

A temperature dependence kinetics study of the reactions of $\text{Cl}(^2P_{3/2})$ with O_3 , CH_4 , and H_2O_2

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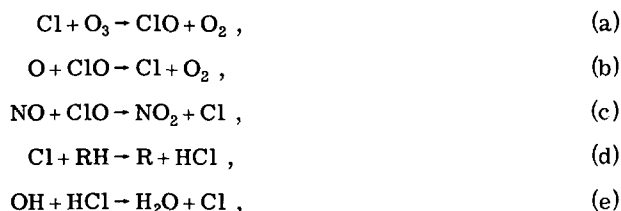
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The technique of flash photolysis-resonance fluorescence has been utilized to study the temperature dependences of two chlorine atom reactions of considerable fundamental importance to stratospheric chemistry. These reactions have been studied using a wide range of experimental conditions to insure the absence of complicating secondary processes. The reactions of interest with their corresponding rate constants are expressed in units of $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$: $\text{Cl} + \text{O}_3 \xrightarrow{k_1} \text{ClO} + \text{O}_2$, $\Delta U_{298} = -164 \text{ kJ mol}^{-1}$, $k_1 = (3.08 \pm 0.30) \times 10^{-11} \exp[-(576 \pm 60/R T)]$, (220–350) K; $\text{Cl} + \text{CH}_4 \xrightarrow{k_2} \text{CH}_3 + \text{HCl}$, $\Delta U_{298} = +6.4 \text{ kJ mol}^{-1}$, $k_2 = (7.44 \pm 0.75) \times 10^{-12} \exp[-(2437 \pm 110/R T)]$, (218–401) K. In addition, the following reaction was studied at 300 K: $\text{Cl} + \text{H}_2\text{O}_2 \xrightarrow{k_3} \text{HCl} + \text{HO}_2$, $\Delta U_{298} = -56.8 \text{ kJ mol}^{-1}$, $k_3 \approx 5.8 \times 10^{-13}$ (\pm factor 2.0), 300 K. A direct implication of the new rate data is the need to revise downward by a factor of 2.4 to 3 the magnitude of the ozone perturbation predicted by earlier model calculations due to the presence of ClO_x species in the stratosphere.

INTRODUCTION

Within the past year, there have been a series of papers appearing in the literature dealing with the possible effects of the presence of chlorine containing species of natural (e.g., CH_3Cl) and anthropogenic (e.g., CF_2Cl_2) origin in the stratosphere.^{1–8} It has been proposed that these contaminants, many of which have been observed in the troposphere and lower stratosphere, can photolyze or react with free radicals to produce Cl atoms or ClO radicals and thus promote the destruction of odd oxygen (odd oxygen $\equiv \text{O}^3P$ and O_3). The results of some model calculations predict that the presence of ClO_x ($\text{ClO}_x \equiv \text{ClO}$; HCl ; Cl ; OCIO ; ClOO) in the stratosphere at concentration levels in excess of 1 ppb (v/v) would cause a significant ($>2\%$) perturbation upon the integrated ozone column density. Quantitative model calculations require knowledge of the net upward flux of chlorine containing species through the tropopause, and their subsequent fate in the stratosphere, as well as accurate rate constant data for the key reactions.

The key chlorine reactions which participate in stratospheric chemistry are



where $\text{RH} \equiv \text{CH}_4$, H_2 , H_2O_2 , and HO_2 . Reactions (a) and (b) are primarily responsible for the conversion of odd oxygen into molecular oxygen. It can be shown that the efficiency (ρ) of the ClO_x catalytic cycle is governed by the rate of reaction (b):

$$\rho \propto 2k_b[\text{O}][\text{ClO}]. \quad (I)$$

Assuming steady state conditions for $[\text{O}]$ and $[\text{ClO}]$, the following alternate expression can be derived:

$$\rho \propto \frac{2k_a k_b k_g J_a [\text{O}_3]^2 [\text{HCl}][\text{OH}]}{k_d [\text{RH}] \{k_b J_a [\text{O}_3] + k_c k_f [\text{NO}][\text{O}_2][\text{M}]\}}, \quad (II)$$

where J_a is the photodissociation constant for O_3 , and k_f

is the rate constant for the third order recombination reaction of oxygen atoms with molecular oxygen. From Eq. (II) it can be seen that the catalytic efficiency is highly dependent upon several rate constants, many of which have received only limited study.

The present work provides an absolute determination of the chlorine atom rate constants with ozone and methane over a wide range of temperature and pressure to insure that the results can be directly applied to atmospheric model calculations. In addition, a limited study of the chlorine atom plus hydrogen peroxide system was performed at 300 K to ascertain whether this reaction is important in the stratosphere. The experimental technique used in this study was that of flash photolysis-resonance fluorescence.

EXPERIMENTAL

The experimental details and operating principles of the flash photolysis-resonance fluorescence technique have been fully described in the literature.⁹ Consequently, only recent modifications and essential details will be discussed.

Two reaction cells were used in this work: (1) a black anodized aluminum cell with an internal volume of $\sim 850 \text{ cm}^3$ for methane, and (2) a Pyrex cell with an internal volume of $\sim 150 \text{ cm}^3$ for ozone and hydrogen peroxide owing to their susceptibility to heterogeneous decomposition on metal surfaces. The cell temperature was controlled to within $\pm 0.5 \text{ K}$ by flowing methanol (235–325 K) or ethylene glycol (298–400 K) from a thermostated circulating bath through the outer jackets of the reaction vessels. Temperatures below 235 K could be controlled to within $\pm 2 \text{ K}$ using cooled dry N_2 . An iron-constantan thermocouple was used in conjunction with a wheatstone bridge resistance box to measure temperature, with a precision of better than 0.5 K.

Atomic chlorine was produced from the flash photolysis of CCl_4 or $\text{CF}_2\text{ClCFCl}_2$ by a N_2 spark discharge lamp in the presence of a reactive reagent (e.g., CH_4 , O_3 , H_2O_2) and a large excess of the diluent gas He or Ar. The mechanism for CCl_4 photodecomposition has been shown to be¹⁰

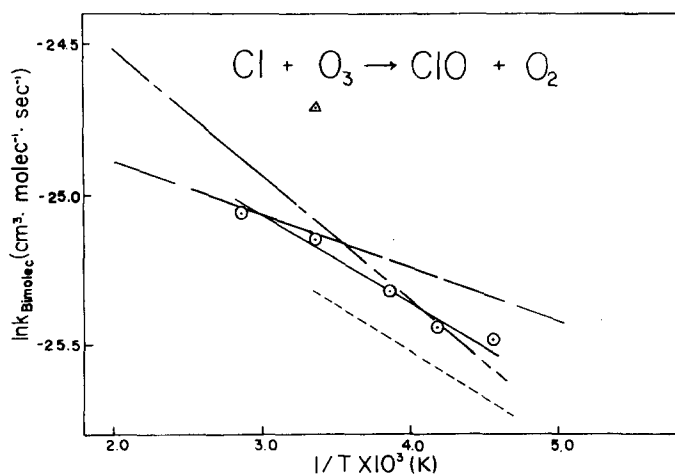
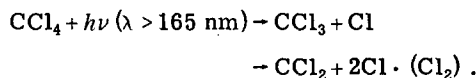


FIG. 1. Arrhenius plot for the $\text{Cl} + \text{O}_3$ reaction: Δ , Ref. 18; — — —, Ref. 21; — — —, Ref. 20; \circ , this work.



The spark discharge lamp was equipped with a window made of LiF , MgF_2 , sapphire, or Suprasil, depending upon the reagent present in the reaction cell. A Suprasil window was normally chosen to eliminate the production of reactive intermediates from the photodecomposition of the added reagent (i. e., $\text{CH}_4 + h\nu \rightarrow \text{CH}_2 + \text{H}_2$),¹¹ whose presence could lead to kinetic complications. Chlorine atoms formed in the $^2P_{1/2}$ state would have been rapidly quenched into the $^2P_{3/2}$ ground state by collision with CCl_4 .¹² For chlorine atoms thermally equilibrated at 300 K, the population of the $^2P_{1/2}$ state should have been 0.8% (the $^2P_{1/2}$ state lies $\sim 800 \text{ cm}^{-1}$ above the $^2P_{3/2}$ state).

Using published absorption cross-section data for CCl_4 ¹³ and flash energy of 80 J based on ethylene actinometry, it was calculated that typical chlorine atom concentrations of $\sim 5 \times 10^{10} \text{ atom cm}^{-3}$ were produced with a CCl_4 concentration of $2 \times 10^{15} \text{ molecule cm}^{-3}$. Initial chlorine atom concentrations were varied from 10^{10} – $2 \times 10^{11} \text{ atom cm}^{-3}$ by varying the flash energy from 20–250 J ($[\text{CCl}_4] = 2 \times 10^{15} \text{ molecule cm}^{-3}$), and from 10^{10} – $10^{11} \text{ atom cm}^{-3}$ by varying $[\text{CCl}_4]$ from 3 – $50 \times 10^{14} \text{ molecule cm}^{-3}$ (flash energy = 80 J).

Chlorine atoms were detected using a discharge-flow chlorine resonance lamp, the gas mixture consisting of $< 1\%$ of Cl_2 in Ar. As in previous studies,⁹ photon-counting electronics were used throughout this study. The linear relationship between chlorine atom concentration and the observed fluorescence intensity was established by varying the $[\text{Cl}]$ via a variation in the flash energy over a range of a factor of 20.

Each reaction was studied using pseudo-first-order kinetic conditions, $[\text{Reagent}]_0 \gg [\text{Cl}]_0$ ($[\text{Reagent}]_0/[\text{Cl}]_0 \geq 600$); and as expected, the chlorine atom concentration decayed exponentially with time. Because the initial chlorine atom concentration was kept low, multiple flashes (5–200) on a single gas mixture were required to produce a single smooth kinetic decay curve. How-

ever, the number of flashes per gas mixture was limited such that the decomposition of the added reagent (CH_4 , H_2O_2 , O_3) was always less than 3%. In some cases, therefore, several fillings of an identical gas mixture were used to develop a single experimental decay curve.

Gas pressures of less than 6 torr were measured using an mks Baratron pressure gauge which was periodically checked against a dibutyl phthalate manometer. The high pressure measurements (20–800 torr) were made with a two-turn Bourdon gauge (Wallace and Tiernan type FA-145). It was estimated that the precision to which CH_4/He gas mixtures could be made was better than $\sim 1\%$, but only $\sim 3\%$ – 5% for O_3/He mixtures due to uncertainties in the determination of ozone concentration caused by (a) small but significant amounts of heterogeneous decomposition and (b) experimental error in the measurement of $[\text{O}_3]$ by uv absorption at 260 nm. The CCl_4 and $\text{CF}_2\text{Cl}-\text{CFCl}_2$ pressures could not be metered so precisely at low temperatures in the Al cell due to absorption effects on the surfaces of the reaction cell. However, an uncertainty in these quantities did not lead to any inaccuracy in the reported rate data, as these species only acted as the precursor of atomic chlorine whose absolute concentration is not required in data analysis.

The CH_4 used in this study was of two types: (a) Matheson Ultra High Purity (stated purity of 99.97%) Gold Label; this was analyzed mass spectrometrically to contain 70 ppm of C_2H_6 and 20 ppm of C_3H_8 , (b) research grade (stated purity of 99.99%) which was shown to contain 20 ppm of C_2H_6 and < 5 ppm of C_3H_8 by mass spectrometric analysis. The CH_4 was thoroughly degassed in liquid N_2 (77 K) prior to use. The helium was Matheson "Gold Label Ultra High Purity" with a stated purity of 99.999%, and was used without further purification. The ozone was generated by flowing molecular oxygen through a commercial ozonizer and collected on silica gel at 196 K. Molecular oxygen was removed from the ozone by vacuum pumping the silica gel for 10–15 min. When required, the ozone was collected in a Pyrex bulb and diluted as required with He. The purity of the ozone was measured by uv spectrophotometry at 255.3 nm and was typically $\sim 90\%$ (10% O_2). The ozone cross section at 255.3 nm was taken from published data¹⁴ to be $137 (\text{atm at } 273)^{-1} \text{ cm}^{-1}$, base 10. Excellent agreement exists between several investigations of the published absorption cross section data for O_3 at 253.7 nm.^{14, 15}

RESULTS

A. $\text{Cl} + \text{O}_3 \xrightarrow{k_1} \text{ClO} + \text{O}_2$

The results for Reaction (1) are shown in Table I and Figure 1. Reaction (1) was studied under a range of temperature (218–350 K), pressure (5–40 torr) and other experimental parameters. Pseudo-first-order kinetic conditions $[\text{O}_3]_0 > [\text{Cl}]_0$, $\{[\text{Cl}]_0 \approx 5 \times 10^{10} \text{ atom cm}^{-3}; [\text{O}_3]_0 \approx (2.5\text{--}25) \times 10^{13}\}$ were employed so that Eq. (III) could be used to analyze the data.

$$-d[\text{Cl}]/dt = k_1[\text{Cl}][\text{O}_3] + k_{\text{diffusion}}[\text{Cl}], \quad (\text{III}) \\ \ln([\text{Cl}]_0/[\text{Cl}]_t) = \{k_1[\text{O}_3] + k_{\text{diffusion}}\}t$$

TABLE I. Reaction rate data for the process $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$.

Temperature (K)	Diluent (torr)	CCl_4 (mtorr)	O_3 (mtorr)	Flash energy (J)	k_1' (s^{-1})	$k_{\text{bimolecular}} \times 10^{12}$ ($\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$)
220	5(He)	65	0.00	88	100	8.57 ± 0.62
			1.11	443		
			1.67	580		
			2.12	925		
			2.51	1111		
			3.13	1325		
			3.65	1570		
			4.38	1920		
			4.46	1710		
			4.70	1940		
239	5(He)	65	1.11	88	730	8.95 ± 1.17
			2.12	1075		
			3.28	1550		
			3.92	1702		
			4.33	1870		
			5.45	2425		
			6.39	2873		
			7.65	2900		
259	5(He)	65	0.80	88	436	10.04 ± 0.5
			1.24	595		
			1.67	775		
			2.09	794		
			2.45	1008		
			2.48	1111		
			3.13	1272		
			3.82	1560		
			5.27	2080		
			6.57	2590		
			298	5(He)	65	
1.04	601					
1.66	740					
1.71	691					
2.11	935					
2.19	20	1040				
2.19	88	1083				
2.19	180	928				
2.19	88	1020				
2.19	88	944				
2.58	1048					
3.13	1366					
3.23	1344					
3.44	1425					
4.38	1818					
4.97	2200					
6.26	2450					
298	40(Ar)	65	0.00	88	40	11.44 ± 0.50
			1.57	547		
			2.17	696		
			3.13	1060		
			3.81	1320		
			4.18	1445		
			5.22	1984		
			7.31	2800		
			350	5(He)	65	
1.72	800					
2.32	1052					
3.00	1250					
3.42	1465					
4.46	1740					

Numerous preliminary experiments were performed to show that ozone did not decay (< 5%) due to heterogeneous decomposition on the reactor surface. The first order rate constant k_1' was determined for a particular gas mixture after the gas was allowed to reside in the reaction cell for different times (0, 2, 5, 10 min) before the experiment was initiated. After an initial "aging" period it was found that k_1' was independent of residence time. However, it was observed that there was a dependence of k_1' upon residence time if the two resonance lamps were on, indicating long term photolytic decomposition of the ozone (k_1' decreased with residence time). Consequently, the time taken to perform an experiment was limited to < 2 min to eliminate inaccuracies in the

measurement of k_1' due to photolytic decomposition of the ozone. Experiments were performed which showed that there was no observable dependence of k_1' upon the flash energy or CCl_4 concentration (Table I). These experiments verified that there was no dependence of the bimolecular rate constant upon initial chlorine atom concentration, and that there was no "flash" decomposition of ozone. Experiments utilizing a variation in the number of flashes per filling of a particular gas mixture showed a decrease in k_1' as the number of flashes increased. This was not due to a regeneration of atomic chlorine, but photolytic decomposition of ozone caused by the increased length of time required to complete the experiment. Consequently the number of flashes per single filling of the reaction cell was limited to ≤ 20 (~ 90 s).

Although there was no significant (< 5%) variation of the bimolecular rate constant with total pressure, there was with temperature. A weighted (dependent upon the number of experiments and reliability of the results) least squares fit of the data was performed at each temperature to determine the bimolecular rate constant at that temperature. A weighted least squares fit of the bimolecular rate constants then produced the following Arrhenius expression:

$$k_1 = (3.08 \pm 0.30) \times 10^{-11} \exp[-576 \pm 50 \text{ cal mol}^{-1}/RT] \\ (220-350 \text{ K}).$$

A total of 60 experiments were performed where the results were used to compute the Arrhenius expression shown above. The most probable systematic error in this study is that of overestimating the ozone concentration due to a small amount of heterogeneous and/or photolytic decomposition (total < 7%).

Possible complicating secondary reactions which must be considered are



Reactions (1a)–(1e) can be rejected for the following reasons. The rate constant for Reaction (1a) has recently been reported¹⁶ to be $\leq 5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which eliminates any possibility that this reaction could regenerate atomic chlorine on the time scale of the experiment. Atomic oxygen could be formed from the photolysis of ozone or molecular oxygen (impurity in the ozone); however, the rate of reaction (b) should be dependent upon the square power of the flash energy. The observed first order rate constants showed no dependence upon flash energy, precluding the need to consider this reaction (in agreement with calculations). The absence of a pressure dependence in the bimolecular rate constant is also in agreement with calculations which indicate that complications due to reactions (c), (d), and (e) should be of negligible importance.

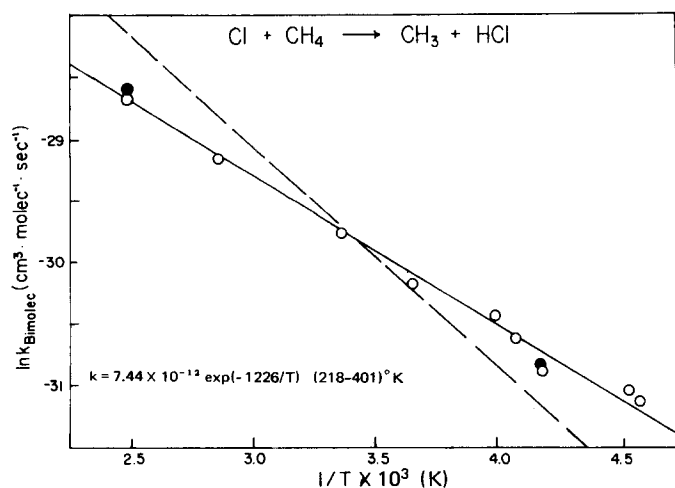


FIG. 2. Arrhenius plot for the $\text{Cl} + \text{CH}_4$ reaction. ———, Ref. 22; o, this work, where CCl_4 was used as the Cl atom precursor; ●, this work, where $\text{CF}_2\text{ClCF}_2\text{Cl}$ was used as the Cl atom precursor.

B. $\text{Cl} + \text{CH}_4 \xrightarrow{k_2} \text{CH}_3 + \text{HCl}$

The results of reaction (2) are presented in complete detail in Table II. This reaction was again studied using pseudo-first-order conditions, $[\text{CH}_4]_0 \gg [\text{Cl}]_0$, so that the individual plots of Cl atom decay with time could be analyzed using Eq. (IV):

$$-d[\text{Cl}]/dt = k_2[\text{Cl}][\text{CH}_4] + k_{\text{diffusion}}[\text{Cl}], \quad (\text{IV})$$

$$\therefore \ln([\text{Cl}]_0/[\text{Cl}]_t) = (k_2[\text{CH}_4] + k_{\text{diffusion}})t.$$

Reaction (2) was thoroughly studied over a range of temperature (218–401 K) and pressure (20–100 torr He; 50 torr Ar). The bimolecular rate constant k_2 , and the individual pseudo-first-order rate constants k_2' (after correction due to differences in the Cl atom diffusion rates for differing total pressures and diluent gases) were found to be invariant with diluent gas pressure, and the nature of the diluent gas (Table II). These observations verify that the reaction studied was bimolecular, as expected, and that complications due to secondary processes which are third order in nature, were not important under the experimental conditions of low ($\sim 10^{11}$ atom cm^{-3}) Cl atom concentration as used in this study. Experiments utilizing variations in CCl_4 concentration (15–150 mtorr) were performed with no significant deviations in the experimental first order rate constants being observed. A series of experiments was performed at 239 and 401 K, where $\text{CF}_2\text{ClCF}_2\text{Cl}$ was substituted for CCl_4 as the precursor of atomic chlorine. The concentration of $\text{C}_2\text{F}_3\text{Cl}_3$ was varied by a factor of 20 (10–200 mtorr) and the bimolecular rate constant k_2 was shown to be independent of $\text{C}_2\text{F}_3\text{Cl}_3$ concentration at each temperature, and within the expected experimental uncertainty of our results ($< 10\%$) yielded a similar value for k_2 , as the experiments where CCl_4 was used as the atomic precursor. Variations in the flash energy by a factor of ~ 12 (20–250 J) also resulted in no significant variations of the bimolecular rate constant. The observation that large variations in initial Cl atom concentration by factors of ~ 13 ($1.1\text{--}14 \times 10^{10}$ at 299 K) and ~ 34 ($0.43\text{--}15 \times 10^{10}$ at

238 K), produced by varying CCl_4 (or $\text{C}_2\text{F}_3\text{Cl}_3$) and the flash energy, resulted in no significant variation in the first order rate constants, is strong evidence that complicating secondary kinetic processes were of no importance in this study. As noted earlier, the flash lamp was equipped with either a sapphire or quartz window to prevent the photolysis of CH_4 below 140 nm, which would result in the production of CH_2 radicals whose presence in concentrations of $\geq 10^{12}$ radical cm^{-3} could cause serious kinetic complications. The experiments which were performed with a large variation in flash energy (20–245 J at 299 K, and 25–245 J at 238.5 K) showed no variation in first order rate constant, which eliminates the possibility of kinetic complications due to labile photolytic fragments reacting rapidly with atomic chlorine.

A third series of experiments was performed in which the number of consecutive flashes per single filling of a particular gas mixture was varied. At 299 and 401 K, the number of flashes per single filling was varied by a factor of 20 (5–100, and 10–200, respectively), and at 239 K by a factor of 10 (20–2000) with no significant variation in the observed first order rate constants. These experiments tend to eliminate kinetic complications due to a buildup in the concentration of a “reactive” stable product.

As stated in the experimental section of this paper, two samples of CH_4 were used in this study. The first was analyzed to contain 70 ppm of C_2H_6 and 20 ppm of C_3H_8 , whereas the second contained 20 ppm of C_2H_6 and < 5 ppm of C_3H_8 . There was no discernable dependence of the bimolecular rate constant on the particular tank of CH_4 used (see Fig. 2), indicating that these low impurity levels caused no inaccuracy in the reported rate data.

Whereas the bimolecular rate constant showed no variation with diluent pressure, flash energy, or initial chlorine atom concentration, it did vary significantly with temperature. A weighted least squared fit of all the data shown in Table II yields the following Arrhenius expression:

$$k_2 = (7.44 \pm 0.75) \times 10^{-12} \exp[-(2436 \pm 100 \text{ cal mol}^{-1}/RT)] \quad (218\text{--}401 \text{ K}).$$

In summary, it can be stated that a total of ~ 180 experiments were performed using a wide range of conditions, such that the probability of the Arrhenius expression being significantly incorrect due to complicating secondary kinetic processes seems extremely low. And it should be noted from Fig. 2 that there is no observable curvature in the Arrhenius plot (to be discussed later) over the temperature range studied.

C. $\text{Cl} + \text{H}_2\text{O}_2 \xrightarrow{k_3} \text{HCl} + \text{HO}_2$

The results of Reaction (3) are shown in Table III. As in the case of Reactions (1) and (2), the study of H_2O_2 was performed using first order conditions where $[\text{H}_2\text{O}_2]_0/[\text{Cl}]_0$ ranged from $9 \times 10^3\text{--}8 \times 10^4$. The results from the study of Reaction (3) were found to be less reproducible than would normally be acceptable, presum-

TABLE II. Reaction rate data for the process $\text{Cl} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{HCl}$.

Temperature (K)	Diluent (torr)	CCl_4 (mtorr)	CH_4 (mtorr)	Flash energy (J)	Flashes per filling	Flash window material	k_2' (s^{-1})	$k_{\text{bimolecular}} \times 10^{14}$ ($\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$)		
218	20(He)	65	0	88	25	S	40	2.98 ± 0.40		
			50			A	82			
			100			P	135			
			150			P	200			
			200			H	271			
			250			I	355			
			300			R	400			
			E							
220	40(He)	65	50	88	25	Q	84	3.31 ± 0.33		
			75			U	117			
			100			A	169			
			125			R	191			
			150			T	240			
			175			Z	272			
			200				322			
238.5	40(He)	65	25	88	25		94	3.86 ± 0.30		
			31		15	95				
			31.65		25	105				
			50		25	122				
			75		25	181				
			99		35	212				
			15		100	45	50		187	
			65		100	88	50		198	
					150		125		Q	283
					150		25		U	324
					150		25		A	268
					150	25	75		R	267
					150	210	10		T	301
					150	88	150		Z	289
					15	150				253
					65	200				382
						200				407
					15	200	45		100	328
					15	200	20		100	326
					65	200	88		50	338
	15	200	30	100	348					
	65	200	106	100	400					
239	40(He)	$10(\frac{T}{13})$	25	88	50	Q	70.3	3.79 ± 0.09		
			100		A	193				
			250		R	417				
					T					
					Z					
	40(He)	$50(\frac{T}{13})$	25	88	50		90.5	4.15 ± 0.50		
			25			105.8				
			100			210				
			100		75	221				
			100			207				
100			20		150	Q	203			
100			245		20	U	240			
160					50	A	313			
250					75	R	450			
250						T	467			
250	25	150	Z	431						
250	245	25		446						
250	88	20		397						
250		200		398						
268		100		543						

TABLE II (Continued)

Temperature (K)	Diluent (torr)	CCl_4 (mtorr)	CH_4 (mtorr)	Flash energy (J)	Flashes per filling	Flash window material	k_2^1 (s^{-1})	$k_{\text{bimolecular}} \times 10^{14}$ ($\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$)
	40(He)	200($\frac{\text{TF}}{13}$)	25 100 250			Q U A R T Z	138.9 245 483	3.81 ± 0.02 3.99 ± 0.18
245	40(He)	65	20 40 60 98.5	88	25	Q U A R T Z	89 137 172 247	4.94×0.30
245	40(He)	65	25 50 75 100 125 150	88	25	Q U A R T Z	87 146 192 231 282 342	5.00 ± 0.26 4.97 ± 0.30
250	20(He)	65	0 20 30 40 40 40 40 50 60 70 80	88 45 211	30 30 50 50 100 100 35 50 50 50 50	S A P P H I R E	40 90 117 138 138 135 144 168 177 216 225	6.01 ± 0.29
	200(He)	65	0 40 80	88	40 75 100	SAP- PHIRE	18 133 212	6.29 ± 0.29
273	20(He)	65	20 30 50 60 70 80	88	50	S A P P H I R E	116 145 185 224 267 278	7.92 ± 0.98
298	20(He)	65	0 15 30 45 45 60 75	88	25 50	S A P P H I R E	36 122 180 225 230 290 331	11.90 ± 1.00
	50(Ar)	65	20 40 60	88	25	SAP- PHIRE	100 175 248	11.4 ± 0.9

TABLE II (Continued)

Temperature (K)	Diluent (torr)	CCl_4 (mtorr)	CH_4 (mtorr)	Flash energy (J)	Flashes per filling	Flash window material	k'_2 (s^{-1})	$k_{\text{bimolecular}} \times 10^{14}$ ($\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$)			
	20(He)	65	0		25		46				
			0				46				
			15		50		123				
			30				180	S			
			30		5		196	A			
			30	45	100		188	P			
			30	215	20		174	P			
			45	88	25		240	H			
			45				232	I			
			45		100		218	R			
			60		25		290	E			
			60				282				
			60		100		300				
			75		25		330				
			90				408				
			90				380				
									11,50 ± 0.60		
				200(He)	65	0	88	30	SAP-	31	
						30		100	PHIRE	151	12,4 ± 2.0
				40(He)	65	0	88	25		45	
15						QUARTZ	103				
30							165				
45							220				
60							280				
90							383				
					120		495	11.4 ± 0.2			
299	40(He)	65		20	88	25		182			
				20				155			
				70				375			
			70			Q	369				
			70		100	U	345				
			70		10	A	368				
			70		25	R	342				
			70	20		T	340				
			70	245	10	Z	363				
			70	45	25		386				
			70	88	25		653				
					150	150	88		707	12,08 ± 0.03	
					65	150					
			350	100(He)	65	0	88	25	S	77	
7		25				A	125				
14		50				P	157				
21						P	221				
28						H	258				
35						I	295				
42						R	330	21,83 ± 1.90			
						E					
401	40(He)	65	25	95	50		460				
			25				462				
			50				676				
			75			Q	933				
			100			U	1104				
			100			A	1004				
			100		200	R	1082				
			100		10	T	1042				
			15	45	50	Z	1118				
			65	150	95		1577				
					200		1905				
					268		2564	35,4 ± 1.2			
401	40(He)	50($\frac{\text{TF}}{15}$)	25	95	50	Q	526				
		20($\frac{\text{TF}}{13}$)	100			U	1203				
		50($\frac{\text{TF}}{13}$)	100			A	1199				
		100($\frac{\text{TF}}{13}$)	100			R	1205				
		50($\frac{\text{TF}}{13}$)	268			T	2778	38,45 ± 0.38			
						Z					

TABLE III. Reaction rate data for the process Cl + H₂O₂ → HCl + HO₂.

Temp (K)	Diluent (torr)	CCl ₄ (mtorr)	H ₂ O ₂ (mtorr)	Flash energy (J)	k ₃ ' (s ⁻¹)	k ^{bimolecular} (cm ³ molecule ⁻¹ s ⁻¹)
298	50(Ar)	65	0	100	15.5	
			6.7		46.5	
			11.7		92.4	
			16.7		138	
			16.7		155	
			20.0		260	
			20.0		216	
			21.65		226	
			21.65		333	
			21.65		256	
			21.65		282	
			26.65		370	
			26.65		445	
			33.3		534	
			33.3		295	
			83.25		1000	
116.6		1667	5.8 × 10 ⁻¹³			

ably due to heterogeneous decomposition of H₂O₂ on the reactor surfaces. Consequently, the uncertainty limits placed upon the final result obtained for the bimolecular rate constant have been made much larger than normal (a factor of 2). A total pressure of 50 torr of argon was used to slow diffusion to the reactor surfaces and thus minimize heterogeneous wall loss. The H₂O₂ concentration was determined by uv spectrophotometry using published absorption cross-section data.¹⁷ These measurements were normally made immediately before mixtures in He were prepared in preconditioned bulbs.

A least squares fit of the data in Table III produce the following bimolecular rate constant:

$$k_3 = 5.8 \times 10^{-13} \pm (\text{factor } 2) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \quad 298 \text{ K.}$$

DISCUSSION AND COMPARISON WITH PREVIOUS RESULTS

A. The Cl + O₃ $\xrightarrow{k_1}$ ClO + O₂ reaction

Figure 1 and Table IV summarize the Arrhenius expressions obtained in this and other studies of the kinetic behavior of the chlorine atom-ozone reaction.

From Table IV it can be seen that a variety of techniques have been employed to study Reaction (1) within the temperature range of the stratosphere (200–270 K). The original determination of k_1 at 298 K¹⁸ utilized the low pressure discharge flow mass spectrometric technique to monitor the decay of ozone (O₃^{*}, $m/e = 48$) in the presence of various excess concentrations of atomic chlorine. The study yielded a value of $(1.85 \pm 0.36) \times 10^{11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is ~50% higher than the mean value $[(1.19 \pm 0.13) \times 10^{11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$ of the four recent studies at 298 K, and just outside the stated uncertainty limits. This apparent discrepancy can only be attributed to the somewhat indirect technique employed to determine the atomic chlorine concentration in the mass spectrometric study. In this and three other recent determinations of the temperature dependence of k_1 ,^{19–21} the decay of atomic chlorine was monitored in the presence of an excess concentration of ozone (pseudo-first order conditions) utilizing the techniques of atomic resonance fluorescence (this work and Refs. 19 and 20) and atomic resonance absorption²¹ to detect the chlorine atoms (²P_{3/2,1/2}). All four studies used uv absorption spectroscopy at ~254 nm to determine the ozone concentration. The absorption cross-section data for the Hartley band of ozone has been well documented and should be considered to be accurate to within ~1%.^{14,15} Consequently, differences in the rate constant data of the four recent studies and the original mass spectrometric study cannot be attributed to an inaccuracy in the ozone cross-section data. The value of k_1 at 298 K obtained from the four recent studies varies by ~30% (1.02 – $1.33 \times 10^{11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$); consequently, the agreement between these studies can only be considered moderately good. At present, it is uncertain whether the mass spectrometric value should be neglected in calculating the best value for k_1 at 298 K. Unit weighting for all five determinations of k_1 results in a mean value of $(1.32 \pm 0.31) \times 10^{11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

As stated above, the agreement between the results of this and three other recent studies at 298 K can be considered moderately good. At 220 K, it is somewhat worse, there being a 40% spread in the values of the re-

TABLE IV. Summary of Arrhenius expressions for the process Cl + O₃ → ClO + O₂.

Reference	Arrhenius expression (cm ³ molecule ⁻¹ s ⁻¹)	k ₁ (298 K) × 10 ¹¹ (cm ³ molecule ⁻¹ s ⁻¹)	Temperature range (K)	Technique ^a
Clyne and Watson ¹⁸	...	1.8 ₅ ± 0.3 ₆	298	DF/MS
Kurylo and Braun ¹⁹	2.72 ± 0.45 × 10 ⁻¹¹ × exp[-(592 ± 78/RT)]	1.02 ± 0.05	213–298	FP/RF
Kaufman <i>et al.</i> ²⁰	(2.17 ± 0.43) × 10 ⁻¹¹ × exp[-(340 ± 60/RT)]	1.22	205–366	DF/RF
Nip and Clyne ²¹	(5.15 ± 0.5) × 10 ⁻¹¹ × exp[-(831 ± 55/RT)]	1.33 ± 0.26	221–629	DF/RA
This study	(3.08 ^{+0.45} _{-0.15}) × 10 ⁻¹¹ × exp[-(576 ± 50/RT)]	1.20 ± 0.10	220–350	FP/RF

^aDF: discharge flow; FP: flash photolysis; MS: mass spectrometry; RF: resonance fluorescence; RA: resonance absorption.

TABLE V. Summary of Arrhenius expression ratios ($k_{\text{H}_2}/k_{\text{CH}_4}$).

Reference	$A_{\text{CH}_4}/A_{\text{H}_2}$	$E_{\text{H}_2}-E_{\text{CH}_4}$	Temperature range (K)
Knox and Nelson ²⁵	0.30	1650 ± 60	193–593
Pritchard, Pyke, and Trotman-Dickenson ²⁴	0.32	1650 ± 150	293–488
Mean value	0.31	1650 ± 100	193–593

ported rate constants ($0.7-1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).

The values reported for the activation energy of Reaction (1) range from 340–831 cal mol⁻¹. Obviously, however, the accurate determination of small (< 1 kcal mol⁻¹) activation energies for a reaction is very difficult when measurements are made over a limited temperature range. Consequently, although the values reported for the activation energy E_1 vary by a factor of ~ 2.5 (340–831 cal mol⁻¹) the agreement must be considered to be reasonably good. A least squares fit of the individual bimolecular rate constants reported in this and the other three recent studies yields the following Arrhenius expressions:

- (a) $(2.69 \pm 1.2) \times 10^{-11} \exp[-(511 \pm 211)/RT]$
(205–298) K ,
- (b) $(3.34 \pm 1.0) \times 10^{-11} \exp[-(615 \pm 150)/RT]$
(205–466) K .

All data points were weighted equally. However, the data published by Kurylo and Braun¹⁹ and Kaufman *et al.*²⁰ have been corrected due to a revision (~ 7.5%) in the value used for the ozone absorption cross section. Expression (a) was evaluated by using all the experimental data collected at 298 K and below, whereas the data points at 350 K (this study); 366 K (Kaufman, *et al.*)²⁰ and 452 K (Clyne and Nip)²¹ were included in the evaluation of expression (b). Both expressions yield essentially the same bimolecular rate constants between 220 and 298 K (e.g., k_1 (240 K): (a) = 9.21×10^{-12} ; (b) = 9.20×10^{-12}). Expression (a) is recom-

mended for use in the model calculations of the stratosphere (discussed later).

B. $\text{Cl} + \text{CH}_4 \xrightarrow{k_2} \text{CH}_3 + \text{HCl}$

Hydrogen abstraction reactions, such as the chlorination of methane, have been the subject of extensive study; however, most of the data was obtained using the competitive photochemical chlorination technique where only relative rate constants could be measured. The reaction between atomic chlorine and molecular hydrogen was used as the primary standard, as its Arrhenius expression was thought to be well established over a wide range of temperature. The only previous direct determination of the temperature dependence of Reaction (2) utilized a low pressure discharge flow system where the decay of methane was monitored mass spectrometrically (CH_4^+ , $m/e = 16$) in the presence of a large excess concentration of atomic and molecular chlorine.²²

Table V presents the results of the competitive chlorination studies^{23,24} in the form of (a) ratio of pre-exponential A factors, and (b) difference in activation energies. The two results differ only by ~ 7% in the magnitude of the pre-exponential factor. Therefore, the mean result of the two competitive studies will be used for comparison purposes with the results of the more recent direct studies. Table VI summarizes the published Arrhenius expressions for the $\text{Cl} + \text{H}_2$ reference reaction. It can be seen that there is considerable variation between the Arrhenius parameters shown in Table VI (to be discussed) which results in a variety of expressions which can be derived for the $\text{Cl} + \text{CH}_4$ reaction. The Arrhenius expressions derived for Reaction (2) from the competitive studies are summarized together with those obtained from the direct studies in Table VII. However, a brief discussion on the preferred Arrhenius expression for the $\text{Cl} + \text{H}_2$ reaction will be necessary before the results of Reaction (2) can be discussed more fully.

As the $\text{Cl} + \text{H}_2$ rate constant data has recently been reviewed,^{13b} it will suffice to present a synopsis of the conclusions. The Arrhenius expressions forwarded by

TABLE VI. Summary of Arrhenius expressions for k ($\text{Cl} + \text{H}_2$).

Reference	Arrhenius expression k_{H_2} ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	Temperature range (K)
Fettis and Knox ^a	$(1.38 \pm 0.1) \times 10^{-10} \exp[-(5500 \pm 140)/RT]$	273–1071
Benson <i>et al.</i> ^b	$(8.0 \pm 2.0) \times 10^{-11} \exp[-(5275 \pm 400)/RT]$	273–1071
Clyne and Walker ^c	(i) $(3.7 \pm 0.6) \times 10^{-11} \exp[-(4264 \pm 100)/RT]$	195–610
	(ii) $(5.6 \pm 1.2) \times 10^{-11} \exp[-(4485 \pm 137)/RT]$	195–496
Watson <i>et al.</i> ^d	(i) $(5.5 \pm 1.0) \times 10^{-11} \exp[-(4750 \pm 100)/RT]$	213–350
	(ii) $(4.7 \pm 0.4) \times 10^{-11} \exp[-(4776 \pm 59)/RT]$	213–1071

^aEvaluation based on all previous data (Refs. 26, 29, 42, 43).

^bEvaluation based on their own data, and reinterpreted data taken from Refs. (26, 29, 42, 43, 40, 44).

^ci. Evaluation based on determinations of both $k_{-\text{H}_2}$ and k_{H_2} (Refs. 27, 31, 40, 44). ii. Evaluation based on $k_{-\text{H}_2}$ (Refs. 31, 40, 44).

^di. Direct determination of k_{H_2} using flash photolysis–resonance fluorescence (Ref. 28). ii. Evaluation based on (di), and data from Refs. 27, 29.

Fettis and Knox²⁶ and Benson *et al.*²⁷ have been updated in favor of that suggested by Watson,²⁵ which was strongly influenced by the recent determination of the temperature dependence of the rate constant using the flash photolysis–resonance fluorescence technique.²⁸ This recent determination [Expression (a)] represents the most extensive single study yet completed of the $\text{Cl} + \text{H}_2$ reaction. Extrapolation of these results²⁸ to higher temperatures are seen to be in excellent agreement with those of Benson *et al.*²⁷ and Steiner and Rideal.²⁹ This combined data base has resulted in Expression 4b in Table VI. The expressions forwarded by Clyne and Walker²² (3a and 3b) were predominantly based on the experimental data for the reverse reaction, $\text{H} + \text{HCl} \rightarrow \text{Cl} + \text{H}_2$, and the assumption that this data could be combined with published thermochemical data to yield an Arrhenius expression for the reaction of Cl with H_2 . It has recently been reported that there is a significant error in the $\text{H} + \text{HCl}$ data,³⁰ the expressions based on this data have been rejected in favor of that using only data from studies of the forward reaction. Therefore, the preferred Arrhenius expression for the $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$ reaction is $4.7 \times 10^{-11} \exp[-4676/RT]$.

Based on the above value of $K_{\text{Cl}+\text{H}_2}$ these authors feel that the best value which can be obtained for k_2 from the competitive chlorination studies is Expression d (Table VII): $1.45 \times 10^{-11} \exp[-(3026/RT)]$. From this expression a value of 0.88×10^{-13} can be obtained for k_2 at 298 K, which is in somewhat better agreement with the direct studies but still nearly 40% lower. A more detailed analysis of the possible reasons for the discrepancy between the competitive chlorination technique and that of direct resonance fluorescence measurements has been presented in another manuscript.²⁸ Suffice it to say, the results of this extensive analysis have indicated that neglecting the reactions $\text{HCl} + \text{CH}_3 \rightarrow \text{CH}_4 + \text{Cl}$ and $\text{Cl} + \text{CH}_3\text{Cl} \rightarrow \text{HCl} + \text{CH}_2\text{Cl}$ in the competitive studies involving CH_4 and H_2 would have resulted in the measuring of too small a value for $E_{\text{H}_2} - E_{\text{CH}_4}$, and hence, too large an activation energy for $\text{Cl} + \text{CH}_4$. It should be noted, however, that at present the actual magnitude of this effect cannot be estimated for lack of accurate rate data and the absence of certain experimental parameters.

The value ($1.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) reported by Davis *et al.*³¹ is ~20% greater than the average of the other two direct studies ($1.24 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).

The Davis *et al.*³¹ study utilized the flash photolysis–resonance fluorescence technique where it was reported that the relationship between the intensity of fluorescence and chlorine atom concentration could be represented by $I_F \propto [\text{Cl}]^{0.9}$. However, if the true relationship had been $I_F \propto [\text{Cl}]$ then the value derived for k_2 would have been $1.35 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, in better agreement with the other studies. It should be noted that the relation $I_F \propto [\text{Cl}]^{0.9}$ in the work by Davis *et al.*³¹ was not based on a direct experimentally measured correlation between I_F and $[\text{Cl}]$, but rather on calculations involving chlorine resonance line shapes, growth curves, and estimated Cl concentrations. The preferred value for k_2 at 298 K is now taken to be $(126 \pm 0.07) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (weighted average of this study, Clyne and Walker²² and the modified value of Davis *et al.*³¹).

There is a large variance in the three values reported for the activation energy of Reaction (2). At present, no explanation can be forwarded for the difference in the results of the two direct studies ($E_a = 2.44$ and 3.56 kcal). However, it should be noted that Clyne and Walker also measured the activation energy for the $\text{Cl} + \text{CH}_3\text{Cl}$ reaction to be ~3.55 kcal; whereas, a value of 2.56 kcal was obtained for this activation energy by these authors. The immediate observation is that the results differ by ~1.0 kcal, as was the case for E_2 . A further point which should be noted is that the values obtained for the $\text{Cl} + \text{CH}_3\text{Cl}$ rate constant at 298 K are in good agreement (4.87×10^{-13} vs 4.50×10^{-13}). Thus, in both cases the rate constants measured at 298 K are in excellent agreement; whereas, the activation energies differ by ~1 kcal mole⁻¹. The most likely source of error in the discharge flow study could have been in the determination of the chlorine atom concentration, but this would normally have propagated an error in the pre-exponential A factor, not in the activation energy.

The experimental pre-exponential A factor derived from this study is significantly lower than would be predicted from the activated complex theory, i. e., $A_2 = 5.5 \times 10^{-11}$.³² However, there are numerous reactions which have low experimental pre-exponential A factors when measured over a restricted low temperature range, e. g.,

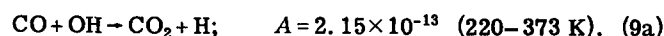
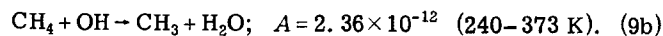


TABLE VII. Summary of Arrhenius expressions for $k(\text{Cl} + \text{CH}_4)$.

Reference	Arrhenius expression ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	$k_{298} \times 10^{14}$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	Temperature range (K)
Competitive chlorination ^{23,24}	(a) $4.28 \times 10^{-11} \exp[-(3850/RT)]$	6.42	193–593
	(b) $2.48 \times 10^{-11} \exp[-(3625/RT)]$	5.44	
	(c) $1.74 \times 10^{-11} \exp[-(2835/RT)]$	14.5	
	(d) $1.45 \times 10^{-11} \exp[-(3026/RT)]^a$	8.75	
Clyne and Walker ²²	$5.1 \times 10^{-11} \exp[-(3560 \pm 37/RT)]$	13.0	300–686
This work	$(7.44 \pm 0.7) \times 10^{-12} \exp[-(2437 \pm 100/RT)]$	11.8	218–401
Davis, Bass, and Braun ³¹	...	15.0	298

^aBest value, based on the preferred value of k_{H_2}

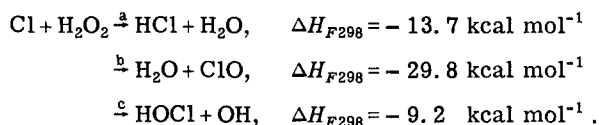


Recent studies of the kinetic behavior of the OH + CO³³ and OH + CH₄³⁴ reactions over a wide range of temperature in a single system (300–900 K) have seemingly verified earlier theories of nonlinear Arrhenius behavior. The apparent nonlinear Arrhenius behavior of the other reactions (e.g., H + CH₄ → CH₃ + H₂, H + C₂H₆ → C₂H₅ + H₂, CH₃ + H₂ → H + CH₄) are in good agreement with that predicted from bond energy–bond order calculations of the rate coefficients.^{35,36}

Therefore, although no significant curvature was observed in the Arrhenius plot of the rate constant data for Reaction (2), its possibility cannot be excluded.

C. Cl + H₂O₂ ^{k₃} → products

This is the first reported study of Reaction (3). Unfortunately, only the rate of removal of atomic chlorine could be monitored. Thus, the following three primary processes which are exoenergetic must receive serious consideration:

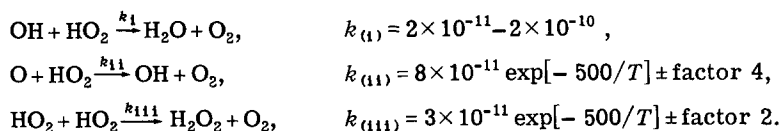


Based on steric conditions, process (a) would be favored; however, the results from kinetic studies of the reaction between atomic hydrogen and hydrogen peroxide would argue that at least two primary processes are probably important.⁴¹ Hence, at the moment it appears that there is no scientific basis for excluding the partitioning of the net rate constant for Reaction (3) into separate *k* values for processes (a), (b), and (c).

ATMOSPHERIC IMPLICATIONS OF NEW RATE DATA

Numerous model calculations have demonstrated that the injection of chlorinated compounds into the stratosphere results in the selective destruction of odd oxygen at midaltitudes (~25–45 km),^{1–8} where the catalytic efficiency (ρ) can be expressed via Eq. (II).

$$\rho \propto \frac{2k_a k_b k_c J a [\text{O}_3]^2 [\text{HCl}] [\text{OH}]}{k_d [\text{RH}] \{k_b J a [\text{O}_3] + k_c k_f [\text{NO}] [\text{O}_2] [\text{M}]\}} \quad (\text{II})$$



The magnitude of [HO]_x and its partitioning (HO_x ≡ H + OH + HO₂ + H₂O₂) is dependent upon the selection of rate constant data for reactions (i)–(iii). The majority of model calculations have performed using a high value for *k*_(i) (2 × 10⁻¹⁰ cm³ molecule⁻¹ sec⁻¹), the predominant chain termination process for HO_x, resulting in a low [HO_x]/([H₂O] + [CH₄] + [H₂]) ratio. Recent rate data³⁸ for O¹D reactions with N₂, O₂ (quenching), H₂O, CH₄, N₂O, and H₂ (reactive) increases the uncertainty in the accuracy of the published [HO_x] profiles. Model calculations which have used high values for *k*_(i) and

This study reinvestigated the kinetic behavior of processes (a), (Cl + O₃ → ClO + O₂), and (d), where *k*_d[RH] can be written:

$$k_d [\text{RH}] = k_2 [\text{CH}_4] + k_3 [\text{H}_2\text{O}_2] + k_4 [\text{H}_2] + k_5 [\text{HO}_2].$$

New results are reported for *k*₂, *k*₃, and *k*₄. The most expedient approach, which can be taken in order to evaluate the effect of the new rate constant data upon the published results of the model calculations, is to assume that the altitude most sensitive to the injection of ClO_x is 35 km, and to discuss the consequences of the new kinetic information at that altitude. The temperature of the standard stratosphere at 35 km is taken to be 237 K.

The early model calculations^{4–7} used a temperature invariant rate constant of 1.85 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ for *k*_a. A value of 9.06 × 10⁻¹² cm³ molecule⁻¹ s⁻¹ was derived for *k*_a at 237 K from the Arrhenius expression obtained in the present study. This is in close agreement with the value of 9.09 × 10⁻¹² cm³ molecule⁻¹ s⁻¹, which was obtained from the “evaluated” Arrhenius expression [see discussion on Reaction (1)]. The new value of *k*_a at 237 K is a factor of 2.0 lower than that used in the early calculations. Consequently, use of Eq. II would predict that the catalytic efficiency (ρ) would be reduced by a factor of 2; however, this simplistic approach predicts the maximum possible change as there will be an increase in the ozone density at lower altitudes produced by the self-healing effect.

The greater the magnitude of *k*_d[RH], the lower the catalytic efficiency of ClO_x due to the “tying up” of chlorine in the inactive form of HCl. Although concentration profiles for both CH₄ and H₂ have been experimentally determined up to ~50 km in the stratosphere,³⁷ neither HO₂ nor H₂O₂ have been directly monitored. Consequently, the only profiles which exist for [HO₂] and [H₂O₂] are those predicted from the one-dimensional photochemical models. Considerable uncertainty exists in the rate constant data for the reactions which exert control over the atmospheric concentrations of HO₂ and H₂O₂ (and OH), e.g.,

*k*_(iii) (2 × 10⁻¹⁰ and 6 × 10⁻¹¹, respectively) predict that [HO₂] at 35 km has a value of ~1.7 × 10⁷ molecule cm⁻³,⁴ whereas, the model calculations which have used low values for *k*_(i) and *k*_(iii) (2 × 10⁻¹¹ and 2 × 10⁻¹¹, respectively) predict that the concentration of HO₂ at 35 km is ~7.8 × 10⁷ molecule cm⁻³.³⁹ The H₂O₂ concentration is predicted to range from ~2–10 × 10⁸ molecule cm⁻³ at 35 km. Unfortunately, not only is the HO₂ concentration uncertain due to a lack of reliable rate constant data for the above processes, but *k*₅ (Cl + HO₂ → HCl + O₂) has not been experimentally measured. The most

TABLE VIII. Magnitudes of various atomic chlorine sinks at 35 km.

Species	Concentration molecule cm ⁻³	$k(237\text{ K})\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$			$k[\text{Reagent}]\text{ s}^{-1}$		
		This study	Clyne- Walker	Others	This study	Clyne- Walker	Others
CH ₄	1.1×10^{11}	4.2×10^{-14}	2.6×10^{-14}	...	4.6×10^{-3}	2.9×10^{-3}	...
H ₂	1.1×10^{11}	2.3×10^{-15}	4.1×10^{-15}	1.1×10^{-15c}	2.5×10^{-4}		1.2×10^{-4c}
H ₂ O ₂	$(2-10) \times 10^8$	$\sim 2.5 \times 10^{-13a}$...	2.2×10^{-15e}	$(5-25) \times 10^{-5}$...	2.4×10^{-4e}
HO ₂	$(1.5-8) \times 10^7$	$\sim 2 \times 10^{-11b}$...	$(1-10) \times 10^{-11d}$	$(3-16) \times 10^{-4}$...	$(1.5-80) \times 10^{-4}$

^aCalculated using an estimated Arrhenius expression of $1 \times 10^{-11} \exp[-(875/T)]$, which is compatible with a mean of $\sim 5.8 \times 10^{-13} \text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ at 298 K.

^bAuthor's estimate.

^cBenson *et al.*²⁷

^dEstimates.

^eWestenberg and deHaas.⁴⁰

probable value for k_5 is estimated to be $\sim 2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, but a range of values from 1×10^{-11} – $1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ have been used in model calculations. Table VIII presents the range of values that can be expected for atomic chlorine loss rates. For these calculations, the mixing ratio for both H₂ and CH₄ was taken to be 0.67 ppm (*v/v*).³⁷ It is unlikely that the mixing ratios are significantly inaccurate although there is a lack of data above 35 km.

From Table VIII it can be seen that either reaction with CH₄ or HO₂ is expected to be the dominant sink for atomic chlorine. Crutzen⁵ used the values of Clyne and Walker for $k_2(\text{CH}_4)$ and $k_4(\text{H}_2)$; $1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $k_5(\text{HO}_2)$; 2×10^{-10} and $2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $k_{(1)}$ and $k_{(11)}$. These k values resulted in an HO₂ concentration of $2.6 \times 10^7 \text{ molecule cm}^{-3}$ at 35 km. Using this concentration for HO₂, the relative rates for Cl atom destruction were 2.9×10^{-3} (CH₄), 4.5×10^{-4} (H₂), and 2.6×10^{-3} (HO₂). The new rate data for k_2 and k_4 would increase $k_2[\text{CH}_4]$ to 4.6×10^{-3} , and decrease $k_4[\text{H}_2]$ to 2.5×10^{-4} . Thus $k_d[\text{RH}]$ would increase from 5.95 to 7.25×10^{-3} ($\sim 22\%$). Wofsy and McElroy⁴ used the values of Clyne and Walker for $k_2(\text{CH}_4)$, and Westenberg and deHaas⁴⁰ for $k_4(\text{H}_2)$; $1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $k_5(\text{HO}_2)$, 2×10^{-10} and $6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $k_{(1)}$ and $k_{(11)}$. This resulted in an HO₂ concentration of $\sim 1.7 \times 10^7 \text{ molecule cm}^{-3}$ at 35 km. With this HO₂ concentration, the relative rates for Cl atom destruction were 2.9×10^{-3} (CH₄), 2.4×10^{-4} (H₂), and 1.7×10^{-4} (HO₂). The new rate data for k_2 and k_4 would increase $k_2[\text{CH}_4]$ to 4.6×10^{-3} , but leave $k_4[\text{H}_2]$ the same. Therefore, $k_d[\text{RH}]$ is increased from 3.3 to 5.0×10^{-3} ($\sim 52\%$). From these simple calculations, it is evident that the new rate constant data causes a small but significant decreases in the catalytic efficiency ρ . A conclusion of this paper is that the Cl + H₂O₂ reaction is not a significant sink ($< 0.05 k_d[\text{RH}]$) for atomic chlorine for any combination of HO₂ rate constants; whereas, experimental data is required for the Cl + HO₂ reaction to determine its importance. If the rate constants for $k_{(1)}$, $k_{(11)}$, and $k_{(111)}$ are 2×10^{-11} , 2×10^{-11} , and $3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively, then the [HO₂] profile will be the maximum possible. Under these conditions, if $k_5 \geq 6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ then the magnitude of $k_5[\text{HO}_2] \geq k_2[\text{CH}_4]$. However, the greatest effect of per-

turbing the above combination of $k_{(1)}$, $k_{(11)}$, and $k_{(111)}$ would be to increase [OH] leading to an enhancement of ρ due to the increased regeneration of atomic chlorine via the OH + HCl reaction.

In summary, the maximum impact of the new rate data reported here would be to decrease the earlier predictions of ozone depletion by a factor of 2.4 to 3.

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