Temperature Dependence of the Rate Constant for the Reaction $F(^2P) + Cl_2 \rightarrow FCl + Cl$ at $T = 180-360$ K

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The absolute rate constant for the reaction $F(^2P)$ with Cl_2 has been measured using the discharge flow kinetics technique coupled to mass spectrometric detection at $T = 180-360$ K and 1 Torr He nominal pressure. Experiments were performed at NASA Goddard Space Flight Center (GSFC) in Greenbelt, MD, and Laboratoire de Combustion et Systemes Reactifs-CNRS in Orleans, France. Results of $k = (5.7 \pm 0.8) \times 10^{-11}$ and $(6.2 \pm 0.8) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} independent of temperature were obtained by each laboratory, respectively. When the results from both laboratories were combined into one data set, an average temperature independent value of $k_1 = (6.0 \pm 1.1) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} was obtained. A very slight positive temperature dependence with $k_1(T) = (6.5 \pm 1.5) \times 10^{-11} \exp\{-(20 \pm 60)/T\}$ cm^3 molecule^{-1} s^{-1} may also be derived from the combined data in the range $T = 180-360$ K.

Introduction

The abstraction of chlorine atoms by fluorine atoms from Cl_2 has been used for years as a convenient and reliable method to determine the concentration of F atoms.[1]

$$F + Cl_2 \rightarrow FCl + Cl \qquad \Delta H_{rxn} = -2 \text{ kcal mol}^{-1} \quad (1)$$

Few investigations of this reaction have been reported in the literature. In a study by Warnatz et al.[2] that covered a temperature range from $T = 232$ to 350 K, a rate constant of 9.5×10^{-11} cm^3 molecule^{-1} s^{-1} at $T = 300$ K was reported. These results provide an activation energy of 1400 cal mol^{-1}. A study by Clyne et al.[1] at $T = 298$ K yielded a rate constant of 1.1×10^{-10} cm^3 molecule^{-1} s^{-1}. A subsequent study from the same laboratory by Appleman et al.[3] at $T = 298$ K gave a rate constant of 1.6×10^{-10} cm^3 molecule^{-1} s^{-1}. Thus at $T = 298$ K a variation of more than 50% is observed in the measurements of the rate constant for reaction 1.

In some instances, for example to correct for undertitration at low [F],[4] the absolute value of k_1 is required as a function of temperature. In light of the limited and conflicting data available, reaction 1 was examined as a function of temperature in two different laboratories. One study was performed at NASA Goddard Space Flight Center (GSFC) in Greenbelt, MD, and the other study was performed at Laboratoire de Combustion et Systemes Reactifs-CNRS in Orleans, France (CNRS). The

work at GSFC covered a temperature range of $T = 180-298$ K. The work at CNRS covered a temperature range of $T = 230-360$ K. Both studies used the technique of discharge flow mass spectrometry (DF-MS).

Experimental Section

Work at NASA/GSFC. *Discharge Flow Reactor.* All experiments were performed in a Pyrex flow tube[4] 60 cm long and 2.8 cm in diameter with the inner surface of the flow tube being lined with Teflon FEP. A diagram of the apparatus is shown in Figure 1. The flow tube has an outer jacket for the circulation of a controlled flow of nitrogen vapor from liquid N_2 or thermostated fluids. The flow tube was coupled via a two-stage stainless steel collision-free sampling system to a quadrupole mass spectrometer (ABB Extrel Corp.) that was operated at low electron energies (typically less than 20 eV). Ions were detected by an off-axis conversion dynode/channeltron multiplier (Detector Technology Corp.). The total pressure was 1 Torr He. The linear flow velocity ranged from 2700 to 3000 cm s^{-1}.

The Cl_2 reactant was introduced into the flow tube via a Pyrex movable injector, which could be changed from a distance of 2 to 44 cm from the sampling pinhole. The helium carrier gas was flowed at 600 sccm at $T = 298$ K and 1100 sccm at $T = 180$ K, into the reaction flow tube through ports at the rear of the flow tube. All gas flows were measured and controlled by mass flow controllers (MKS Instruments). The mass flow controllers were calibrated using the pressure drop method. In this method, the gas flow originates from a bulb of known volume, and the pressure of the gas in the bulb is recorded as a function of time. Using the pressure change with time ($\Delta P/\Delta t$), the known volume (V_0), and the temperature (T), the gas

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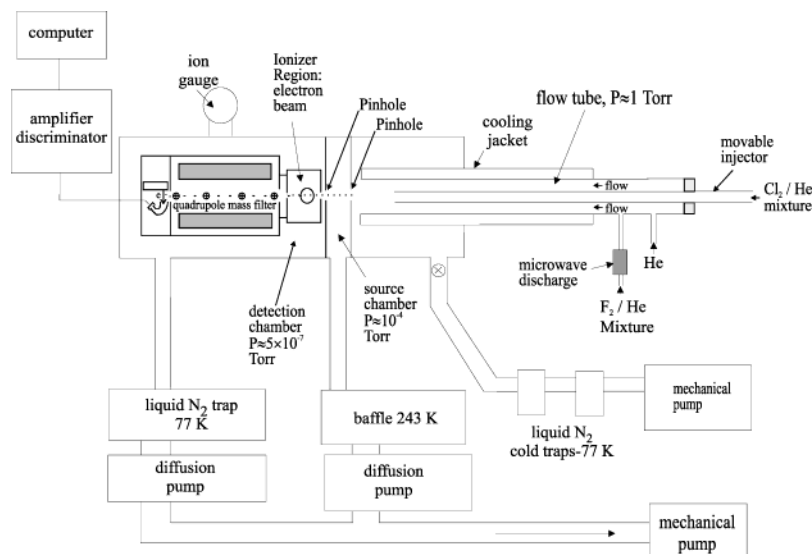† Also at Department of Natural Sciences, Coppin State College, Baltimore, MD 21216.

Figure 1. Diagram of the apparatus at NASA/GSFC.

flow (*F*) can be calculated from $F = (V_0/RT)(\Delta P/\Delta t)$. This calculated flow is compared with the flow reading of the flow controller. This calibration is done for several gas flows covering the range of the flow controller to yield a calibration factor.

Atomic Fluorine Production and Titration. Fluorine atoms were generated by passing molecular fluorine (ca. 5% diluted in helium) through a sidearm at the upstream end of the flow tube that contained a microwave discharge ($\sim$50 W, 2450 MHz Opthos Instruments). The discharge section consisted of a $^3/_8$ in. ceramic discharge tube coupled to a glass arm.

The concentration of fluorine atoms in the kinetic studies was determined by measuring the Cl_2 consumption in the fast titration reaction 1. With Cl_2 in excess, the F atom concentration was determined by measuring the decrease in the Cl_2^+ signal ($m/z = 70$) at an electron energy of $\sim$14 eV when the discharge was initiated. The diluted Cl_2/He mixture was admitted via the movable injector. The position of the injector was chosen to ensure that reaction 1 went to completion during the titration, and that this position was close to the middle of the decay range for Cl_2 under reaction conditions for the rate constant measurement. The absolute F atom concentration is given by

$$[F] = [Cl_2]_{\text{DiscOff}} - [Cl_2]_{\text{DiscOn}} \equiv (\Delta Cl_2 \text{ signal})[Cl_2]_{\text{DiscOff}} \quad (2)$$

where (ΔCl_2 signal) is the fractional decrease in the Cl_2^+ mass spectrometric signal (*S*) when the microwave discharge is turned on and is calculated from

$(\Delta Cl_2 \text{ signal}) =$
$\quad [S(\text{discharge off}) - S(\text{discharge on})]/S(\text{discharge off})$

Typically, 65–75% of the F_2 was dissociated and initial F atom concentrations were $(1.3-10.7) \times 10^{13}$ molecule cm^{-3} for the kinetic studies. $[Cl_2]$ was 3–4 times greater than [F] to yield fractional reductions in $[Cl_2]$ of 0.2–0.3. The reaction time for the titration was typically 1–4 ms, which was less than the typical flow time from the probe position to the sampling hole to the mass spectrometer.

Materials. Helium (99.9995%, Air Products) and F_2 (4.92% in helium, Air Products) were used as obtained. Cl_2 (VLSI grade, Air Products) was degassed at liquid nitrogen temperature.

Work at Laboratoire de Combustion et Systemes Reactifs-CNRS. *Discharge Flow Reactor.* Experiments were carried out
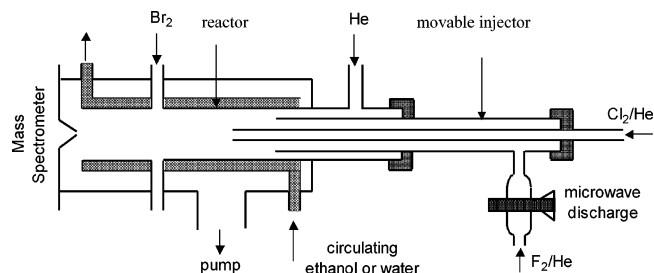

Figure 2. Diagram of the apparatus at CNRS.

in a discharge flow reactor using a modulated molecular beam mass spectrometer[5] as the detection method. The reactor consisted of a Pyrex tube (45 cm length and 2.4 cm i.d.) with a jacket for the circulation of the thermostated liquid (ethanol or water). The configuration of the movable double injector used for the introduction of the reactants into the reactor is shown in Figure 2. To reduce the wall loss of F atoms, the inner surfaces of the reactor and the injector were coated with halocarbon wax. F atoms were generated in a microwave discharge of F_2 diluted in He, which was used as the carrier gas in all the experiments. It was verified by mass spectrometry that more than 90% of F_2 was dissociated in the microwave discharge. The fluorine atoms were detected at their parent peak (F^+, $m/e = 19$) and also as FBr at $m/e = 100$, after scavenging by Br_2 at the end of the reactor through the fast reaction:[6]

$$F + Br_2 \rightarrow FBr + Br \qquad k_3 = 2.2 \times 10^{-10} \text{ cm}^3$$
$$\text{molecule}^{-1} \text{ s}^{-1} \quad (3)$$
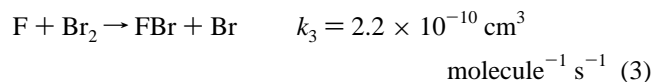
Br_2 was added 5 cm upstream of the sampling cone.

This last method of F atom detection was preferred to the direct detection at $m/e = 19$ (F^+), when working with low concentrations of F atoms (kinetics of F consumption in excess of Cl_2, see below), because detection sensitivity of the mass spectrometer for FBr was better than for F atoms. In addition, in this case one does not need to make corrections on the possible contribution at $m/e = 19$ of FCl, product of reaction 1. All the other relevant species were detected at their parent peaks: $m/e = 38$ (F_2^+), 70 (Cl_2^+), 160 (Br_2^+).

Absolute concentration of F atoms was measured from the titration reaction 3 using an excess of Br_2. In this case, $[F] = \Delta[Br_2] = [FBr]$. Another method of the absolute calibration of
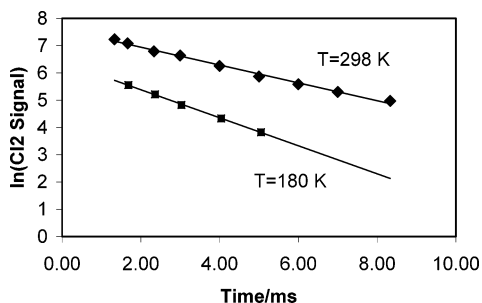
Figure 3. Examples of the kinetic runs of Cl_2 consumption in reaction with excess F atoms: $T = 298$ K and $T = 180$ K.

the F signal consisted of titration of F atoms by an excess of Cl_2; $[F] = \Delta[Cl_2]$. Results obtained by these two approaches were always consistent within a few percent. The concentrations of the stable species in the reactor were calculated from their flow rates obtained from the measurements of pressure drop of mixtures of the species with helium in calibrated volume flasks.

Materials. The purities of the gases were as follows: He > 99.9995% (Alphagaz) was passed through liquid nitrogen traps; Cl_2 > 99% (Ucar); Br_2 > 99.99% (Aldrich); F_2 (5% in helium, Alphagaz).

Results

Work at NASA/GSFC. The rate constant measurements for reaction 1 were performed under pseudo-first-order conditions with $[F]_0 > [Cl_2]_0$ and $[F]_0/[Cl_2]_0$ ranging from 6 to 41 at a total pressure of 1 Torr He. The initial concentrations of Cl_2 were $(2.0-9.9) \times 10^{11}$ molecules cm^{-3}. The first-order decay of Cl_2 is given by the expression

$$\ln[Cl_2]_t = -k_{obs}(d/v) + \ln[Cl_2]_0 \qquad (4)$$

where k_{obs} is the measured pseudo-first-order decay constant, d is the distance from the tip of the movable injector to the sampling pinhole, and v is the linear velocity. Linear least-squares analysis of plots of $\ln(Cl_2$ signal) at $m/z = 70$ versus contact time yielded the observed pseudo-first-order rate constant, k_{obs}. Figure 3 shows two examples of such plots. The experimental first-order decay constants were corrected (2.5%) for axial diffusion of the Cl_2 in helium gas with the relationship

$$k_{corr} = k_{obs}(1 + k_{obs}D/v^2) \qquad (5)$$

where v is the linear flow velocity and D is the diffusion coefficient of Cl_2 in helium. The diffusion coefficient for Cl_2
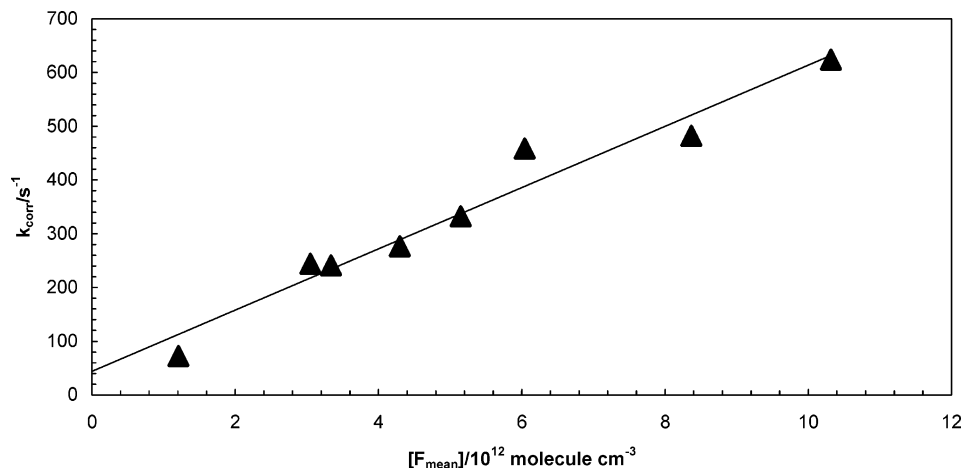
TABLE 1: Experimental Conditions and Results for the Study of the F + Cl_2 Reaction: Kinetics of Cl_2 Consumption in Excess of F Atoms

no. of decays	T (K)	$[F]_{mean}{}^a$	$k_1{}^b$	lab.
9	360	1.8–13.4	6.1 ± 0.8	CNRS
8	320	1.6–9.9	6.0 ± 0.9	CNRS
8	298	1.21–10.3	5.68 ± 0.54	GSFC
8	294	0.9–9.6	6.0 ± 0.7	CNRS
8	273	1.3–9.1	6.2 ± 0.8	CNRS
7	250	0.8–6.7	7.0 ± 0.8	CNRS
9	230	0.4–7.5	6.5 ± 0.8	CNRS
4	220	2.76–8.51	6.53 ± 1.18	GSFC
8	200	2.32–9.15	5.81 ± 1.16	GSFC
8	180	2.54–8.63	4.87 ± 0.47	GSFC

^{a} Units of 10^{12} molecules cm^{-3}. ^{b} Units of 10^{-11} cm^3 molecule^{-1} s^{-1}; errors are 1σ plus 10%.

in He was estimated from that of Ar in He according to the method of Lewis et al.[7] to be $D = 197$ cm^2 s^{-1} at $T = 180$ K and $D = 367$ cm^2 s^{-1} at $T = 298$ K. A $T^{3/2}$ dependence of D on T was assumed in estimating D at other temperatures. A small (8%) stoichiometric correction to $[F]_0$ was made to allow for the depletion of F during the reaction.

$$[F]_{mean} = [F]_0 - {}^1\!/_2[Cl_2]_0 \qquad (6)$$

The bimolecular rate constant k_1 is related to the corrected pseudo-first-order rate constant k_{corr} through the expression

$$k_{corr} = k_1[F]_{mean} + k_{loss} \qquad (7)$$

where $[F]_{mean}$ is calculated from eq 6 and k_{loss} is the first-order rate constant for the loss of Cl_2 on the walls or other first-order processes. Figure 4 shows a plot of k_{corr} versus $[F]_{mean}$ at $T = 298$ K. The slope of this plot gives $k_1(298K) = (5.68 \pm 0.54) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Similar plots give $k_1(220K) = (6.53 \pm 1.18) \times 10^{-11}$, $k_1(200K) = (5.81 \pm 1.16) \times 10^{-11}$, and $k_1(180K) = (4.87 \pm 0.47) \times 10^{-11}$, all in units of cm^3 molecule^{-1} s^{-1}. The errors are $\pm 1\sigma + 10\%$ for systemic error. The results are summarized in Table 1.

Work at Laboratoire de Combustion et Systemes Reactifs-CNRS. All the experiments were carried out at 1 Torr total pressure of helium. Two series of experiments were performed to measure the rate constant of the reaction F + Cl_2: one by monitoring Cl_2 consumption kinetics in excess of F atoms and another by monitoring of F decays in excess of Cl_2 molecules.

Cl_2 Kinetics in an Excess of F Atoms. In this series of experiments reaction 1 was studied under pseudo-first-order
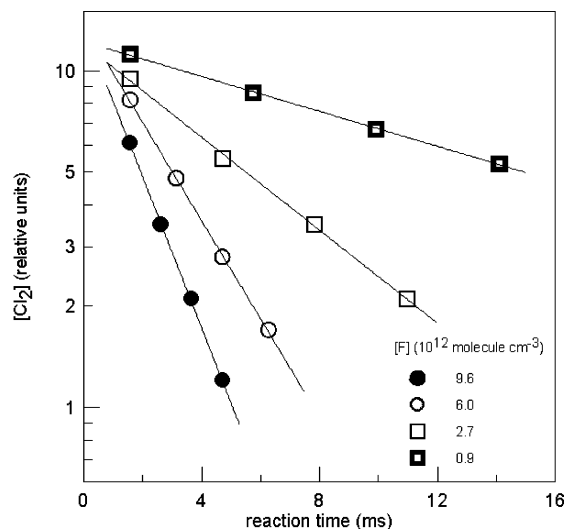

Figure 4. Plot of pseudo-first-order rate constants versus the mean fluorine atom concentration at $T = 298$ K.

Rate Constant for the Reaction F(^{2}P) + Cl$_2$ $\rightarrow$ FCl + Cl

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Figure 5. Example of the kinetic runs of Cl$_2$ consumption in reaction with excess F atoms: $T = 294$ K
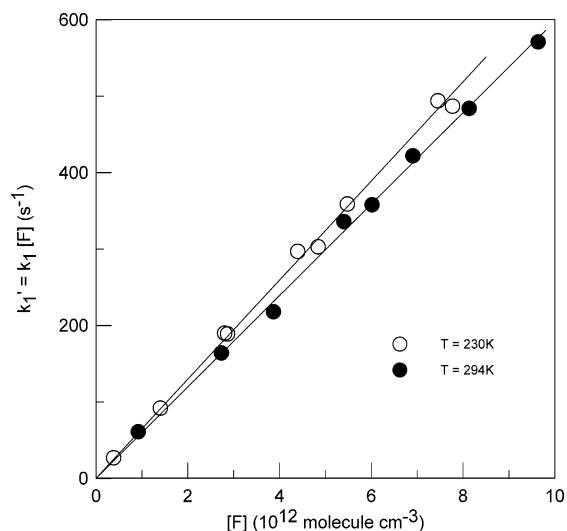

Figure 6. Example of pseudo-first-order plots of Cl$_2$ consumption in reaction with excess F atoms.

conditions using an excess of F atoms over Cl$_2$ molecules. Experiments were carried out in the temperature range $T = 230-360$ K. The initial concentrations of Cl$_2$ were $(1.2-4.0) \times 10^{11}$ molecule cm^{-3}; the range of F concentrations is shown in Table 1. Flow velocities in the reactor were $(1500-2300)$ cm s^{-1}. The wall loss rate of Cl$_2$ was negligible (<1 s^{-1}). The consumption of excess reactant, F atoms, was negligible ($<10\%$) in all the experiments, and was taken into account using the mean F concentration over the whole reaction time for the calculation of k_1. An example of the kinetic runs of the exponential decay of Cl$_2$ measured with different concentrations of F atoms is shown in Figure 5. Figure 6 shows an example of the dependence of the pseudo-first-order rate constant, $k'_1 = k_1[F]$, on the concentration of F atoms. All the pseudo-first-order rate constants, k'_1, were corrected for axial and radial diffusion of Cl$_2$.[8] The diffusion coefficient of Cl$_2$ in He was calculated from that of Kr in He.[9] The maximum correction was about 10%. The values of k_1 were obtained from the slope of the linear least-squares fit to the experimental data, as shown in Figure 6. All the results obtained for k_1 at the different temperatures of the study are reported in Table 1.

F Atom Kinetics in an Excess of Cl$_2$. In this series of experiments to measure the rate constant of reaction 1, k_1, F

TABLE 2: Experimental Conditions and Results for the Study of the F + Cl$_2$ Reaction, Kinetics of F Consumption in Excess of Cl$_2$ (CNRS)

no. of decays	T (K)	[Cl$_2$]$_{\text{mean}}$[a]	k_1[b]
8	360	0.5–8.1	5.8 ± 0.7
7	335	0.4–7.2	5.8 ± 0.7
8	240	0.5–6.5	6.1 ± 0.8

[a] Units of 10^{12} molecule cm^{-3}. [b] Units of 10^{-11} cm^{3}molecule^{-1}s^{-1}; errors are 1σ plus 10%.
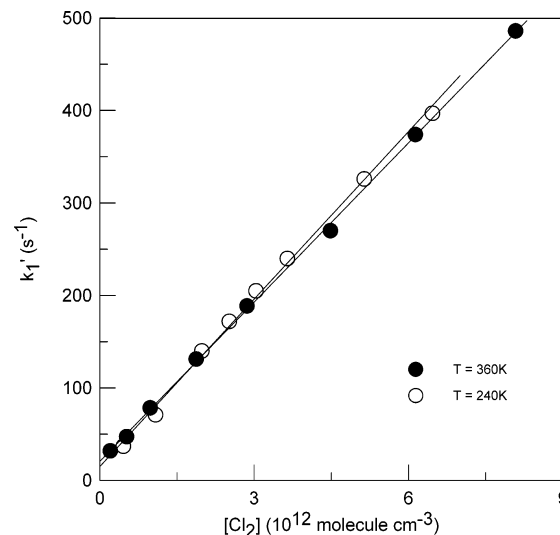

Figure 7. Example of pseudo-first-order plots of F atoms consumption in reaction with excess Cl$_2$.

atom decay kinetics were monitored in the presence of excess of Cl$_2$. Because both F atoms and Cl$_2$ were introduced through the double movable injector (see Figure 2), the F atom signal was monitored as a function of position and, therefore, time. Experiments were carried out at three temperatures, $T = 360$, 335, and 240 K. The initial concentration of F atoms (detected as FBr, see Experimental Section) was $(3.5-5.0) \times 10^{11}$ molecule cm^{-3}, and the initial concentration of Cl$_2$ was varied in the range $(0.4-8.1) \times 10^{12}$ molecule cm^{-3} (see Table 2). The flow velocity in the reactor was $1540-2160$ cm s^{-1}. The concentrations of Cl$_2$ and F atoms were simultaneously measured as a function of reaction time. A consumption of excess reactant, Cl$_2$, was also observed. In most cases, this consumption was less then 10% and it reached 30% in a few kinetic runs, where insufficient excess of Cl$_2$ over the F atom concentration was used. For the rate constant calculations the mean values of [Cl$_2$] over the reaction time of the F kinetics were used. The examples of the pseudo-first-order plots measured from F atom decay kinetics are shown in Figure 7. The pseudo-first-order rate constant values were corrected to take into account the axial and radial diffusion of F atoms. The diffusion coefficient of F in He, was calculated from $D_{\text{O-He}}$ to be $D_{\text{F-He}} = 2.77 \times 10^{-2}T^{1.8}$.[10] Maximum corrections were around 10%. The values of k_1 obtained from the slopes of the straight lines in Figure 7 are presented in Table 2. The intercepts in Figure 7, 15 ± 10 s^{-1}, are in fair agreement with the F loss rate 8–15 s^{-1} measured in absence of Cl$_2$.

As noted above, F atoms were scavenged by Br$_2$ at the end of the reactor to be detected as FBr molecules. This procedure implies that any secondary reaction could not affect the FBr concentration after its formation and therefore could not affect the observed kinetics of F decay. Br atoms are the only active species present at the zone of the reactor downstream of Br$_2$ addition point. They are formed simultaneously with FBr in
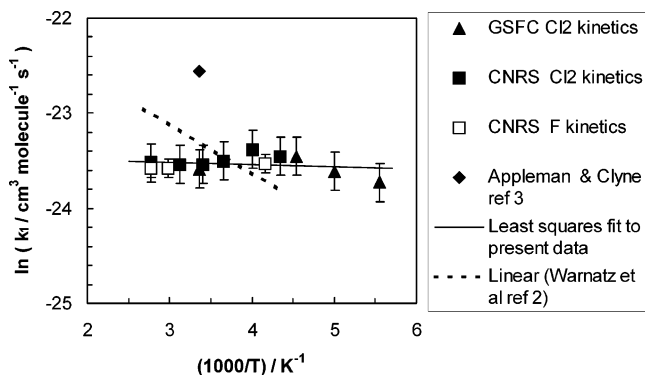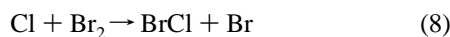
Figure 8. For the combined data set the temperature dependence of the rate constant of the reaction $F + Cl_2 \rightarrow Cl + FCl$. Continuous and dashed lines represent the exponential fit to the experimental data from this study and ref 2, respectively.

reaction 3 and also in reaction 8 of Cl atoms (product of reaction 1) with Br_2:[11]

$$Cl + Br_2 \rightarrow BrCl + Br \qquad (8)$$

$$k_8 = 2.3 \times 10^{-10} \exp(-135/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Considering that reaction 9 of Br atoms with FBr is endothermic by approximately 14 kcal mol^{-1}, its possible influence in the present experiments can be ruled out:

$$Br + FBr \rightarrow F + Br_2 \qquad (9)$$
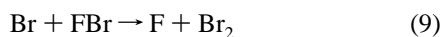
Excellent agreement between the results obtained for k_1 under different experimental conditions (see Tables 1 and 2) is additional evidence that the procedure used for F atom detection was correct.

Discussion

From the GSFC laboratory the average temperature independent rate constant is $k_1 = (5.7 \pm 0.8) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. An Arrhenius plot of these data for the temperature range $T = 180-298$ K shows a relatively flat temperature dependence. For the results from the CNRS laboratory the least-squares analysis of the data provides the Arrhenius expression: $k_1 = (4.8 \pm 0.5) \times 10^{-11} \exp\{(70 \pm 60)/T\}$ cm^3 molecule^{-1} s^{-1} for $T = 230-360$ K, where the quoted uncertainties represent 2σ for the activation energy and 1σ for the preexponential factor. Thus, this shows no more than a small negative temperature dependence of the rate constant of the F + Cl$_2$ reaction. In fact, considering the experimental uncertainty, the temperature independent value of $k_1 = (6.2 \pm 0.8) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at $T = 230-360$ K can be also recommended from the CNRS set of results.

When the two sets of laboratory results from CNRS and GSFC are combined and treated as one set of results, the average temperature independent value derived for k_1 is $(6.0 \pm 1.1) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for the temperature range $180-360$ K. In Figure 8 all the results from both laboratories are plotted according to the Arrhenius equation. The least-squares analysis of the combined results provides the following Arrhenius

expression with a very weak positive temperature dependence:

$$k_1 =$$
$$(6.5 \pm 1.5) \times 10^{-11} \exp\{-(20 \pm 60)/T\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
$$T = 180-360 \text{ K} \quad (10)$$

The results for the rate constant for reaction 1 from this study differ significantly from those previously published. The only other temperature study is that of Warnatz et al.[2] in a discharge flow mass spectrometer system that covered a temperature range from $T = 232$ to 350 K. As shown by the dashed line in Figure 8, this earlier study measured a much steeper temperature dependence for k_1 than was found in this present work. Their derived Arrhenius expression is

$$k_1 = 9.1 \times 10^{-10} \exp(-700/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
$$T = 232-373 \text{ K}$$

where the activation energy is more than a factor of 10 greater than that derived in this work. Figure 8 also shows the value of 1.6×10^{-10} cm^3 molecule^{-1} s^{-1} measured by Appelman and Clyne[3] at $T = 298$ K in a discharge flow mass spectrometer system; this value of k_1 is about a factor of 2 greater than that measured in this present study.

It is generally accepted that there is no secondary chemistry in the F + Cl$_2$ reaction system.[1] In addition, the previous studies[1-3] as well as the present one all employed the same experimental technique of discharge flow mass spectrometry. Therefore, there is no obvious explanation for the discrepancy in the values of k_1 between those from the present study and those from the earlier studies.[1-3]

References and Notes

(1) Clyne, M. A. A.; McKenney, D. J.; Walker, R. F. *Can. J. Chem.* **1973**, *51*, 3596.
(2) Warnatz, Von J.; Wagner, H. Gg.; Zetzsch, C. *Ber. Bunsen-Ges. Phys. Chem.* **1971**, *75*, 119.
(3) Appelman, E. H.; Clyne, M. A. A. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 2072.
(4) Cody, R. J.; Payne, W. A., Jr.; Thorn, R. P., Jr.; Nesbitt, F. L.; Iannone, M. A.; Tardy, D. C.; Stief, L. J. *J. Phys. Chem. A* **2002**, *106*, 6060.
(5) Poulet, G.; Lancar, I. T.; Laverdet, G.; Le Bras, G. *J. Phys. Chem.* **1990**, *94*, 278.
(6) Bemand, P. P.; Clyne, M. A. A. *J. Chem. Soc. Faraday Trans. 2* **1976**, *72*, 191.
(7) Lewis, R. S.; Sander, S. P.; Wagner, W.; Watson, R. T. *J. Phys. Chem.* **1980**, *84*, 2009.
(8) Kaufman, F. *J. Phys. Chem.* **1984**, *88*, 4909.
(9) Marrero, T. R.; Mason, E. A. *J. Phys. Chem. Ref. Data* **1972**, *1*, 3.
(10) Zelenov, V. V.; Kukui, A. S.; Dodonov, A. F. *Sov. J. Chem. Phys.* **1990**, *5*, 1109.
(11) Bedjanian, Y.; I. T.; Laverdet, G.; Le Bras, G. *J. Phys. Chem. A* **1998**, *102*, 953.