore and Tschuikow-Roux for 190-200 nm and the data of Cox and Hayman [29], DeMore and Tschuikow-Roux [32], and Burkholder et al. [13] for the wavelength range 200-360 nm. Data at

$\lambda > 360$ nm are from a log-linear extrapolation and are given by the expression $\log[\sigma(\lambda)] = 7.589 - 0.01915 \times \lambda$ where λ is in nm and σ is in units of 10^{-20} cm² molecule⁻¹.

Bloss et al. [9] measured a value for $\sigma(210$ nm) in a pulsed photolysis ClO + ClO + M kinetics study over the temperature range 183 – 245 K that is ~25% greater than the current recommendation. Recently, Chen et al. [23] used a new experimental method involving pulsed laser photolysis of ClOOCl in a molecular beam combined with mass spectrometric detection to determine $\sigma(\lambda)\Phi(\lambda)$ where $\Phi(\lambda)$ is the ClOOCl photolysis quantum yield, the quantity needed for atmospheric photolysis rate calculations, at 308 and 351 nm. Their experimental method is not sensitive to spectral interference from Cl₂ and the lower-limit for the ClOOCl cross sections, assuming $\Phi(\lambda) = 1$, for measurements made at 200 and 250 K are in good agreement at 308 nm and ~40% greater at 351 nm than the current recommendation. Additional studies of the ClOOCl absorption spectrum by Papanastasiou et al. [93] and $\sigma(\lambda)\Phi(\lambda)$ by the Anderson group [46] at Harvard are currently in preparation for publication but were not considered in this evaluation.

Cross-Section Uncertainties: The uncertainties in the ClOOCl absorption cross section have been re-evaluated from JPL-2006. Over the wavelength range 200 – 300 nm, we estimate the uncertainty in $\sigma(\lambda)$ to be $\pm 35\%$. The estimated uncertainty increases towards longer wavelengths and the upper and lower limits for $\sigma(\lambda > 300$ nm) are given by: $\sigma(\lambda)^+ = 1.35 \times \sigma(300$ nm) $\times \exp[-0.038(\lambda - 300)]$ and $\sigma(\lambda)^- = (1/1.35) \times \sigma(300$ nm) $\times \exp[-0.0525(\lambda - 300)]$. The estimated error limits cover a range in $\sigma(\lambda)$ that includes the values reported by Burkholder et al. (upper limit) and the extrapolated values of Huder and DeMore (lower limit). The results reported in the Pope et al. study fall outside the currently estimated range of uncertainty for $\sigma(\lambda)$. Further studies of the peak cross section and spectrum at $\lambda > 300$ nm that reduce uncertainties in the calculated atmospheric photolysis rate of ClOOCl are desired.

Photolysis Quantum Yields and Product Studies: Molina et al. {Molina, 1990 #939} reported a quantum yield, Φ , of approximately unity (1.03 ± 0.12) for the Cl + ClOO pathway from a flash photolysis study at 308 nm, in which the yield of Cl atoms was measured using time-resolved atomic resonance fluorescence. These results are in agreement with the steady-state photolysis study of Cox and Hayman [29]. In a molecular beam/flash-photolysis study Moore et al.[86] measured the relative Cl:ClO product yields from which the branching ratio for both photolysis channels ClOO + Cl and ClO + ClO was derived. At 248 nm, they obtained 0.88 ± 0.07 and 0.12 ± 0.07 respectively, and at 308 nm, 0.90 ± 0.1 and 0.10 ± 0.01 . Plenge et al. [97] measured the primary products from ClOOCl photolysis at 250 and 308 nm using photoionization mass spectrometry. At both wavelengths 2Cl + O₂ was observed as the exclusive products corresponding to a primary Cl quantum yield near unity at 250 nm $\Phi_{\text{Cl}} \geq 0.98$ and at 308 nm $\Phi_{\text{Cl}} \geq 0.90$. At both photolysis wavelengths the pathway leading to ClO was not observed corresponding to $\Phi_{\text{ClO}} \leq 0.02$ at 250 nm and $\Phi_{\text{ClO}} \leq 0.10$ at 308 nm.

A quantum yield of $\Phi_{\text{Cl}} = 1.0 (\pm 0.1)$ is recommended for $\lambda < 300$ nm while $\Phi_{\text{Cl}} = 0.9 (\pm 0.1)$ is recommended for $\lambda > 300$ nm. The determination of photolysis quantum yields and product branching ratios at wavelengths > 300 nm are desired.

Theoretical Studies: Toniolo et al.[128], Peterson and Francisco [96], and Matus et al. [78] report theoretical calculations for the electronic transitions of the ClOOCl UV absorption spectrum that include transitions to excited singlet and triplet states. Peterson and Francisco report that the strongest triplet transition is dissociative to Cl + ClOO, centered near 385 nm, and is three orders of magnitude weaker than the strongest singlet transition at shorter wavelengths. Kalekin and Morokuma [58] studied the ClOOCl photodissociation dynamics and predict the synchronous and sequential formation of 2Cl + O₂ at 308 nm, and three possible fragmentation routes at 248 nm: 2Cl + O₂, Cl + O(³P) + ClO, and 2Cl + 2O(³P). Similar theoretical calculations performed by Toniolo et al. [127] for excitation at 264, 325 and 406 nm found that 2Cl + O₂ was produced at all wavelengths with only a small yield of 2ClO at the shortest wavelength.

Table 4.xx Summary of ClOOCl UV absorption spectrum studies

Reference	Year	Temperature(K)	λ (nm)	$10^{20} \sigma(\lambda)(\text{cm}^2)$
Cox and Hayman [29]	1988	200 – 300	220 – 360	$640 \pm 60^*$
Permien et al. [95]	1988	235	211 – 290	– ^{\$}
Burkholder et al. [13]	1990	205 – 250	212 – 410	$650 +80/-50^*$
DeMore and Tschuikow-Roux [32]	1990	206	190 – 400	$680 \pm 80^*$
Vogt and Schindler [135]	1990	230	204 – 350	– ^{\$}
Huder and DeMore [53]	1995	195	200 – 310	– ^{\$.@}
Bloss et al. [9]	2001	183 – 245	210	294 ± 86
McKeachie et al. [81]	2004	223	235 – 400	– ^{\$}
Pope et al. [99]	2008	193	226 – 355	– ^{\$}
von Hobe et al. [136]	2009	10	220 – 400	– ^{\$.#}
Chen et al. [23]	2009	200	308	$49^{\&}$
		250	308	50.9
		200	351	11.2
		250	351	12.6

* Absorption cross section values at the peak of the spectrum, 245 nm. Cross section data also given over the reported range of wavelengths. ^{\$} Reported ClOOCl absorption spectrum without absolute cross section determination. [#] Solid-phase ClOOCl absorption spectrum measured in a Ne matrix. [@] ClOOCl absorption spectrum at wavelengths reported at >310 obtained using a log-linear extrapolation. [&] ClOOCl cross section obtained assuming a unit photolysis quantum yield.

Table 4-85. Absorption Cross Sections of ClOOCl

λ (nm)	$10^{20} \sigma$ (cm ²)	λ (nm)	$10^{20} \sigma$ (cm ²)	λ (nm)	$10^{20} \sigma$ (cm ²)	λ (nm)	$10^{20} \sigma$ (cm ²)
190	565.0	256	505.4	322	23.4	388	1.4
192	526.0	258	463.1	324	21.4	390	1.3
194	489.0	260	422.0	326	19.2	392	1.2
196	450.0	262	381.4	328	17.8	394	1.1
198	413.0	264	344.6	330	16.7	396	1.0
200	383.5	266	311.6	332	15.6	398	0.92
202	352.9	268	283.3	334	14.4	400	0.85
204	325.3	270	258.4	336	13.3	402	0.78
206	298.6	272	237.3	338	13.1	404	0.71
208	274.6	274	218.3	340	12.1	406	0.65
210	251.3	276	201.6	342	11.5	408	0.60
212	231.7	278	186.4	344	10.9	410	0.54
214	217.0	280	172.5	346	10.1	412	0.50
216	207.6	282	159.6	348	9.0	414	0.46
218	206.1	284	147.3	350	8.2	416	0.42
220	212.1	286	136.1	352	7.9	418	0.38
222	227.1	288	125.2	354	6.8	420	0.35
224	249.4	290	114.6	356	6.1	422	0.32
226	280.2	292	104.6	358	5.8	424	0.29
228	319.5	294	95.4	360	5.5	426	0.27
230	365.0	296	87.1	362	4.5	428	0.25
232	415.4	298	79.0	364	4.1	430	0.23
234	467.5	300	72.2	366	3.8	432	0.21
236	517.5	302	65.8	368	3.5	434	0.19
238	563.0	304	59.9	370	3.2	436	0.17
240	600.3	306	54.1	372	2.9	438	0.16
242	625.7	308	48.6	374	2.7	440	0.15
244	639.4	310	43.3	376	2.4	442	0.13
246	642.6	312	38.5	378	2.2	444	0.12
248	631.5	314	34.6	380	2.1	446	0.11
250	609.3	316	30.7	382	1.9	448	0.10
252	580.1	318	28.0	384	1.7	450	0.09
254	544.5	320	25.6	386	1.6		

Note: 190-200nm, DeMore and Tschuikow-Roux [32], 200-360 nm, mean of Cox and Hayman [29], Burkholder et al. [13], Permien et al. [95], and DeMore and Tschuikow-Roux [32], 362-450 nm, $\log[\sigma(\lambda)] = 7.589 - 0.01915 \times \lambda$ extrapolation where λ is in nm and σ is in units of $10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$.

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