



# A laser flash photolysis resonance fluorescence kinetics study of the reaction CI (2 P) + CH4 $\rightarrow$ CH3+HCI

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# A laser flash photolysis-resonance fluorescence kinetics study of the reaction $Cl(^{2}P) + CH_{4} \rightarrow CH_{3} + HCl$

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The technique of laser flash photolysis-resonance fluorescence is employed to study the kinetics of the reaction  $Cl(^2P) + CH_4 \rightarrow CH_3 + HCl$  over the temperature range 221-375 K. Chlorine atoms are produced by photolysis of  $Cl_2$  at 355 nm. At temperatures  $\leq 241$  K the apparent bimolecular rate constant is found to be dependent upon the identity of the chemically inert gases in the reaction mixture. For  $Cl_2/CH_4/He$  reaction mixtures (total pressure = 50 Torr) different bimolecular rate constants are measured at low  $(k_{11})$  and high  $(k_{1H})$  methane concentrations. For  $Cl_2/CH_4/CCl_4/He$  and  $Cl_2/CH_4/Ar$  reaction mixtures, the bimolecular rate constant  $(k_1)$  is independent of methane concentration with  $k_1 \approx k_{1L}$ .  $k_1$  and  $k_{1L}$  are in good agreement with previous results obtained using the flash photolysis-resonance fluorescence and competitive chlorination techniques. At 298 K the measured bimolecular rate constant is independent of the identity of the chemically inert gases in the reaction mixture and in good agreement with all previous investigations. The low temperature results obtained in this investigation and all previous investigations can be rationalized in terms of a model which assumes that the  $Cl(^2P_{1/2})$  state reacts with CH<sub>4</sub> much faster than the  $Cl(^2P_{3/2})$  state. Extrapolation of this model to higher temperatures, however, is not straightforward.

## INTRODUCTION

The reaction of atomic chlorine with methane

 $Cl^{(2}P) + CH_4 - CH_3 + HCl$ <sup>(1)</sup>

is very important in stratospheric chemistry because it is the principal pathway via which chlorine atoms are removed from the ClO, cycle which catalytically destroys ozone.<sup>1-3</sup> For this reason, many investigations have been carried out in recent years where the rate constant has been measured over a broad range of temperature utilizing several experimental techniques; these include discharge flow-mass spectrometry (DF-MS), 4-6 flash photolysis-resonance fluorescence (FP-RF), 7-9 discharge flow-resonance fluorescence (DF-RF), <sup>10,11</sup> steady state competitive chlorination (CC), <sup>6</sup> and very low pressure pyrolysis (VLPP).<sup>12</sup> The availability of such a large data base has resulted in the absolute rate constant being known reasonably accurately, particularly at ambient temperatures. However, some aspects of the available data suggest the need for further experimentation.

In several of the studies referenced above, a non-Arrhenius temperature dependence for  $k_1$  was observed, 8-11 the apparent activation energy being greater at higher temperatures than at lower temperatures. However, the CC studies, which were carried out with sufficient precision to observe non-Arrhenius behavior, yielded a linear  $\ln k$  vs  $T^{-1}$  dependence. Model calculations by some investigators<sup>9,10</sup> showed that the "curvature" in the temperature dependence of  $k_1$  could be rationalized in terms of transition state theory only if allowance is made for quantum mechanical tunneling. The use of an adjustable parameter in both calculations, however, makes it possible to obtain results which are consistent with a broad spectrum of experimental data. Also, the uncertainty in the height and shape of the barrier through which tunneling could occur further reduces the predictive power of such calculations. Thus, one

must conclude that a reasonable explanation for the observed non-Arrhenius behavior exists, but that this explanation remains unproven.

In Table I, we have compiled results obtained in the more recent investigations of Reaction (1). With the exception of the forementioned difference between the CC results and those obtained by other methods, the Arrhenius parameters reported in the various studies agree quite well. However, close examination of the results shows that some discrepancies arise at low temperatures (200-250 K). It is apparent that the measured rate constant at 231 K, a typical stratospheric temperature, is systematically dependent upon one of two factors: (a) the Cl atom precursor-Cl<sub>2</sub><sup>13</sup> vs heavier chlorinated species-or (b) the nature of the experimental technique-FP-RF vs DF-RF and CC. The FP-RF studies, all of which were carried out using Cl atom precursors other then  $Cl_2$ , give rate constants which are ~20% higher than those obtained in the three studies which employed other experimental techniques and Cl<sub>2</sub> as the Cl atom precursor.

We have undertaken a new study of the kinetics of Reaction (1) in an attempt to gain some insight into the nature of the problems discussed above. Employing a laser as the photolysis source, we have produced measurable densities of Cl atoms by photolyzing very small quantities of Cl<sub>2</sub> in a high pressure, flash photolysis apparatus where only heavier chlorinated species have previously been used as photolytic precursors. We find that at the lower temperatures investigated (221, 231, and 241 K), the kinetics of Reaction (1) are affected by the identity and density of the chemically inert gases in the reaction mixture. This observation serves to empirically unite all previously reported measurements at stratospheric temperatures. However, more experimental information is needed before a complete understanding of our results will be possible.

TABLE I. Recent rate data for the reaction  $Cl(^{2}P) + CH_{4} \rightarrow CH_{3} + HCl$ .

Exptl. technique <sup>a</sup>	Cl atom precursor	Temperature range of study (K)	Arrhenius expression		Temperature	b at 231 K	
			$10^{12} A \pm 1 \sigma$	$-E/R \pm 1\sigma(A)$	range (K)	$(10^{-14} \text{ cc/molecule s})$	Reference
FP-RF	CCl4	218-401	$7,94 \pm 0.70$	$1260 \pm 35$	218-401	3.40	7
FP-RF	CCl <sub>4</sub>	218 - 322	$7.93 \pm 1.53$	$1272 \pm 50$	218 - 322	3.15	8
FP-RF	$COCl_2$	200-500	$6.51 \pm 0.79$	$1229 \pm 27$	200-299	3.24	9
			$18.4 \pm 2.8$	$1545 \pm 52$	318 - 500		
DF-RF	$Cl_2$	200-500	$8.2 \pm 0.6$	$1320\pm20$	200-300	2.70	10
			$22.5 \pm 3.1$	$1623 \pm 40$	300-500		
DF-RF	$Cl_2$	220+423	$7.4 \pm 2.0$	$1291 \pm 68$	220-298	2.77	11
			$16.5 \pm 3.2$	$1530 \pm 68$	298 - 423		
CC	$Cl_2$	198 - 296	18.8 $\pm$ 1.7 <sup>b</sup>	$1564 \pm 31^{b}$	198 - 296	2.66	6
DF-MS	CL	300-686	$50.8 \pm 4.5$	$1792 \pm 37$	300 - 686		5
DF-MS	Cl	295-490	$19.2 \pm 5.8^{\circ}$	$1439 \pm 95^{\circ}$	295-490		4
DF-MS	Cl <sub>2</sub>	268 - 423	$10.6 \pm 2.5$	$1415 \pm 80$	268 - 423		6
VLPP		298-	$0.093 \pm 0.003$	0	298		12

<sup>a</sup>FP-RF: flash photolysis-resonance fluorescence; DF-RF, discharge flow-resonance fluorescence; CC: competitive chlorination; DF-MS: discharge flow-mass spectrometry; VLPP: very low pressure pyrolysis.

<sup>b</sup>Calculated assuming a rate constant of  $(7.84 \pm 0.3) \times 10^{-11} \exp[(-126 \pm 23)/T]$  for the reference reaction  $Cl(^{2}P) + C_{2}H_{6} + C_{2}H_{6} + HCl$ .

<sup>c</sup>Recalculated from the original data by Whytock et al. (Ref. 9).

#### **EXPERIMENTAL**

 $Cl_{-}$ 

Details of the flash photolysis-resonance fluorescence apparatus and its adaptation to the study of chlorine atom reactions have been previously published, <sup>14,15</sup> so only those facets of the experimental technique which are unique to this study will be discussed.

All experiments were carried out under "slow flow" conditions. The concentration of each component in the reaction mixture was determined from measurements of the appropriate flow rates and the total pressure. The flow rate was slow enough that the system was kinetically identical to a static system, but fast enough to provide a fresh reaction mixture for each laser flash (rep. rate = 1 Hz). A schematic of the experimental apparatus as well as a more detailed description of the slow flow reactor is given elsewhere.<sup>16</sup>

All gases were obtained from Matheson Gas Products and had the following stated purities:  $Cl_2$  (99.96% analyzed; He (99.9999%); Ar (99.9995%);  $CH_4$  (99.99%). The  $CH_4$  sample was analyzed using GLC and found to contain <5 ppm  $C_2H_6$ .  $CCl_4$  was Fisher Certified, with a stated purity of 99%.  $Cl_2$  and  $CCl_4$  were degassed several times at 77 K before use, while  $CH_4$  was passed from tank to storage bulb through a glass bead filled trap at 77 K. He and Ar were used as supplied.

Chlorine atoms were produced by photolyzing  $Cl_2$  with a pulsed, frequency tripled, Nd : YAG laser (20 mJ per pulse in the reaction zone, 2 cm<sup>2</sup> beam cross section, 10 ns pulse width):

$$h\nu$$
 98% 2Cl( $^{2}P_{3/2}$ ) (2a)

$$\begin{array}{c} C_{2} 355 \text{ nm} \\ 2\% \\ Cl(^{2}P_{3/2}) + Cl(^{2}P_{1/2}) \\ \end{array}$$
(2b)

[The relative importance of photolysis channels (2a) and (2b) is estimated based on the theoretical work of Mulliken, <sup>17</sup> and subsequent experimental verification. <sup>16, 19</sup>] Due to partial reversal of the atomic lines emitted by the chlorine atom resonance lamp, the relative sensitivity of the detection system for  $Cl(^{2}P_{3/2})$  and  $Cl(^{2}P_{1/2})$  could not be determined. However, knowledge of these relative sensitivities is not needed to interpret the kinetic data.

#### RESULTS

All experiments were carried out under pseudo-first order conditions with  $CH_4$  in excess. Typical experimental conditions were  $[Cl] \le 1 \times 10^{11}$  cm<sup>-3</sup>,  $[Cl_2] \sim 1 \times 10^{13}$ cm<sup>-3</sup>, and  $[CH_4]/[Cl] \ge 2000$ . Each  $Cl(^2P)$  decay curve was generated by averaging sufficient laser shots (100– 5000 depending upon the signal-to-noise ratio) to allow the temporal profile to be defined for a minimum of three, and in some cases six, 1/e times. The experiments were carried out over a period of 3 months. Many experiments, particularly those at low temperatures, were repeated several times. The results were found to be exceptionally reproducible.

In a reaction mixture containing  $Cl_2$ ,  $CH_4$ , and inert diluent gases, the temporal behavior of  $Cl(^2P)$  is governed by the following reaction scheme:

 $\operatorname{Cl}^{(2}P) + \operatorname{CH}_{4} - \operatorname{CH}_{3} + \operatorname{HCl},$  (1)

$$CH_3 + Cl_2 - CH_2Cl + Cl(^2P) , \qquad (3)$$

$$C1(^{2}P) \xrightarrow{h_{a}} loss by diffusion and reaction (4) with background impurities.$$

Reaction (3) could cause secondary chemistry problems if it were fast enough to regenerate  $Cl^{(2P)}$  before Reaction (1) could go to completion. However, with a laser as the photolytic light source, sufficiently low concentrations of  $Cl_2$  could by employed so as to make Reaction (3) unimportant. To experimentally verify the insignificance of Reaction (3) and any biradical processes, both the laser energy (factor of 5) and the  $Cl_2$  concentration (factor of 4) were varied at most of the temperatures studied; the measured rate constants were independent of these two parameters. Experiments were carried out at room temperature where the concentration of  $Cl_2$  was increased to >  $1 \times 10^{14}$  molecule/cc. Under these conditions,

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FIG. 1. Plots of pseudo-first order rate constant vs methane concentration for 249 K < T < 375 K. All data shown were obtained with He/Cl<sub>2</sub>/CH<sub>4</sub> reaction mixtures except at 298 K where Ar/Cl<sub>2</sub>/CH<sub>4</sub> mixtures (shown by open squares) were also studied. Measured pseudo-first order rate constants at zero methane concentration are omitted for the sake of clarity.

nonexponential decays were observed which are attributed to regeneration of  $Cl(^{2}P)$  via Reaction (3).

Since our experiments were run under conditions where only reactions (1) and (4) contributed to the  $Cl(^{2}P)$ temporal behavior, the data were analyzed using the following relationship:

$$\ln\{[C1(^{2}P)]/[C1(^{2}P)_{0}]\} = (k_{1}[CH_{4}] + k_{d})t \equiv k_{1}'t.$$
(5)



FIG. 2. Plots of pseudo-first order rate constant vs methane concentration for T=221, 231, and 241 K. For the sake of clarity, many of the data points obtained at low methane concentrations are omitted. Data obtained with  $He/Cl_2/CH_4$  reaction mixtures at intermediate methane concentrations gave nonexponential decays. Since accurate pseudo-first order rate constants could not be deduced from this data, the results are not plotted.  $\bullet$ :  $He/Cl_2/CH_4$  reaction mixtures:  $\Box$ :  $He/Cl_2/$  $CCl_4/CH_4$  reaction mixtures;  $\circ$ :  $Ar/Cl_2/CH_4$  reaction mixtures.



FIG. 3. Chlorine atom temporal profiles in the presence of varying amounts of methane: T = 221 K. [CH<sub>4</sub>] in units of  $10^{15}$  molecule/CC: (a) 1.4, (b) 5.1, (c) 13.5. The measured temporal profile for the intermediate methane concentration does not obey simple first order kinetics.

The measured pseudo-first order rate constant  $(k_1')$  for a particular experiment was obtained from the slope of a  $\ln[Cl(^2P)]$  vs t plot. Values for  $k_1$  were then obtained from the slopes of  $k_1'$  vs  $[CH_4]$  plots. These plots are shown in Figs. 1 and 2. (We have chosen a graphic rather than a tabular representation of the experimental results because the space required to tabulate over 300 experiments is prohibitive. For the sake of clarity, some pseudo-first order rate constants are not plotted in Figs. 1 and 2; however, the lines drawn through the data points were determined from a linear least squares analysis of all measured pseudo-first order rate constants.) Figure 1 shows the dependence of  $k_1'$  on  $[CH_4]$  in the temperature range 249 < T < 375 K;  $k_2'$  was found to vary linearly with [CH<sub>4</sub>] at all temperatures in this range. Figure 2 shows the dependence of  $k_1'$  on  $[CH_4]$  at temperatures below 249 K. When helium was used as the diluent gas (total pressure = 50 torr), the dependence of  $k_1'$  on [CH<sub>4</sub>] was found to be nonlinear. The lower and higher  $[CH_4]$  values of  $k_1$  fell on two distinct lines (both having the same  $[CH_4] = 0$  intercept), thereby giving two different values for  $k_1$ . In the intermediate range of  $[CH_4]$  (i.e., the range where the transition from low  $[CH_4]$  to high  $[CH_4]$ behavior occurred),  $\ln(Cl(^2P))$  vs t plots were found to be nonlinear (Fig. 3). When 20 mtorr CCl<sub>4</sub> was added to the  $Cl_2/CH_4/He$  reaction mixture, the dependence of  $k_1'$  on [CH<sub>4</sub>] became linear; the  $k_1$  values at 221 and 231 K obtained with CCl<sub>4</sub> present were nearly equal to the low  $[CH_4]$  values obtained in the absence of  $CCl_4$ , but significantly higher than the high [CH<sub>4</sub>] values measured in the absence of CCl<sub>4</sub>. When argon was substituted for helium as the diluent gas and no CCl<sub>4</sub> was added, the results were nearly identical to those obtained with He/  $Cl_2/CH_4/CCl_4$  reaction mixtures. All measured values of  $k_1$  are tabulated in Table II.

An Arrhenius plot of the experimental data obtained using  $Cl_2/CH_4/He$  reaction mixtures is shown in Fig. 4. The rate constants measured under conditions of low temperature and high  $[CH_4]$  using  $Cl_2/CH_4/He$  reaction mixtures are in good agreement with previous DF-RF and CC results (agreement with CC results is only obtained over the temperature range 221-241 K). In con-

Temp.	$10^{14} \times k_1 \text{ cm}^3/\text{molecules}$						
(K)	He/Cl <sub>2</sub> /CH <sub>4</sub>	mixture	He/Cl <sub>2</sub> /CCl <sub>4</sub> /CH <sub>4</sub> mixture	Ar/Cl <sub>2</sub> /CH <sub>4</sub> mixture			
375	$28.6 \pm 1$	. 0					
352	$19.6 \pm 1.0$	. 3					
333	$16.4 \pm 0.1$	4					
315	$12.3 \pm 0.2$	5					
298	9.80 $\pm$ 0.45			$9.50 \pm 0.40$			
283	$7.56 \pm 0.23$						
272	$6.31 \pm 0.27$						
260	$5.14 \pm 0.36$						
249	$4.46 \pm 0.15$						
	low [CH <sub>4</sub> ]	high [CH4]					
241	$4.05 \pm 0.20$	$3.42 \pm 0.16$	$4.00 \pm 0.20$	$4.02 \pm 0.13$			
231	$3.40 \pm 0.15$	$2.68 \pm 0.10$	<b>3</b> . $17 \pm 0$ . 06	$3.27 \pm 0.05$			
221	$2.78 \pm 0.16$	$2.14 \pm 0.07$	$2.60 \pm 0.10$	$2.70 \pm 0.08$			

TABLE II. Rate constants for the reaction  $Cl(^{2}P) + CH_{3} \rightarrow CH_{3} + HCl$  as a function of temperature and reaction mixture composition. Errors are  $2\sigma$  and refer to precision only.

junction with the rate constants measured at higher temperatures, this data gives a slightly curved Arrhenius plot. Over the entire temperature range investigated, this data agrees most closely with the DF-RF results of Zahniser *et al.*<sup>10</sup> The rate constants measured under conditions of low temperature and low [CH<sub>4</sub>] using Cl<sub>2</sub>/ CH<sub>4</sub>/He reaction mixtures are in good agreement with previous FP-RF results, as are the rate constants obtained with Cl<sub>2</sub>/CH<sub>4</sub>/CCl<sub>4</sub>/He and Cl<sub>2</sub>/CH<sub>4</sub>/Ar reaction mixtures. These rate constants, when considered in conjunction with the higher temperature results, indicate substantial curvature in the Arrhenius plot. At T = 298 K, our results are in reasonably good agreement with all previous determinations.

# DISCUSSION

The most striking result obtained in this investigation is the  $k'_1$  vs  $[CH_4]$  behavior observed at low temperature. In reaction mixtures where He was the inert diluent gas, we measured different values of  $k_1$  at low  $(k_{1L})$  and high  $(k_{1H})$  methane concentrations. However, when a small amount of CCl<sub>4</sub> was added to the reaction mixture, or when Ar was substituted for He as the diluent gas, the usual linear  $k'_1$  vs  $[CH_4]$  dependence was observed; the rate constant  $(k_1)$  obtained under these conditions was nearly equal to  $k_{1L}$ .

The fact that the kinetics of Reaction (1) are found to depend upon the nature of the chemically inert gases in the reaction mixture strongly suggests that nonthermal reactant internal state distributions are causing kinetic complications. A plausible model which qualitatively links our results with all previous studies can be constructed around the hypothesis that the two spin-orbit states of chlorine have different reactivities toward  $CH_4$ :

$$Cl(^{2}P_{1/2}) + CH_{4} \rightarrow HCl + CH_{3}, \qquad (1a)$$

$$Cl(^{2}P_{3/2}) + CH_{4} \rightarrow HCl + CH_{3}.$$
 (1b)

An adiabatic correlation diagram for Reaction (1) is shown in Fig. 5. Only the ground state reactants  $Cl({}^{2}P_{3/2})$ +  $CH_4({}^{1}A_1)$  can adiabatically be converted into energetically accessible products. Thus, one would expect that at high temperatures, where energetics become unimportant, Reaction (1b) would be considerably faster than Reaction (1a). [It has been shown both experimentally<sup>20</sup> and theoretically<sup>21</sup> that in hydrogen atom abstraction reactions of halogen atoms, where the adiabatic correlation diagram is qualitatively similar to that for Reaction (1) but differs in that reaction to form ground state products is highly exothermic from both the  ${}^{2}P_{1/2}$ and  ${}^{2}P_{3/2}$  states, the  ${}^{2}P_{3/2}$  reaction is significantly faster than the  ${}^{2}P_{1/2}$  reaction.] Because Reaction (1b) is slightly endothermic while Reaction (1a) is exothermic, it is reasonable to expect that  $k_{1\rm s}/k_{1\rm b}$  will increase significantly at lower temperatures. At the same time, of course, the thermal population in the  $Cl({}^{2}P_{1/2})$  state becomes smaller at lower temperatures.



FIG. 4. Arrhenius plot for the reaction  $Cl(^2P) + CH_4 \rightarrow CH_3 + HCl$ . At low temperatures, where the rate constant is found to depend upon the methane concentration, the results obtained with low methane concentrations are indicated by open circles. All data were obtained with  $Cl_2/CH_4/He$  reaction mixtures at a total pressure of 50 Torr. Error bars are  $2\sigma$  and refer to precision only.



FIG. 5. Adiabatic correlation diagram for the reaction  $Cl(^{2}P)$  +  $CH_{4} \rightarrow CH_{3}$  + HCl.

Recently, Fletcher and Husain<sup>22,23</sup> have studied the quenching process

$$Cl(^{2}P_{1/2}) + M \xrightarrow{k_{0}^{m}} Cl(^{2}P_{3/2}) + M$$
 (5)

for several collision partners including all species used in our study except  $CH_4$ . Their results are summarized in Table III. Also, given in Table III are values for the reverse process

$$Cl({}^{2}P_{3/2}) + M \xrightarrow{k_{-Q}^{M}} Cl({}^{2}P_{1/2}) + M$$
, (6)

at the temperature extremes of our study; the rate constants  $k_{-Q}^{M}$  were calculated by assuming Reactions (5) to be temperature independent and applying the principle of detailed balance. It is clear from Table III that addition of 20 mtorr CCl<sub>4</sub> to the reaction mixture or substitution of Ar for He as the diluent gas dramatically increases the rate of interchange between the two spin-orbit states. Furthermore, in our experiments with Cl<sub>2</sub>/CH<sub>4</sub>/He reaction mixtures, the rate of interchange between the spinorbit states was not much faster than, but rather of the same order of magnitude as, the rate of Reaction (1).

If we assume that at low temperatures  $k_{1a} \gg k_{1b}$ , then our low temperature experimental results can be rationalized as follows: Under most experimental conditions, the rate of interconversion between  $Cl(^{2}P_{1/2})$  and  $Cl({}^{e}P_{3/2})$  is fast enough to maintain a thermal population distribution throughout the  $Cl(^{2}P)$  decay time. However, under the conditions where the rate constants  $k_{1H}$  were measured, the fraction of Cl atoms in the  ${}^{2}P_{1/2}$  state is depleted rapidly due to enhanced reaction with CH4, and the remaining  $Cl(^{2}P_{3/2})$  atoms react with  $CH_{4}$  at a rate which is sufficiently fast to prevent re-establishment of a thermal  $Cl(^{2}P_{1/2})$  population. All previous data for Reaction (1) in the 220-240 K temperature range can also be rationalized in the same manner. The DF-RF studies employed He diluent at total pressures of less than 5 torr. Therefore, the major collision partner for interconversion between the spin-orbit states was either CH<sub>4</sub> or the walls of the flow reactor. The CC studies were carried out in several atm CH4 with no added diluent. Thus, in all studies where relatively low values of  $k_1 \approx k_{1H}$ were obtained, the experimental conditions were such that the collision partner which was dominant in coupling

the  $\operatorname{Cl}(^{P}P_{1/2})$  and  $\operatorname{Cl}(^{P}P_{3/2})$  states could have been  $\operatorname{CH}_{4}$ . All three previous FP-RF studies were carried out with Ar as the diluent gas and/or  $\operatorname{CCl}_{4}$  as the photolytic precursor. Therefore, in all studies where relatively high values of  $k_{1}$  were measured, the experimental conditions were such that a thermal distribution of spin-orbit states was maintained through collisions with one of the chemically inert gases in the reaction mixture.

At 298 K, we find that the measured rate constant is independent of whether He or Ar is used as the diluent gas. Thus, it appears that at 298 K, Reaction (1a) is not fast enough compared to Reaction (1b) to overcome the large excess population in the  ${}^{2}P_{3/2}$  state and be a factor in the overall Cl decay kinetics. This observation represents a possible inconsistency in the proposed explanation of the experimental results. The thermal population in the  ${}^{2}P_{1/2}$  state increases by about a factor of 4 between 220 and 298 K, while the measured rate constant also increases by about a factor of 4. Therefore, if  $k_{1\#} = k_{1b}$  as the proposed explanation might lead one to assume, and if  $k_{1a}$  is temperature independent, then Reaction (1a) should make the same contribution to the overall Cl decay kinetics at 298 as at 220 K. Only if Reaction (1a) has a negative activation energy would a consistent rationalization of all experimental data be possible within the confines of the above assumption.

$$Cl({}^{2}P_{1/2}) + M \xrightarrow{k_{0}}{m_{0}} Cl({}^{2}P_{3/2}) + M.$$

 $k_Q^{\mathsf{M}}$  were measured by Fletcher and Husain;  $k_{-Q}^{\mathsf{M}}$  were calculated by assuming that  $k_Q^{\mathsf{M}}$  is independent of temperature and applying the principle of detailed balance. All rate constants are in units of cc/molecules.

М	kQ	$k_{-Q}^{M}$ (T = 221 K)	$k_{-Q}^{M}$ (T = 375 K)
Не	3.8 $\times 10^{-15}$	6. $1 \times 10^{-18}$	$6.5 \times 10^{-17}$
Ar	$1.1 \times 10^{-12}$	$1.8 \times 10^{-15}$	$1.9 \times 10^{-14}$
CCl <sub>4</sub>	2.0 $\times$ 10 <sup>-10</sup>	$3.2 \times 10^{-13}$	3. $4 \times 10^{-12}$
Cl <sub>2</sub>	$4.5 \times 10^{-11}$	$7.2 \times 10^{-14}$	$7.7 \times 10^{-13}$
CH <sub>4</sub>	Unknown		

30

A negative activation energy is usually associated with an attractive potential well along the reactant approach path—a situation which does not seem likely in this case. It is very possible, of course, that at low temperatures  $k_{1H} \neq k_{1b}$  but rather contains contributions from Reaction (1a) [i.e., competition between reaction and quenching by CH<sub>4</sub> could result in a "pseudo-steady-state"  ${}^2P_{1/2}$ fraction which is lower than the thermal fraction but not zero—an analogous situation to that proposed by Snyder<sup>24</sup> for the reaction Cl( ${}^2P$ ) + H<sub>2</sub> + H( ${}^2$ S) + HCl]; then a zero or even a positive activation energy for  $k_{1a}$  would be consistent with all experimental data. Unfortunately, the state resolved reaction and relaxation rates needed to quantitatively assess this possibility are not known.

In summary, we have reported experimental results which strongly suggest that, under some experimental conditions, measurements of  $k_1$  can be influenced by the presence of nonthermal reactant internal state distributions. Over the temperature range 220-240 K, our data and all previously reported data can be rationalized in terms of an hypothesis which assumes that  $\operatorname{Cl}({}^2P_{1/2})$  reacts with  $\operatorname{CH}_4$  much faster than  $\operatorname{Cl}({}^2P_{3/2})$ . The hypothesis seems reasonable in light of the energetics of Reaction (1) and recent measurements of  $\operatorname{Cl}({}^2P_{1/2})$  quenching rates, but is not easily extrapolated to higher temperatures. More experimental information is needed to test the hypothesis. In particular, knowledge of the following state-selected rate constants as a function of temperature is desirable;

$$-Cl(^{2}P_{3/2}) + CH_{4}$$
, (7)

$$\operatorname{Cl}^{(2}P_{1/2}) + \operatorname{CH}_{4} \longrightarrow \operatorname{CH}_{3} + \operatorname{HCl},$$
 (1a)

$$Cl(^{2}P_{3/2}) + CH_{4} - CH_{3} + HCl$$
 (1b)

#### IMPLICATIONS FOR STRATOSPHERIC MODELING

Our results suggest that a simple average of all reported rate constants may not be the most suitable choice of  $k_1$  for stratospheric modeling. In the stratosphere, the  $Cl(^2P)$  lifetime is sufficiently long that a thermal distribution of spin-orbit states must exist at all times. Therefore, if the hypothesis discussed above proves to be correct, the rate constants measured by the flash photolysis technique would be most suitable for model-ing purposes.

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