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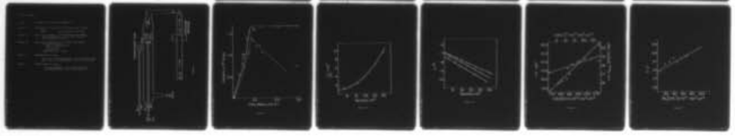

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Atomic fluorine was reacted with HCl in a flow system to see if the $F + HCl \overset{\text{yields}}{\rightarrow} HF + Cl$ reaction could be used as a titration for determination of F atom concentration, with an endpoint indicated by the intensity of chlorine atom recombination emission.

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20. Abstract (continued)

A sharp intensity maximum of this emission was observed near the endpoint, indicating the rapid removal of chlorine atoms by excess HCl. Since kinetic studies indicated that this removal process was third order overall and first order in [Cl], the $Cl + HCl + M \xrightarrow{\text{yields}} HCl_2 + M$ reaction was hypothesized. Third order rate constants were determined for M = HCl, Ar, and N_2. The relative efficiencies were found to be $Ar:N_2:HCl = 1:7.9:19.5$, and $k_{Ar} = 8.2 \pm 1.2 \times 10^{14}\ cm^6\ mole^{-2}\ sec^{-1}$.

INTRODUCTION

One method used for the determination of atomic fluorine concentration for kinetic studies has been titration using H_2[1], NOCl[2], and Cl_2[3,4] as titrants. In particular, when F_2 is used as the fluorine atom source, molecular chlorine is most useful as a titrant due to the fact that reaction (1) is about four orders of magnitude faster than reaction (2)[3]

$$F + Cl_2 \rightarrow FCl + Cl \qquad (1)$$

$$Cl + F_2 \rightarrow FCl + F \qquad (2)$$

so that virtually no Cl atoms are lost or F_2 molecules consumed by reaction (2). Instead, the Cl atoms recombine homogeneously to form molecular chlorine in both ground ($X^1\Sigma$) and excited ($A^3\Pi$) states[5]. Visible emission from the latter can then be used as a measure of Cl (and thus F) concentration.

$$Cl + Cl + M \rightarrow f\,Cl_2(A^3\Pi) + (1-f)Cl_2(X^1\Sigma) + M \qquad (3)$$

$$Cl_2(A^3\Pi) \rightarrow Cl_2(X^1\Sigma) + h\nu \qquad (4)$$

$$Cl_2(A^3\Pi) + M \rightarrow Cl_2(X^1\Sigma) + M \qquad (5)$$

Reaction (5), the collisional deactivation of the excited Cl_2 species, is indicated as an alternative to the chemiluminescent decay.

It was the original purpose of this study to determine if the reaction of F atoms with HCl,

$$F + HCl \rightarrow HF + Cl \qquad (6)$$

followed by reactions (3)-(5) would also be a suitable chemiluminescent titration for atomic fluorine. When it was determined that another process was occuring in the F/HCl system, becoming evident at higher HCl concentrations, the present study turned to the investigation of this other process.

EXPERIMENTAL

Fluorine atoms were produced by passing F_2/Ar mixtures through a 2450 MHz microwave discharge produced in an alumina discharge tube by an Evanson cavity excited by a Raytheon Microwave Power Generator. The F/F_2/Ar mixture then entered the reaction cell, a Teflon coated quartz tube 3.3 cm in diameter and 55 cm in length, where HCl and chlorine and, where necessary, nitrogen were added through a moveable multi-perforated Teflon inlet (Figure 1). Fluorine, HCl and chlorine flows were monitored by standard flow meters. Fluorine (Matheson) flow was controlled by a Nupro stainless steel fine metering valve. Flows of HCl (Linde) and chlorine (Matheson) were controlled by a Granville-Phillips Variable Leak. Argon (Linde) flowed through an Oxytrap column (Alltech) and a P_2O_5 trap, while nitrogen (Linde) was passed through an Oxysorb column (Alltech). Pressure was monitored by both a tilting McCleod Gauge and Hastings DV-4 and DV-6 Vacuum Gauges. The flow system was pumped through liquid nitrogen and charcoal traps by a Welch Model 1402 Vacuum Pump, having a pumping speed of 160 liters/min. Flow rates varied from 100-500 μmol/sec, depending on the object of the particular experiment.

The emission was detected by a RCA IP28 phototube powered by a Fluke Model 415B High Voltage Power Supply and monitored by a Keithley Model 610C Electrometer. The emission was filtered by a Wrattan 16A filter having a 5160-6200 Å bandpass. Both the photocell and Teflon inlet tube could be moved along the length of the reaction cell, allowing measurements of intensity vs time to be made, while circumventing local wall conditions.

RESULTS AND DISCUSSION

The reaction of F atoms with Cl_2 in an argon atmosphere was studied at varying Cl_2 concentrations. $Cl_2(A\rightarrow X)$ emission intensity was monitored at a position 3 cm downstream from the inlet, so that all initial mixing would be complete. A plot of intensity vs. Cl_2 concentration (Figure 2, solid line) showed a good reproduction of the earlier Ganguli and Kaufman titration[3], with an easily identified endpoint and emission intensity increasing as the square of the Cl atom concentration up the the endpoint.

The results of the analogous F + HCl reaction is shown in Figure 2 by the dotted line. While at low concentrations, the square relationship is maintained, there is a sharp and dramatic decrease in intensity at higher HCl concentrations. Although a systematic study was not undertaken, the experiments performed indicated that a comparison of the two titrations, run consecutively using the same F atom concentration produced the same endpoint. Thus HCl would seem to be as effective as Cl_2 as a chemiluminescent titrant for F atoms. In fact, the sharp endpoint may make HCl preferable to Cl_2.

On the other hand, the results left open the question of what process was responsible for the sharp intensity dropoff. Reaction (6) is well documented as the initial step of the F/HCl reaction[6,7]. If the subsequent reactions are assumed to be reactions (3)-(5), a steady state treatment of $Cl_2(A^3\Pi)$ arrives at the result that the intensity is proportional to the square of the Cl atom concentration:

$$I \;\alpha\; [Cl_2(A^3\Pi)] \;\alpha\; \frac{fk_3[M][Cl]^2}{(k_4+k_5[M]} \qquad (7)$$

If the decay of Cl atoms were second order as in reaction (3), a plot of $1/I^{1/2}$ vs time would be linear. Figure 3a shows this not the case. Figure 3b shows the linearity of a plot of $\ln I^{1/2}$ vs time, indicating that the decay of Cl atoms is first order.

The following reaction mechanism for the decay of Cl atoms is thus hypothesized:

$$Cl + HCl + M \rightarrow HCl_2 + M \qquad (8)$$

$$HCl_2 + Cl \rightarrow HCl + Cl_2 \qquad (9)$$

$$Cl\ (wall) \rightarrow 1/2\ Cl_2 \qquad (10)$$

The HCl_2 complex has been discussed[8,9] although there is some controversy as to its existence[10]. This type of mechanism would result in a first order decay of Cl atoms, provided reaction (8) is the rate determining step, and is rapidly followed by reaction (9). A predominant collisional dissociation of HCl_2 (reverse of reaction (8)) is ruled out, as it would result in a second order Cl atom decay, as can be seen if a steady state approximation is applied to HCl_2. The heterogeneous recombination of Cl atoms (reaction (10)) is also included as a well-known[7] first order decay process.

To determine the rate constant k_8 for the rate determining step, pseudo-first order conditions were used in the experiments, with the concentrations of HCl and third body being in large excess (at least twenty times greater) of the F atom (and therefore Cl atom) concentrations. Under these conditions, pseudo-first order rate constants, k', were determined as the slope of the ln $I^{1/2}$ vs time plots (Figure 3b) and could be related to the third order rate constants as follows:

$$k' = k_{8(Ar)}[Ar][HCl] + k_{8(HCl)}[HCl]^2 + k_{10} \qquad (11)$$

Only Ar and HCl were present in sufficient concentration to be important third bodies for reaction (8).

The rate constant for argon as a third body, $k_{8(Ar)}$ was determined first by finding k' for a number of different argon concentrations while holding the HCl concentration constant. Plotting k' vs

[Ar][HCl] gives a slope corresponding to $k_{8(Ar)}$. A typical series of runs for this process is shown plotted in Figure 4, and a summary of all such measurements appears in Table 1. The value found for $k_{8(Ar)}$ was $(8.2 \pm 1.2) \times 10^{14}$ cm^6 mol^{-2} s^{-1}. Once this value was determined, runs were made in which the HCl concentration was varied while argon concentration was held constant. Since $k_{8(Ar)}$ is now known, the term $k_{8(Ar)}$ [Ar][HCl] can be subtracted from k' in equation (11). Plots of $k'-k_{8(Ar)}[Ar][HCl]$ vs $[HCl]^2$ for various HCl concentrations results in a slope corresponding to $k_{8(HCl)}$, with an intercept corresponding to the rate constant for the wall reaction, k_{10}. A typical series of runs used for the determination of $k_{8(HCl)}$ appears in Figure 4 for comparison with $k_{8(Ar)}$, and the summary of all values obtained for $k_{8(HCl)}$ and k_{10} is shown in Table 1. The value for $k_{8(HCl)}$ is found to be $(1.6 \pm 0.4) \times 10^{16}$ cm^6 mol^{-2} s^{-1}, while k_{10}, although subject to much more scatter, is 11.7 ± 3.2 s^{-1}, corresponding to $\gamma = (9.1 \pm 2.5) \times 10^{-4}$. Neither $k_{8(Ar)}$ nor $k_{8(HCl)}$ show any pressure dependence, indicating that reaction (8) is indeed a third order reaction.

An interesting result is that HCl appears to be about twenty times as efficient a third body as is Ar for the production of HCl_2. In order to determine which properties of HCl are responsible for the greatly enhanced efficiency, a number of experiments were performed with N_2 as an added third body. Although N_2 is a diatomic molecule, it is inert and nonpolar. A typical series of runs used to determine $k_{8(N_2)}$ is shown in Figure 5. Here both Ar and HCl concentrations are fixed, and N_2 concentration is varied for different runs. A plot of k' vs $[HCl][N_2]$ gives a slope equal to $k_{8(N_2)}$. The value for this rate constant was found to be $(7.3 \pm 2.0) \times 10^{-15}$ cm^6 mol^{-2} s^{-1}. Thus, the efficiency of N_2 as a third body is nearly nine times that of argon, but only about one-half that of HCl. Therefore while the polarity of HCl appears to be a factor in its efficiency as a third body, the dominant factor appears to be the availability of internal degrees of freedom to remove the energy.

In Table 2, the results of this work is summarized giving both absolute rate constants for $k_{8(M)}$, and rates relative to $k_{8(Ar)}$. In addition, for the sake of comparison, also listed are the relative efficiencies of third bodies in the homogeneous recombination of chlorine atoms (reaction (3)) as found by various authors[12-14]. The nature of the third body employed seems more important in the production of a complex such as HCl_2 than in the production of a simple substance such as Cl_2.

The mechanism proposed here for the reaction of Cl + HCl lends more support for the existence of HCl_2. This species has been the subject of some controversy over the past few years. Experimentally, Noble and Pimentel[8] assigned spectral features produced when HCl/Cl_2/Ar mixtures were passed through a discharge and condensed in a matrix to HCl_2. Spencer and Glass[9] postulated HCl_2 as a species produced by reaction of Cl atoms with HCl at the chamber walls following the H + HCl reaction. Their measured cross-section for broadening of Cl EPR lines by HCl was also indicative of a strong long range attraction between Cl and HCl. HCl_2 has also been predicted by the BEBO calculations of Truhlar, Olson and Parr[15], and employed in the trajectory analysis of Thommarson and Berend[16]. In addition, the fact that vibrational relaxation of HCl by Cl atoms has been found to be very rapid[17], indicates that a HCl_2 intermediate is likely. The existence of HCl_2 in the matrix studies, however, has been disputed by Milligan and Jacox[10] and by Wight, Ault and Andrews[18] who claimed the species in question was actually HCl_2^-. In addition, Klein and Persky[19] calculated a high energy barrier to the formation of HCl_2.

The species present in the current research is certainly not ionic in nature. In addition, the fact that the Cl atom decay is first order, yet reaction (8) is dependent also on HCl concentration and that of the third body indicates the formation in a three-body reaction of an intermediate which could be only HCl_2. This is in contrast with the work of Spencer and Glass[9], where HCl_2 formation was assumed to largely occur on the walls, in order to explain its varying importance when different wall coatings of their vessel were employed.

Recently, Cohen and Bott reviewed the HCl chemical laser. In their report, they designated the primary recombination mechanism for Cl atoms to be

$$Cl + M \rightarrow ClM^* \qquad (12)$$

$$ClM^* + Cl \rightarrow Cl_2 + M \qquad (13)$$

In comparing the relative efficiencies of the various M's, they stated that qualitatively HCl would be only half as efficient as Ar due to the potential barrier to HCl_2 formation. The fact that in the current research we find a better than order-of-magnitude increase in HCl third body efficiency over Ar is further proof for the existence of HCl_2.

Finally, it should be pointed out that the titration comparison shows the sharp dropoff in intensity only past the endpoint - where HCl is present. This indicates that while Cl atoms will react with HCl to form the HCl_2 complex, no similar reaction occurs between Cl and HF.

Table 1

Compilation of Data for $k_{8(HCl)}$, $k_{8(Ar)}$, and k_{10}

Series	$k_{8(HCl)}$ ($cm^6\ mol^{-2}\ s^{-1}$)	Total Pressure (Torr)
1	1.6×10^{16}	1.0
9	1.8	3.7
11	1.8	6.05
13	1.1	6.05
21	1.1	5.0
22	2.0	4.1

Mean $k_{8(HCl)} = (1.6 \pm 0.4) \times 10^{16}\ cm^6\ mol^{-2}\ s^{-1}$

Series	$k_{8(Ar)}$ ($cm^6\ mol^{-2}\ s^{-1}$)	Total Pressure (Torr)
6	8.0×10^{14}	2.95 - 5.8
14	6.6	4.15 - 6.9
15	8.9	4.15 - 6.4
16	9.3	6.05 - 8.0

Mean $k_{8(Ar)} = (8.2 \pm 1.2) \times 10^{14}\ cm^6\ mol^{-2}\ s^{-1}$

Series	k_{10} (s^{-1})	Total Pressure (Torr)
1	7.7	1.0
5	13.5	3.8
9	8.3	3.7
10	9.9	4.0
11	8.9	6.05
12	12.1	4.3
13	13.0	6.05
21	16.8	5.0
22	14.9	4.1

Mean $k_{10} = 11.7 \pm 3.2\ s^{-1}$

Table 2

Summary of Results

M =	Ar	N_2	HCl	Cl_2	Ref
Cl + HCl + M:					
$k_{8(M)} \times 10^{-15}$ ($cm^6\ mol^{-2}\ s^{-1}$)	0.82 (±0.12)	7.3 (±2.0)	16 (±4)	--	This Work
Relative Efficiencies	1	8.9	19.5	--	This Work
Comparison with Cl + Cl + M:					
Relative Efficiencies	1	--	--	4.6	12
	1	--	--	6.8	13
	1	2	--	--	14

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LIST OF FIGURES

Figure 1 Diagram of the Fast Flow Apparatus

Figure 2 Comparison of Cl_2 and HCl as Titrants for F Atoms
○ Cl_2
□ HCl Total Pressure: 2.9 Torr

Figure 3a Decay of Cl Atoms as a Second Order Relationship
HCl Concentration = 1.3×10^{-9} mol cm^{-3}
Total Pressure = 1 Torr

Figure 3b Decay of Cl Atoms as a First Order Relationship
HCl Concentration =
○ 1.3×10^{-9} mol cm^{-3}
□ 2.2×10^{-9}
△ 3.7×10^{-9}
Total Pressure = 1 Torr

Figure 4 Determination of $k_{8(M)}$
○ M = Ar, HCl Concentration = 7.7×10^{-9} mol cm^{-3}
□ M = HCl, Ar Concentration + 208×10^{-9} mol cm^{-3}

Figure 5 Determination of $k_{8(N_2)}$
Ar Concentration = 275.6×10^{-9} mol cm^{-3}
HCl Concentration = 8.9×10^{-9} mol cm^{-3}

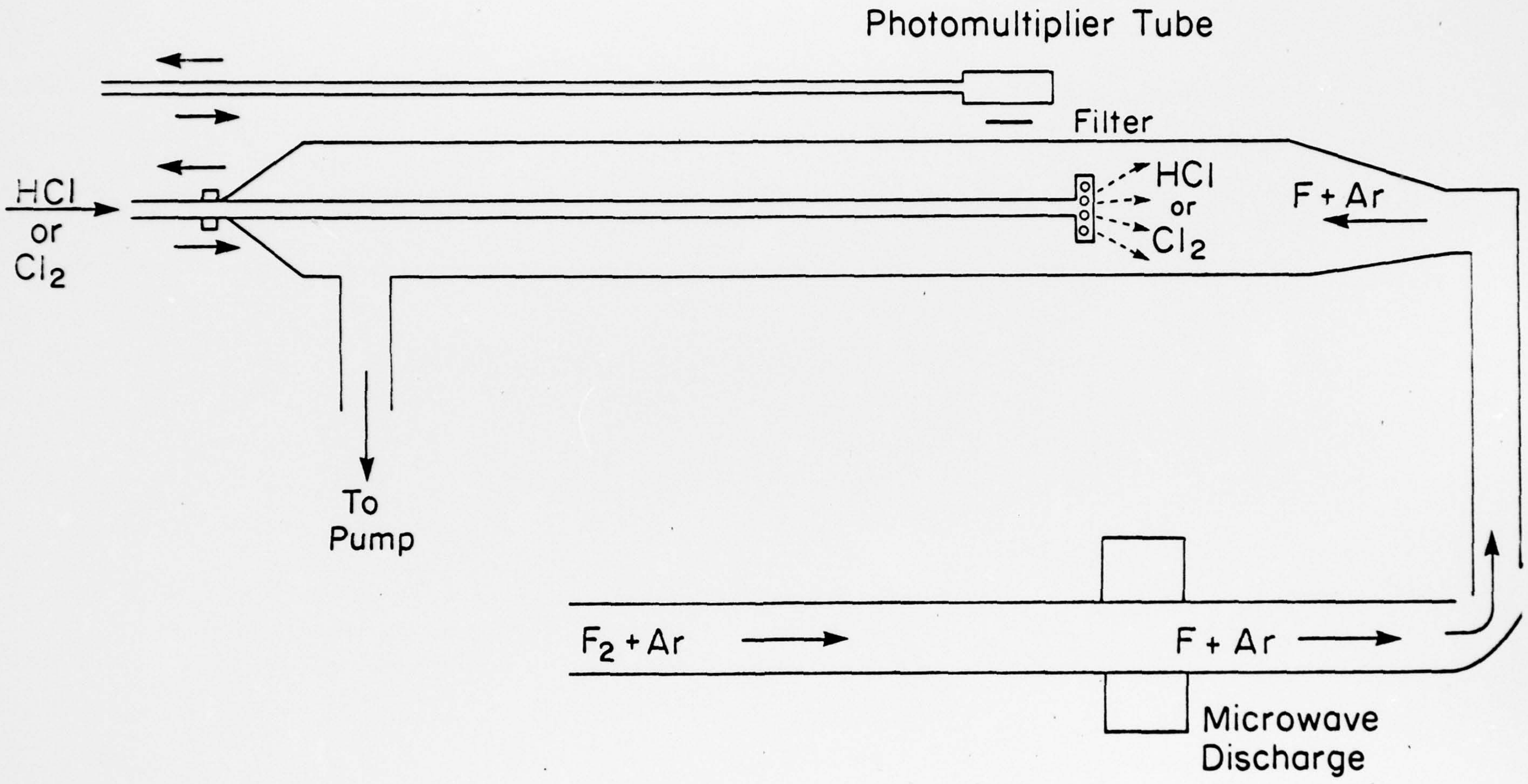
Photomultiplier Tube
Filter
HCl or Cl_2
HCl or Cl_2
F + Ar
To Pump
F_2 + Ar
F + Ar
Microwave Discharge

Figure 1

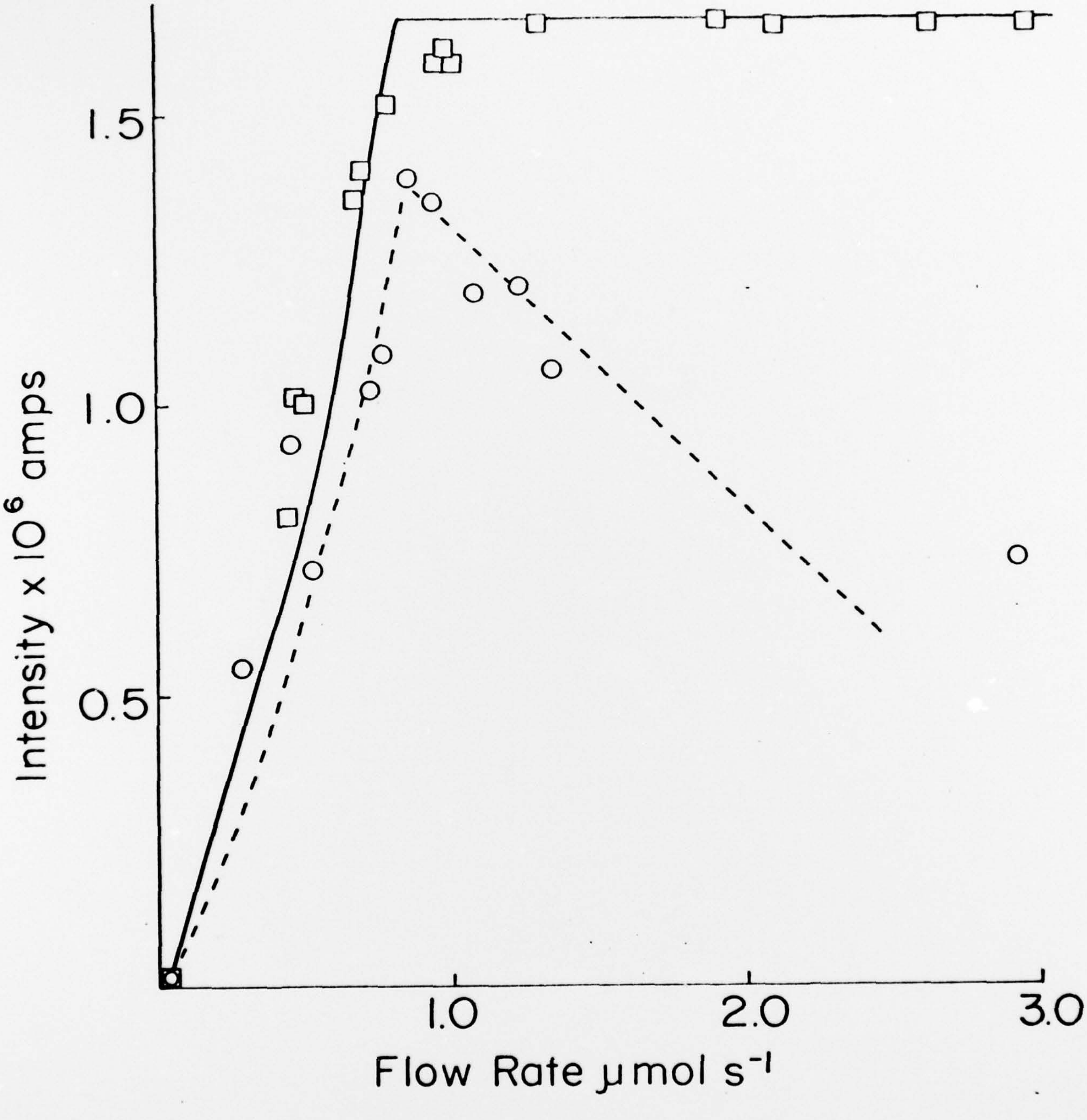

Figure 2

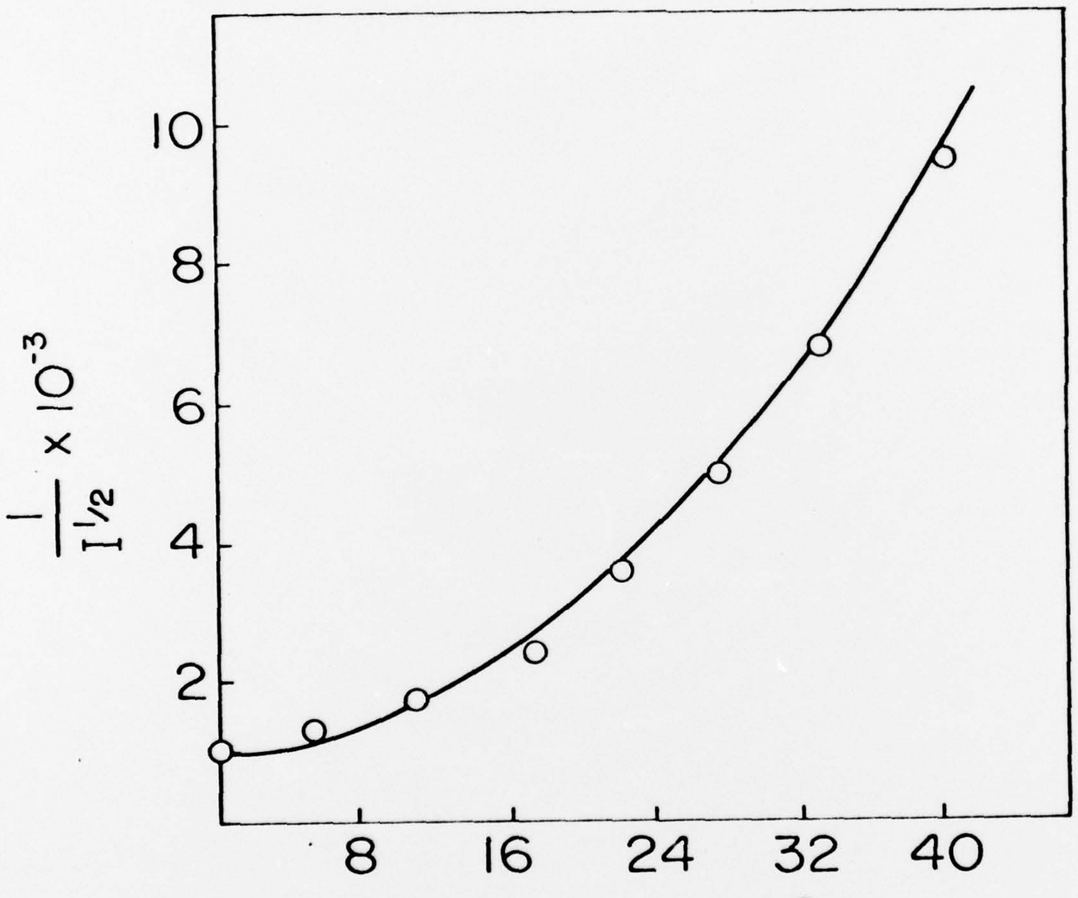

Figure 3a

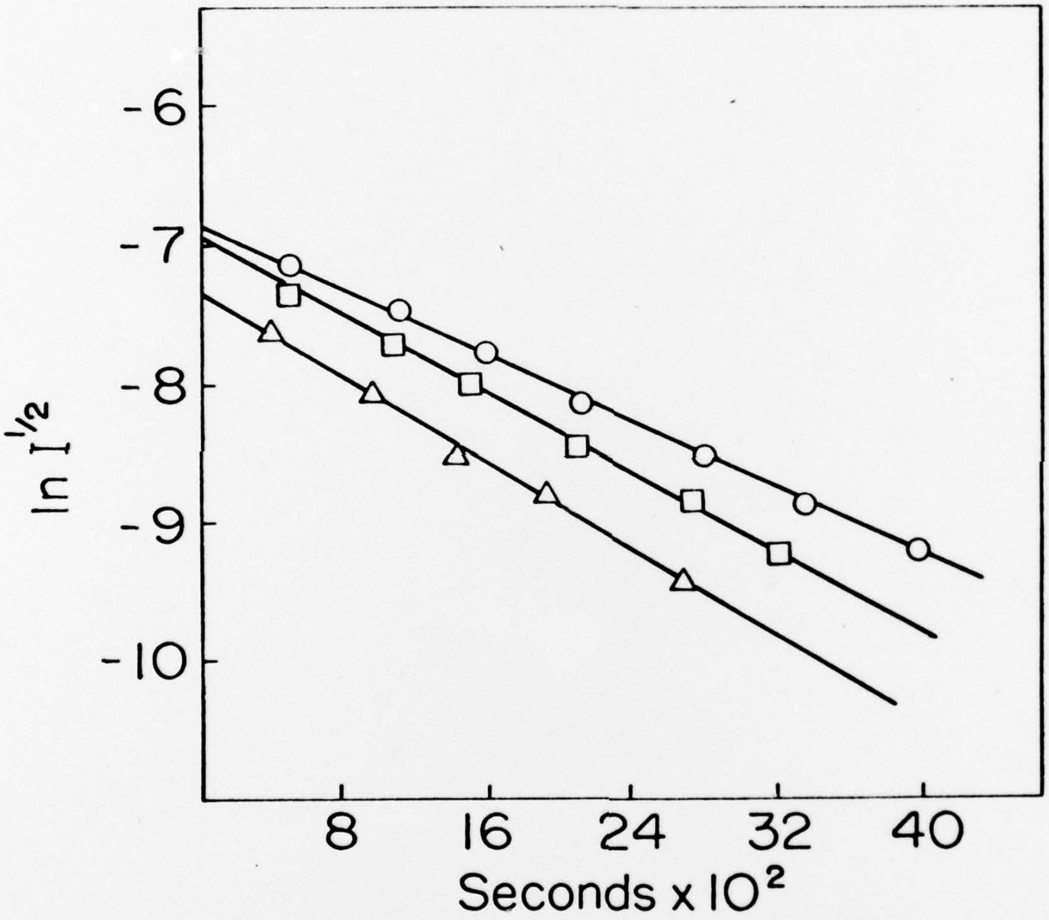

Figure 3b

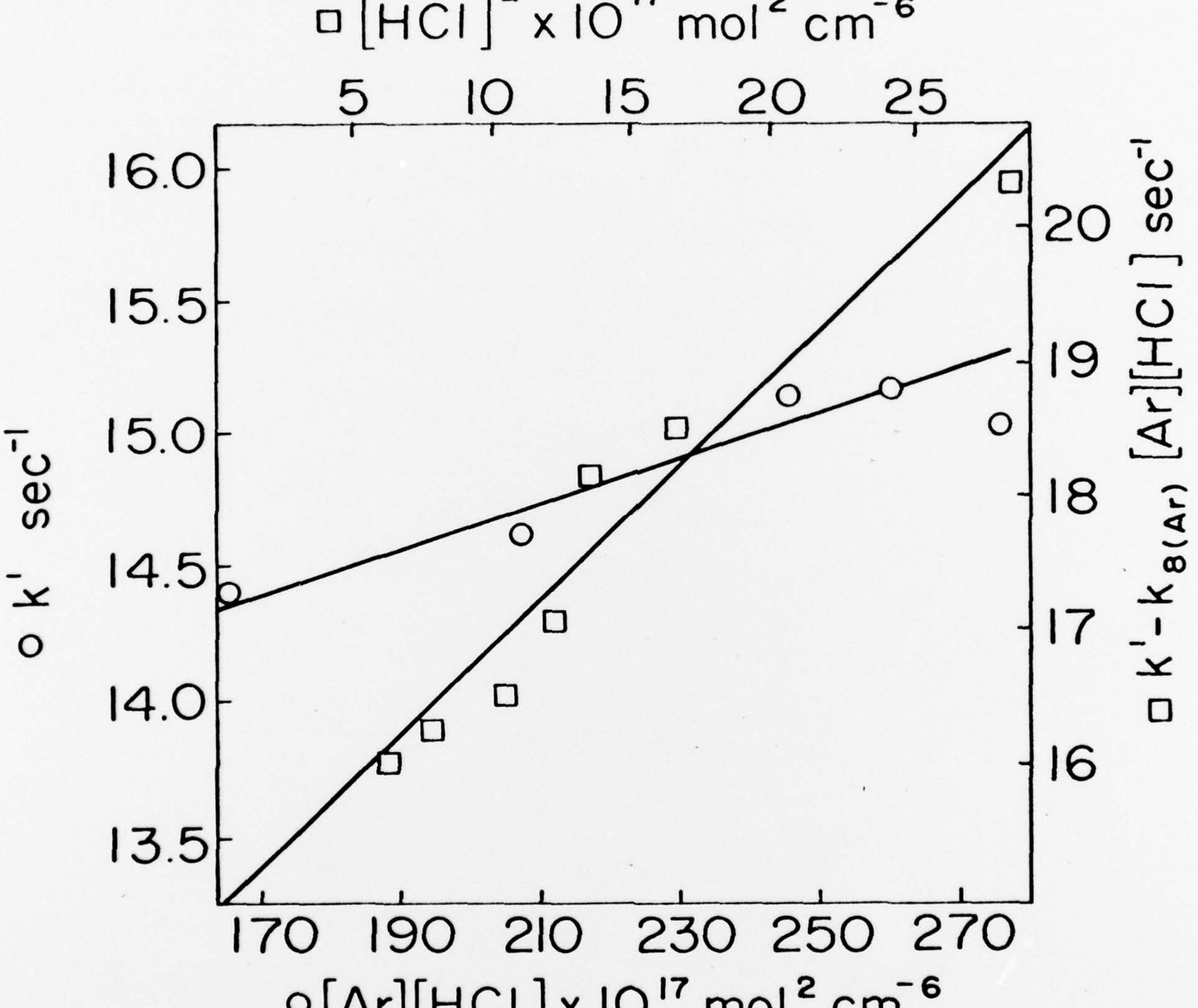
□ $[HCl]^2 \times 10^{17}$ mol^2 cm^{-6}
5
10
15
20
25
○ k' sec^{-1}
16.0
15.5
15.0
14.5
14.0
13.5
□ $k' - k_{8(Ar)}$ [Ar][HCl] sec^{-1}
20
19
18
17
16
170
190
210
230
250
270
○ [Ar][HCl] $\times 10^{17}$ mol^2 cm^{-6}

Figure 4

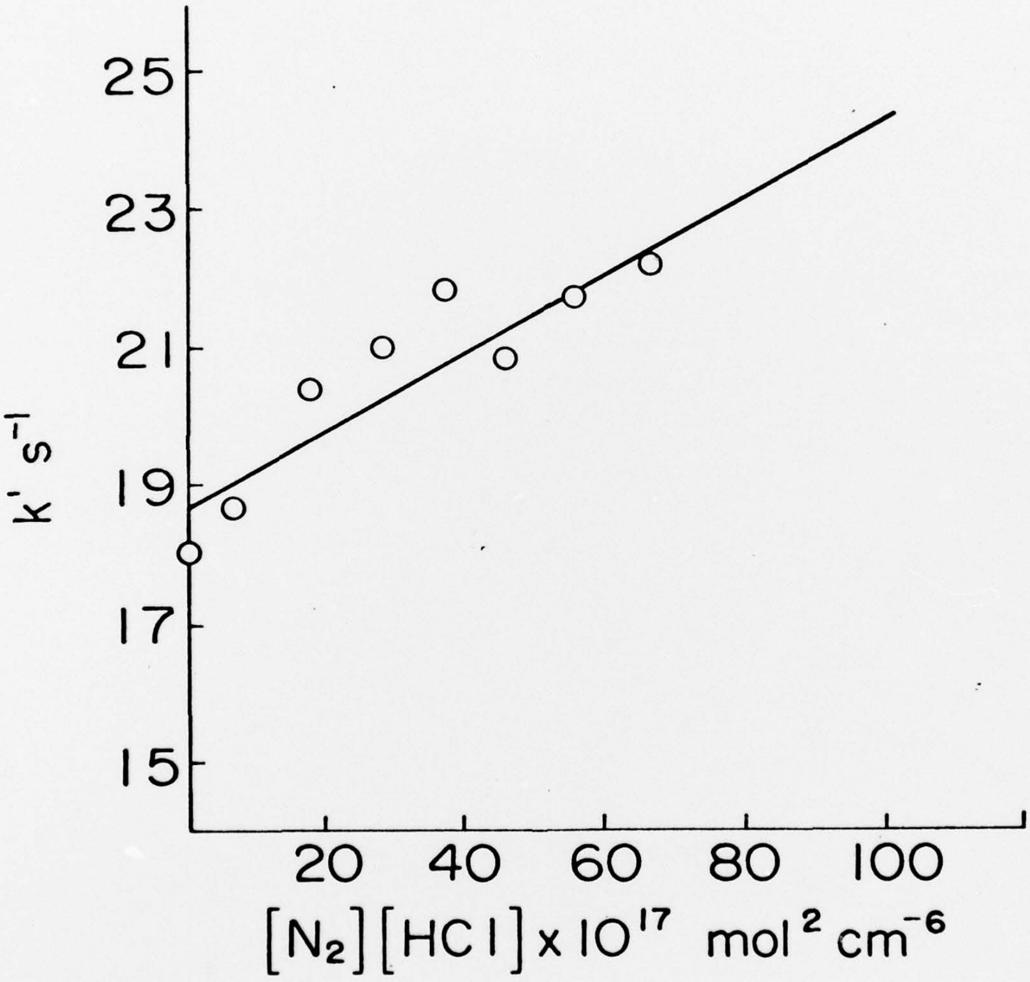

Figure 5