

$\geq 10$ –20 ns. (The rise time of Arai and Firestone's system was 40 ns.) Thus we conclude that the emission decays observed by Arai and Firestone are due to the same reaction sequence as the slow process observed by us and by Hanle et al., and which our analysis suggests involves a dissociative ion-recombination reaction. The fast process observed by Hanle et al. is the same as the fast process observed in the present work, where the 2p levels are produced both by direct excitation and by cascade from higher electronic levels.

## References and Notes

- (1) Work performed in part under the auspices of the Division of Physical Research of the U.S. Energy Research and Development Administration and in part under the auspices of the Australian Research Grants Committee.
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## A Temperature Dependent Kinetics Study of the Reactions of HCl with OH and O(<sup>3</sup>P)

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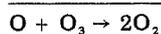
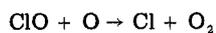
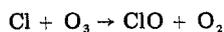
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The flash photolysis-resonance fluorescence technique was employed to determine the temperature dependencies of the rate constants for the reaction of O(<sup>3</sup>P) and OH radicals with HCl. These reactions were studied under pseudo-first-order conditions and in the absence of interfering secondary reactions. The Arrhenius expression for each bimolecular rate constant is given as follows in units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>:  $k_1 = (3.3 \pm 0.3) \times 10^{-12} \exp[-(937 \pm 78) \text{ cal mol}^{-1}/RT]$  250–402 K, OH + HCl → H<sub>2</sub>O + Cl (1) and  $k_2 = (5.2 \pm 1.0) \times 10^{-11} \exp[-(7510 \pm 750) \text{ cal mol}^{-1}/RT]$  350–454 K, O(<sup>3</sup>P) + HCl → OH + Cl (2). The stratospheric implications of this new rate data are discussed.

## Introduction

According to present atmospheric models, hydrogen chloride is predicted to be one of the principal chlorine containing species in the stratosphere.<sup>1</sup> Recent measurements of the HCl concentration in the lower stratosphere now support this prediction.<sup>2</sup> In the stratosphere the formation of HCl proceeds through the reaction of chlorine atoms with RH species (i.e., CH<sub>4</sub>, H<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, and/or HO<sub>2</sub>), thus removing reactive chlorine from the catalytic cycle:



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The chlorine atom in HCl, however, can be reintroduced into the catalytic ozone destruction cycle via reaction of OH or O(<sup>3</sup>P) with HCl and/or by photolysis of HCl, e.g.



Since HCl is the dominant "temporary sink" for Cl atoms in the stratosphere, reliable rate constants for reactions 1 and 2 are essential for stratospheric modeling calculations.

Five measurements of the rate constant  $k_1$  have been reported. Wilson et al.<sup>4</sup> measured  $k_1$  at high temperatures, while Takacs and Glass<sup>5</sup> and Hack et al.<sup>6</sup> obtained room temperature values. In addition, there have been two measurements of  $k_1$  over an extended temperature range, one by Smith and Zellner<sup>7</sup> and the other by Zahniser et al.<sup>8</sup> All measurements are in very good agreement at 300

K; however, at stratospheric temperatures of 225 K, the  $k_1$  value reported by Zahniser et al. is approximately 20% higher than that of Smith and Zellner.

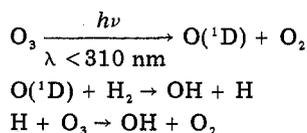
Several investigations of reaction 2 have been reported over an extended temperature range where the activation energy could be evaluated. Balakhnin et al. were the first to study the kinetic behavior of reaction 2. These authors reported an activation energy of 4.52 kcal/mol. Brown and Smith<sup>10</sup> later obtained an  $E$  value of 5.95 kcal/mol, a number which agrees well with some recent work reported by Singleton and Cvetanovic.<sup>11</sup> Hack et al.<sup>6</sup> and Wong and Belles,<sup>12</sup> however, have reported values for reaction 2 of 6.44 and 7.2 kcal/mol<sup>-1</sup>, respectively. Thus, at the present time the activation energy for process 2 must be considered to be in only fair shape.

Reported here are the results of a new study on both reactions 1 and 2, the purpose of which was to further test the reliability of the earlier rate data using a completely different experimental technique—flash photolysis-resonance fluorescence.

### Experimental Section

Detailed descriptions of the flash photolysis-resonance fluorescence technique employed in this investigation have been described previously.<sup>13-15</sup> In this manuscript, therefore, we have pointed out only those experimental features necessary for an understanding of the present study. In this investigation, an all-Pyrex cell with an internal volume of ~150 cm<sup>3</sup> was used to study both reactions 1 and 2. The reaction mixture was maintained at a known constant temperature by circulating either methanol (250–300 K) or silicone oil (300–450 K) from a thermostated circulating bath through an outer jacket of the reaction cell. The temperature of the reaction cell was measured with an iron-constantan thermocouple. The transient species OH and O(<sup>3</sup>P) were formed by the photolysis of a suitable photolyte using a nitrogen spark discharge.

The technique for detection of OH radicals by resonance fluorescence has been documented elsewhere.<sup>13</sup> The OH radicals in this study were produced either by directly photolyzing H<sub>2</sub>O or by photolyzing a mixture of 50 mTorr of O<sub>3</sub> and 100 mTorr of H<sub>2</sub>. In the latter case, OH was formed through the sequence of reactions:



Photolysis of H<sub>2</sub>O was used as the source of OH at temperatures above 270 K. Below 270 K, the photolysis of O<sub>3</sub> and H<sub>2</sub> was employed as a means of avoiding the problem of HCl absorbing on the water-coated reaction vessel walls. To demonstrate that the rate constant for reaction 1 was independent of the OH source,  $k_1$  was measured at 298 K using both photolytes. The results listed in Table I clearly show this independence.

O(<sup>3</sup>P) was produced by the vacuum-UV photolysis of 150 mTorr of O<sub>2</sub>. Since 100 Torr of Ar was used as the diluent gas in these experiments, all O(<sup>1</sup>D) formed during the photolysis was quenched to O(<sup>3</sup>P) within a few microseconds after its formation. The concentration of O(<sup>3</sup>P) was monitored using an atomic oxygen resonance lamp as described in previous work from this laboratory.<sup>14,15</sup> One minor change in our present investigation was the inclusion of an EMR solar blind vacuum-UV photomultiplier tube (Model 542G) to detect atomic oxygen resonance radiation at ~1300 Å. In all cases, a calcium fluoride window was

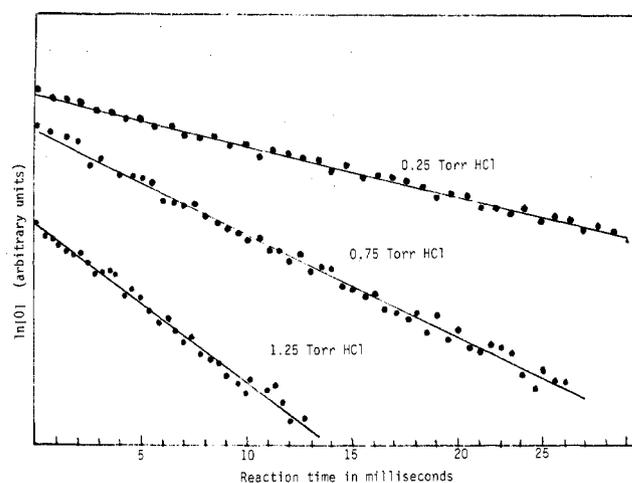


Figure 1. Plots of [O] vs. reaction time for different concentrations of HCl.

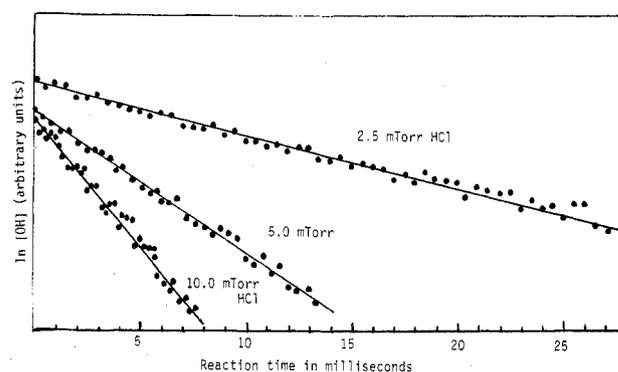


Figure 2. Plots of [OH] vs. reaction time for different concentrations of HCl.

placed over the photomultiplier tube to filter out any background Lyman- $\alpha$  radiation. Reaction 2 was not studied at temperatures below 350 K due to the very small value of  $k_2$  which dictated the use of very high concentrations of HCl. These high concentrations of HCl resulted in a significant decrease in the signal and the signal-to-noise ratio, making high-precision measurements difficult. This loss in signal can be correlated with the decrease in the intensity of the resonance radiation reaching the reaction zone and the attenuation of the fluorescence light arriving at the photomultiplier tube, both due to the absorption of the 1303-Å atomic oxygen resonance line by HCl.<sup>16,17</sup> Hence, we attribute our lower signal levels primarily to an absorption by HCl rather than quenching of the upper excited states of oxygen atoms by HCl.

Reactions 1 and 2 were studied under pseudo-first-order conditions, with the concentration of HCl in excess. In this investigation, the decay rates of O(<sup>3</sup>P) and OH were followed for at least two mean lifetimes. The plots of ln [O] and ln [OH] vs. reaction time, shown in Figures 1 and 2, were linear. This linearity confirms the existence of pseudo-first-order conditions in the system. Under these conditions, the typical concentrations of OH and O(<sup>3</sup>P) were in the range of  $1 \times 10^{11}$  to  $5 \times 10^{11}$ /cm<sup>3</sup>. The ratios of reactants were as follows: [HCl]/[O(<sup>3</sup>P)] > 10<sup>4</sup> and [HCl]/[OH] > 600.

A MKS Baratron and a two turn bourdon gauge (Wallace and Tiernan Type FA145) were used to measure low pressures (1–300 mTorr) and high pressures (800 Torr), respectively. The precision with which reaction gas mixtures could be made up was ~4%.

The argon and oxygen used in this study were Air Products UHP grade gases with a stated purity of

TABLE I: Reaction Data for OH + HCl → H<sub>2</sub>O + Cl

Temp, K	Diluent	Photolyte	P <sub>HCl</sub> , mTorr	Flash energy, J	k <sub>1</sub> <sup>'</sup> , s <sup>-1</sup>	10 <sup>13</sup> k <sub>bimol</sub> <sup>e</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	
250	40 Torr of He	50 mTorr of O <sub>3</sub> + 100 mTorr of H <sub>2</sub>	0.0	88	90	4.8 ± 0.2	
			2.5		125		
			5.0		166		
			10.0		263		
			15.0		361		
			20.0		438		
270	50 Torr of He	150 mTorr of H <sub>2</sub> O	0.0	88	47	5.9 ± 0.6	
			2.5		53		
			5.0		89		
			7.5		169		
			10.0		207		
			12.5		256		
			15.0		293		
			17.5		414		
			20.0		444		
298	20 Torr of He	150 mTorr of H <sub>2</sub> O	0.0	88	55 <sup>a</sup>	6.7 ± 0.4	
			5.0		150 <sup>a</sup>		
			10.0		270 <sup>a</sup>		
			15.0		393		
			20.0		472		
	40 Torr of He	50 mTorr of O <sub>3</sub> + 100 mTorr of H <sub>2</sub>	0.0	88	120	6.4 ± 0.6	
			5.0		215		
			10.0		320		
	20 Torr of He	150 mTorr of H <sub>2</sub> O	5.0	250	160		
			10.0		88		260 <sup>c</sup>
			10.0		88		250 <sup>b,d</sup>
	356	50 mTorr of He	150 mTorr of H <sub>2</sub> O	0.0	88	40	8.8 ± 0.6
2.5				62			
5.0				142			
7.5				173			
10.0				260			
15.0				397			
402	50 mTorr of He	150 mTorr of H <sub>2</sub> O	0.0	88	130	9.9 ± 1.0	
			2.5		179		
			5.0		238		
			10.0		335		
			12.5		413		
			15.0		500		

<sup>a</sup> Average of two runs. <sup>b</sup> Not used in the calculation of bimolecular rate constant. <sup>c</sup> Experiments carried out 10 min after the reactants were introduced into the cell. <sup>d</sup> Similar to c, however, with a 15-min delay. <sup>e</sup> The quoted errors for the values of k<sub>bimol</sub> are two standard deviations.

TABLE II: Reaction Rate Data for O(<sup>3</sup>P) + HCl → OH + Cl

Temp, K	P <sub>HCl</sub> , Torr	Flash energy, J	k <sub>2</sub> <sup>'</sup> , s <sup>-1</sup>	10 <sup>15</sup> k <sub>bimol</sub> <sup>a</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>
350	0.0	88	16	(0.99 ± 0.09)
	0.5		31	
	1.0		48	
	1.5		58	
	2.0		71	
392	1.0	210	85	
	1.0		37	
401	0.0	88	22	(4.8 ± 0.4)
	0.25		52	
	0.25		63	
	0.50		87	
	0.75		118	
	1.00		136	
	1.00		145	
454	0.0	88	28	(11.6 ± 0.4)
	0.25		73	
	0.50		131	
	0.75		213	

<sup>a</sup> The quoted errors for the values of k<sub>bimol</sub> are two standard deviations.

99.999%. Matheson "Electronic grade" HCl was purified to remove Cl<sub>2</sub> by bulb-to-bulb distillation at 195 K and was degassed before use. O<sub>3</sub> was prepared by passing O<sub>2</sub> through an Ozonator and stored at 195 K. Before use, ozone was purified by continuously pumping while at 195 K; its purity was checked by UV spectroscopy. Matheson UHP hydrogen was used without further purification. The H<sub>2</sub>O used in this investigation was glass distilled and degassed at liquid N<sub>2</sub> temperatures prior to use.

## Results and Discussion

The results from the OH-HCl study are shown in Table I. Reaction 1 was studied at five temperatures and over a wide range of experimental parameters. As pointed out earlier, pseudo-first-order conditions (i.e., [HCl] ≫ [OH]) were maintained throughout the investigation. In those experiments where water was used as the source of OH radicals, the first-order rate constant k<sub>1</sub> was also measured as a function of the residence time for the HCl gas mixture in the reaction cell (e.g., 0, 10, and 15 min). As can be seen from Table I, k<sub>1</sub> at 298 K was found to be only slightly dependent on the residence time of the gas mixture up to times of 15 min. These measurements indicate that HCl was not being depleted by its dissolution into water ab-

TABLE III: Summary of Rate Data for OH + HCl → H<sub>2</sub>O + Cl

Ref	Arrhenius expression, cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	10 <sup>13</sup> k <sub>1(298)</sub> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Temp range, K	Technique <sup>a</sup>
8		6.4 ± 1.5 (295 K)		DF/ESR
<i>b</i>		6.5 ± 0.4		FF/RF
6		6.7 ± 1.7 (293 K)		DF/ESR
7	(4.1 <sup>+2.0</sup> <sub>-1.4</sub> ) × 10 <sup>-12</sup> exp[-(1050 ± 50)/RT]	6.9 ± 1.0	220-480	FF/RA
8	(2.0 ± 0.1) × 10 <sup>-12</sup> exp[-(620 ± 20)/RT]	6.7 ± 0.4	224-440	DF/RF
This work	(3.3 ± 0.3) × 10 <sup>-12</sup> exp[-(937 ± 78)/RT]	6.6 ± 0.4	250-402	FF/RF

<sup>a</sup> FF/RF, flash photolysis with resonance fluorescence detection system; FF/RA, flash photolysis with resonance absorption detection system; DF/RF, discharge flow with resonance fluorescence detection system; DF/ESR, discharge flow with electron spin resonance detection system. <sup>b</sup> Davis et al., unpublished results.

sorbed on the reaction cell wall within the normal operating time of 5 min. In another series of tests at 270 K, *k*<sub>1</sub> was shown to decrease by ~10% in 10 min. Hence, at this temperature, all experiments were carried out within 3 min after the introduction of the reactant gas mixture to ensure only a very minor loss of reactant on the cell walls.

At each temperature, the bimolecular rate constant, *k*<sub>1</sub>, was computed from the measured pseudo-first-order rate constant using a linear least-squares analysis. The quoted errors on each *k*<sub>bi</sub> are 2σ. A plot of ln *k*<sub>1</sub> against 1/*T* is shown in Figure 3. A least-squares fit of this data produced the following Arrhenius expression:

$$k_1 = (3.3 \pm 0.3) \times 10^{12} \exp[-(937 \pm 78) \text{ cal mol}^{-1}/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Again the quoted errors are 2σ for the temperature range covered. This expression has been defined from a total of 39 experiments.

In previous kinetic investigations of our laboratory of the OH radical, under conditions similar to the present measurements, it was demonstrated that radical-radical reactions of the type H + OH and OH + OH were of negligible importance. Moreover, both calculations, as well as experimental variations of the OH concentration in this study, tend to confirm the negligible contribution of the above processes, as well as others (e.g., OH + Cl) to the measured rate constants (see Table I).

The results obtained from the O(<sup>3</sup>P) + HCl study are shown in Table II. We could not measure *k*<sub>2</sub> below 350 K since below this temperature (i.e., 298 K) there was no measurable increase in the observed decay rate of O(<sup>3</sup>P), even when 1 Torr of HCl was present in the reaction cell. Since the flash photolysis-resonance fluorescence technique in this case was capable of measuring a change of 10 s<sup>-1</sup> in *k*<sub>2</sub>', it can be concluded that the value of *k*<sub>2</sub> is less than 3 × 10<sup>-16</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K. This result suggests that the HCl pressure would have to be greater than 10 Torr to obtain an accurate value for *k*<sub>2</sub> at 298 K. At these high HCl concentrations, however, numerous complications develop, as were described earlier in the Experimental Section.

At 392 K, experiments were carried out to determine the possible importance of secondary reactions resulting from the high concentrations of HCl employed. In this case, the flash energy was varied by a factor of ~6. As seen from Table II, this variation in the radical concentration did not affect our measured value of *k*<sub>2</sub>'. These results would tend to indicate that our measured values of *k*<sub>2</sub>' were free of major errors originating from radical-radical processes.<sup>18</sup>

The bimolecular rate constant, *k*<sub>2</sub>, at each temperature was computed by subjecting the pseudo-first-order data to a linear least-squares analysis. From these temperature

TABLE IV: Summary of Rate Data for O(<sup>3</sup>P) + HCl → OH + Cl(<sup>2</sup>P<sub>3/2</sub>)

Ref	Arrhenius expression, cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Temp range, K	Technique <sup>a</sup>
9	(1.75 ± 0.6) × 10 <sup>-12</sup> exp(-2260/ <i>T</i> )	295-371	DF/ESR
10	(2.5 <sup>+1.2</sup> <sub>-0.8</sub> ) × 10 <sup>-12</sup> × exp[-(2970 ± 150)/ <i>T</i> ]	293-440	F/AG
12	(1.9 ± 0.3) × 10 <sup>-11</sup> × exp[-(3584 ± 70)/ <i>T</i> ]	356-628	SF/MS
This work	(5.2 ± 0.9) × 10 <sup>-11</sup> × exp[-(3755 ± 200)/ <i>T</i> ]	350-454	FF/RF
6	(8.5 ± 1.7) × 10 <sup>-12</sup> × exp[-(3220 ± 150)/ <i>T</i> ]	293-718	DF/ESR

<sup>a</sup> DF/ESR, discharge flow with ESR as the detection system; F/AG, flow tube with after glow as the detection system; SF/MS, stirred flow reactor with mass spectrometer as the detection system. FF/RF, flash photolysis with resonance fluorescence as the detection system.

dependent bimolecular rate constants, the following Arrhenius expression was derived:

$$k_2 = (5.2 \pm 1.03) \times 10^{11} \exp[-(7510 \pm 750) \text{ cal mol}^{-1}/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The quoted errors are 2σ for both *k*<sub>bi</sub> and *k*<sub>2</sub>. It is to be noted that the larger error in the *A* factor for reaction 2 vs. reaction 1 is the result of the more limited temperature range covered, the higher degree of uncertainty in each of the individual measurements, and the more limited number of experiments performed.

### Comparison with Previous Studies

Table III lists the three Arrhenius expressions which have now been reported for reaction 1. The calculated 298 K rate constants are seen to be in remarkably good agreement with each other. These values suggest that at room temperature, *k*<sub>1</sub> can be given as (6.6 ± 0.6) × 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The temperature dependence of *k*<sub>1</sub> obtained in the present study is seen to be in reasonably good agreement with previous measurements. The most significant disagreement is with the work of Zahniser et al.<sup>8</sup> As can be seen from Figure 3, the error bars on *k*<sub>1</sub>, measured in this work, overlap the Arrhenius lines of both Zahniser et al.<sup>8</sup> and Smith and Zellner<sup>7</sup> at temperatures higher than 270 K. Below 270 K, our *k*<sub>1</sub> values are in good agreement with those of Smith and Zellner, but are ~20% lower than those measured by Zahniser et al.<sup>8</sup> at temperatures of 225 K. At the present time, we can give no explanation for this observed difference in *k*<sub>1</sub> at low temperatures.

Concerning reaction 2, the results from four previous studies, as well as the present investigation, are listed in Table IV. The most recent results obtained by Singleton

TABLE V: Rate of HCl Degradation in the Stratosphere

Altitude (A), km	Temp (T), K, at A	$k_1^c$ at $T \times 10^{13}$	OH concn, radicals per $\text{cm}^3$ at A $\times 10^{-7}$	$k_1[\text{OH}] \times 10^9$	$k_2^d$ at $T \times 10^{17}$	$\text{O}(^3\text{P})^a$ atom concn, atoms per $\text{cm}^3$	$k_2[\text{O}(^3\text{P})] \times 10^9$	$k_1[\text{OH}]/k_2[\text{O}]$	$J_{\text{HCl}}^b$
20	220	4.2	0.11	463	0.20	0.02	0.004	$1.2 \times 10^5$	$< 10^{-10}$
25	220	4.2	0.18	737	0.20	0.14	0.03	$2.6 \times 10^4$	$\sim 6 \times 10^{-10}$
30	230	4.6	0.30	1370	0.42	0.62	0.26	$5.3 \times 10^3$	$\sim 8 \times 10^{-9}$
35	240	5.0	0.63	3120	0.83	2.4	2.0	$1.6 \times 10^3$	$\sim 2.5 \times 10^{-8}$
40	250	5.3	1.4	7450	1.6	8	12	$6.0 \times 10^2$	$\sim 4 \times 10^{-8}$
45	265	5.9	1.6	9380	3.7	22	80	$1.2 \times 10^2$	$\sim 5.5 \times 10^{-8}$
50	270	6.0	1.1	6640	4.7	36	171	$3.9 \times 10^1$	$\sim 6.5 \times 10^{-8}$

<sup>a</sup> Reference 20. <sup>b</sup> Reference 19. <sup>c</sup>  $k_1$  from this work. <sup>d</sup>  $k_2$  from this work.

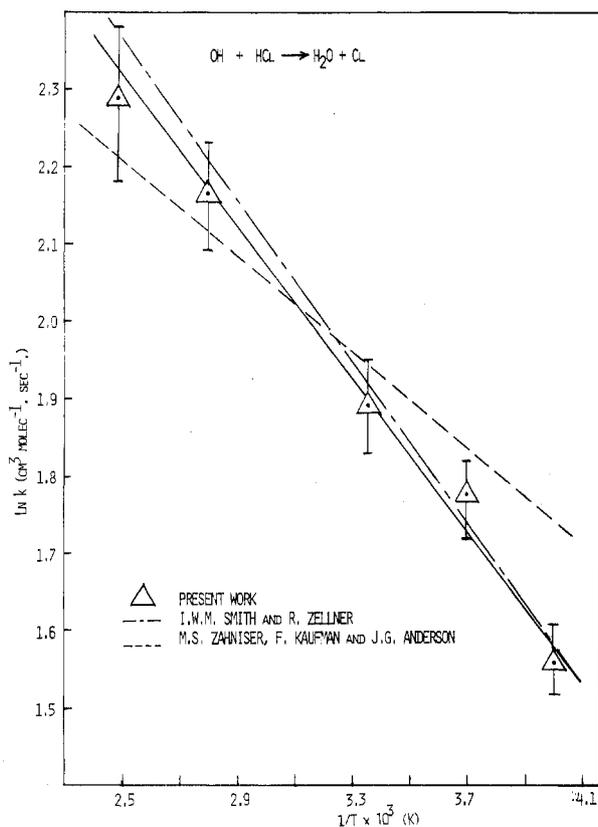


Figure 3. Arrhenius plots for the reaction  $\text{OH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}$ .

and Cvetanovic<sup>11</sup> have not been included in Table IV since these authors have yet to provide printed rate data at different temperatures. However, a value for  $E_{\text{act}}$  was verbally reported by these investigators<sup>11</sup> as  $\sim 6 \text{ kcal mol}^{-1}$ . From Table IV, it would appear that the activation energy of  $4.5 \text{ kcal mol}^{-1}$ , obtained by Balakhnin et al.,<sup>9</sup> is quite low and probably incorrect. There is a discrepancy of  $\sim 1.5 \text{ kcal mol}^{-1}$  between Brown and Smith's<sup>10</sup> value of  $E_2$  and that reported in this work. The results from the other three investigations lie between these two values. At this juncture, there appears to be no basis for rejecting or accepting any one of these five values for  $E_2$  (i.e.,  $6,^{10} \sim 6,^{11} 6.44,^6 7.15,^{12}$  and  $7.5 \text{ kcal mol}^{-1}$ ). It should be noted, in fact, that the seemingly large discrepancy of  $\sim 25\%$  in  $E_2$  is not that unreasonable in view of the small value for the bimolecular rate constant. However, there is a large discrepancy in the values of the individual bimolecular rate constants measured at a given temperature by different authors. For example, at 401 K, the value of  $k_2$  measured by Smith and Brown is a factor of 3 lower than that measured by us. In virtually all studies reported, involving four different techniques, it appears that the sensitivity

of each apparatus was at its ultimate limit.

### Atmospheric Implications

The three processes which reintroduce Cl atoms into the stratospheric  $\text{O}_3$  destruction cycle are chemical reactions 1 and 2 and the photochemical process 3. At photochemical equilibrium with respect to Cl atoms, it can be shown that

$$[\text{Cl}]/[\text{HCl}] = (k_1[\text{OH}] + k_2[\text{O}(^3\text{P})] + J_{\text{HCl}})/k_4[\text{RH}] \quad (\text{I})$$

where  $J_{\text{HCl}}$  is the photodissociation rate constant for HCl and process 4 is given as



Presented in Table V are the values of  $k_1[\text{OH}]$ ,  $k_2[\text{O}(^3\text{P})]$ , and  $J_{\text{HCl}}$  as a function of altitude. From this table, it can be seen that reaction 1 totally dominates the conversion of HCl back to active chlorine atoms below 50 km. In point of fact, at the most favorable altitude of 50 km, reaction 2 makes only an approximate 3% contribution to the total conversion process. Thus, below 50 km, eq I can be simplified to

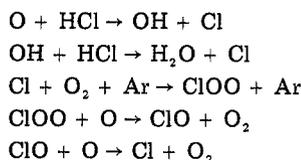
$$\frac{[\text{Cl}]}{[\text{HCl}]} = \frac{k_1[\text{OH}]}{k_4[\text{RH}]} \quad (\text{II})$$

The maximum impact on stratospheric models from the  $k_1$  value reported in this work would be in the stratospheric region of 13 to 30 km. In this region, our value of  $k_1$  would predict an approximate 20% lower value for the steady-state Cl atom concentration than that suggested from the measurements of Zahniser et al.<sup>8</sup> It should again be noted, however, that no basis presently exists for excluding the Zahniser et al.<sup>8</sup> value; hence, it would seem reasonable to take a simple average of the  $k_1$  values for modeling purposes.

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Even if we assume that each  $O(^3P)$  atom in the system led to the formation of one ClOO radical through the proposed reaction mechanism, the concentration of ClOO would be  $\sim 10^{10} \text{ cm}^{-3}$  during the decay of  $O(^3P)$ , since the pseudo-first-order rate constant for the formation of ClOO through the reaction,  $Cl + O_2 + Ar \rightarrow ClOO + Ar$ , is at most  $86 \text{ s}^{-1}$  under our experimental conditions (it is very likely to be an order of magnitude lower). Hence, the contribution of  $ClOO + O \rightarrow ClO + O_2$  toward the measured pseudo-first-order rate constant  $k_2'$  would be at most 15%. When the flash energy was increased by a factor of 6, the concentrations of O atoms and ClOO would both be 6 times higher. Thus, this flash energy variation would have indicated the importance of that reaction.

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## Direct Measurement of the Radiative Lifetime and Collisional Quenching of the $C^3\Pi_u$ State of Nitrogen as Studied by Pulse Radiolysis

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The optical emission of  $N_2(C^3\Pi_u \rightarrow B^3\Pi_g)$ , the second positive system, has been measured by pulse radiolysis of pure nitrogen, helium–nitrogen, and argon–nitrogen gas systems as a function of total gas pressure in the range 50–20 000 Torr. The radiative lifetime,  $\tau_0$ , was found to be  $40.8 \times 10^{-9} \text{ s}$  and the quenching rate constants for nitrogen and helium were found to be  $7.1 \times 10^{-12}$  and  $7.8 \times 10^{-14} \text{ cm}^3 \text{ particles}^{-1} \text{ s}^{-1}$ , respectively.

### Introduction

The identity, lifetime, and reactivity of the short-lived transient species produced in a chemical reaction constitutes a central problem in the elucidation of reaction mechanisms. This information is often obtained from fast reaction techniques which generally involve a short-lived perturbation of the system from an external source, followed by the direct observation of some physical parameter as a function of time. Pulse radiolysis is a useful technique for determining this type of information.<sup>1–14</sup>

The recent development of the plasma chromatograph and atmospheric pressure ionization sources for mass spectrometry has created an interest in the fate of electronically excited ions and neutral molecules at total gas pressures of 1 atm and above.<sup>5–9</sup> In this work, the technique of gas phase pulse radiolysis was employed to directly measure the lifetime of the second positive emission bands of nitrogen,  $C^3\Pi_u \rightarrow B^3\Pi_g$  transition, at total pressures ranging from 50 to 20 000 Torr.

### Experimental Section

A schematic of the gas phase pulse radiolysis arrangement is shown in Figure 1. A 1-MeV Van de Graaff electron accelerator produces electron pulses of 1-, 3-, 10-, 30-, and 100-ns duration with a average pulse current of 0.5 A per pulse. The accelerator is capable of operating in a single or repetitive pulsing mode with a maximum of 150 pulses per second. The reaction cell is aligned on axis

with the exit window of the accelerator and the light emissions are analyzed with a SPEX Model 1500, 3/4 meter, Czerny-Turner mount, optical grating spectrometer with a Bausch and Lomb 600 line/mm grating blazed at 3000 Å. A head-on, 12-stage, RCA 8575 photomultiplier is used to detect the light emission. The signal from the photomultiplier is transmitted through coaxial cable to a Tektronix 564B sampling-storage oscilloscope and is subsequently recorded on a Hewlett-Packard 7035B X–Y recorder. The photomultiplier tube, quartz light pipes, quartz prism, and the reaction cell are lead shielded to reduce the effects of x-rays and interfering Cerenkov radiation.

For the purpose of recording gross spectra, the quartz prism and exit slit of the monochromator could be removed and replaced by a film holder. The film holder is designed to contain a 2-in. piece of 35-mm film upon which a maximum of ten spectra, each covering 1000 Å, can be recorded. The excited species are then identified from their emission spectra.

Three gas mixtures were examined in this study at various total pressures ranging from 50 to 20 000 Torr. The gases were He + 0.1%  $N_2$ , pure  $N_2$  (99.999 mol %), and Ar + 0.5%  $N_2$ . These gases were obtained from Matheson Gas Products, Inc., East Rutherford, N.J. The composition of the gases prior to irradiation were analyzed with a CEC Model 21-130 cycloidal focusing mass spectrometer.

### Results and Discussion

The emission spectra resulting from the irradiation of pure nitrogen were studied in the region 2000–6000 Å. The

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