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Kinetics and Products of the Reactions of Fluorine Atoms with ClNO and Br_2 from 295 to 950K

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Kinetics and Products of the Reactions of Fluorine Atoms with ClNO and Br_2 from 295 to 950K

ABSTRACT

The kinetics and products of the reactions of F atoms with Br_2 and ClNO have been studied in a flow reactor coupled with an electron impact ionization mass spectrometer at nearly 2 Torr total pressure of helium and over a wide temperature range, T = 295 – 950 K. The rate constant of the reaction F + ClNO → products (1) was determined under pseudo-first order conditions, monitoring the kinetics of F-atom consumption in excess of ClNO. The measured temperature independent rate constant, $k_1 = (1.29 \pm 0.13)\times10^{-10}$ $cm^3 molecule^{-1} s^{-1}$ (T = 299-950 K), was found to be in excellent agreement with the only previous low temperature study which allowed to recommend the value of k_1 in an extended temperature range, (228 – 950) K. FCl and Cl atoms were observed as the reactions products (corresponding to two reaction pathways: Cl-atom abstraction and replacement with fluorine atom, respectively) with the independent of temperature, in the range 295 – 948 K, yields of 0.68 ± 0.10 and 0.32 ± 0.05, respectively. Rate constant of the reaction F + Br_2 (2), $k_2 = (1.28 \pm 0.20) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}, determined using both absolute and relative rate methods, was found to be independent of temperature at T = (299 - 940) K.

1. INTRODUCTION

Reactions of F atoms, as a rule, are extremely rapid with the rate constants often approaching to bimolecular collision frequency.[1] This specificity of the reactions of fluorine atoms provokes, in addition to general, a practical interest for these reactions, especially for laboratory studies of gas-phase reactions. For instance, reactions of F atom with stable molecules are frequently used as titration reactions in order to detect and/or measure the absolute concentrations of F-atoms and other species (e.g., refs 2-5) or as a source of various atoms and radicals (e.g., refs 6-7). On the other hand, the rapidity of the elementary reactions of F atoms makes them difficult to study, in particular, due to presence of a rapid secondary chemistry and need of a high detection sensitivity. This may be the reason why the database for reactions of fluorine atoms remains limited and highly uncertain: the rate constants of many reactions studied are poorly defined even at room temperature.[1]

In the present work we report the results of an experimental study of the reactions of F atoms with Br_2 and ClNO in an extended temperature range (from room temperature to 950K):

$$F + ClNO \rightarrow \text{products} \qquad (1)$$

$$F + Br_2 \rightarrow FBr + Br \qquad (2)$$

There is only one previous measurement of the rate constant of reaction 1 in the temperature range (228-353) K,[8] whereas the products of the reaction have never been studied. In fact, reaction 1 is very interesting from mechanistic point of view, since it can proceed through two competing pathways, C1-atom abstraction channel and FNO + Cl forming one, which until now was considered as negligible:[8]

$$F + ClNO \rightarrow FCl + NO \qquad \Delta_r H° = -98.3 \text{ kJ mol}^{-1} \qquad (1a)$$

$$\rightarrow Cl + FNO \qquad \Delta_r H° = -99.6 \text{ kJ mol}^{-1} \qquad (1b)$$

The thermochemical data used for the calculations of $\Delta_r H°$ are from ref. 9. The rate constant of reaction (2) was measured at room temperature in two previous studies;[2-3] however even for this frequently used in laboratory reaction, the value of the rate constant at room temperature is uncertain by a factor of nearly 1.5.

In the present paper, we report the temperature dependence of the rate constants of the title reactions and the branching ratio for two reactive pathways of reaction 1 as function of temperature between 295 and 950 K.

2. EXPERIMENTAL

Experiments were carried out in a discharge flow reactor using a modulated molecular beam mass spectrometer with electron impact ionization as the detection method. The flow reactor operated at temperatures T = 295 – 950 K and nearly 2 Torr total pressure of Helium and consisted of an electrically heated Quartz tube (45 cm length and 2.4 cm i.d.) with water-cooled extremities (Figure S1, Supporting Information).[10] Temperature in the reactor was measured with a *K*-type thermocouple positioned in the middle of the reactor in contact with its outer surface. Temperature gradients along the flow tube measured with a thermocouple inserted in the reactor through the movable injector was found to be less than 1%.[10]

F atoms were formed in the microwave discharge of F_2/He mixtures. In order to reduce F atom reactions with glass surface inside the microwave cavity, a ceramic (Al_2O_3) tube was inserted in this part of the injector. It was verified by mass spectrometry that more than 90% of F_2 was dissociated in the microwave discharge. Fluorine atoms were detected at m/z = 98/100 (FBr^+) after being scavenged with an excess of Br_2 (added in the end of the reactor 6 cm upstream of the sampling cone, see Figure S1) through reaction 2. This reaction was also used for the determination of the absolute concentrations of FBr: [FBr] = $\Delta[Br_2]$, i.e. concentration of FBr was determined from the consumed fraction of $[Br_2]$. Similarly, F atoms

could be detected as FCl (m/z = 54) upon chemical conversion in reaction with an excess of Cl_2:

$$F + Cl_2 \rightarrow FCl + Cl \quad (3)$$

This reaction was also used for the absolute calibration of FCl, one of the products of reaction 1: [FCl] = $\Delta[Cl_2]$. Another product of reaction 1, Cl-atom, was detected as BrCl at m/z = 114/116 ($BrCl^+$) after being scavenged with Br_2:

$$Cl + Br_2 \rightarrow Br + BrCl \quad (4)$$

Absolute concentration of BrCl was determined from the consumed fraction of [Br_2]: [BrCl] = $\Delta[Br_2]$. The absolute concentrations of Br_2 as well as of other stable species (Cl_2, ClNO) in the reactor were calculated from their flow rates obtained from the measurements of the pressure drop of their mixtures in He stored in calibrated volume flasks.

The purities of the gases used were as follows: He >99.9995% (Alphagaz), passed through liquid nitrogen trap; Br_2 >99.99% (Aldrich); F_2, 5% in helium (Alphagaz); Cl_2 > 99.6% (Alphagaz); ClNO >99.2% (Matheson).

3. RESULTS AND DISCUSSION

3.1. Rate Constant of Reaction 1. The rate constant of reaction 1 was determined from kinetics of F-atom consumption in excess of ClNO, basically, under pseudo-first order conditions. The initial concentration of F atoms was in the range (0.6 - 1.7) $\times 10^{11}$ molecule cm^{-3}, the concentrations of ClNO are shown in Table 1. The flow velocity in the reactor was in the range (2400-3600) cm s^{-1}.

Table 1. Summary of the Measurements of the Rate Constant of the Reaction F + ClNO.

T (K)	number of kinetic runs	[ClNO] (10^{12} molecule cm^{-3})	k_1^a (10^{-10} $cm^3 molecule^{-1} s^{-1}$)
299	10	0.36-4.36	1.31

356	7	0.30-3.64	1.26
454	7	0.39-5.23	1.29
613	8	0.26-4.96	1.25
950	9	0.41-5.10	1.32

[a] estimated uncertainty on k_1 is 15 %.

The concentrations of F atoms and ClNO were simultaneously measured as a function of reaction time. The observed consumption of ClNO, although low (≤ 10%), was taken into account in calculations of k_2. Examples of exponential F-atom decays observed at different concentrations of ClNO are shown in Figure 1.

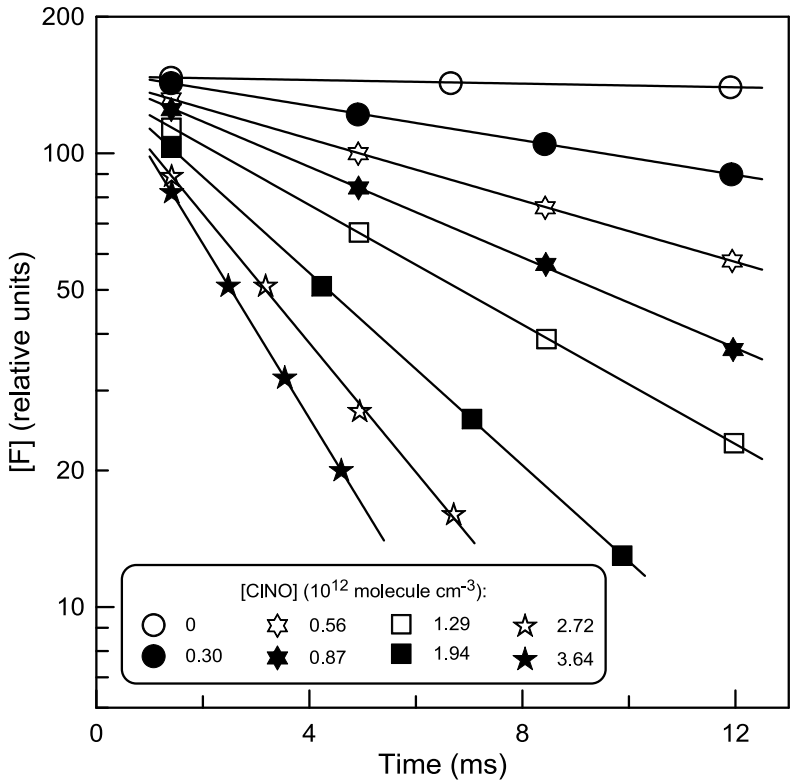

Figure 1. Reaction F + ClNO: examples of F-atom consumption kinetics observed with different concentrations of ClNO at T = 356 K.

Figure 2 shows the pseudo-first order rate constant, $k_1' = k_1[\text{ClNO}] + k_w$, as a function of the concentration of ClNO at T = 299 and 356 K. Pseudo-first order plots observed at three other temperatures (454, 613 and 950 K) are shown in Figures S2-S4 (Supporting Information). k_w

represents the rate of F decay in the absence of ClNO in the reactor and was measured in separate experiments.

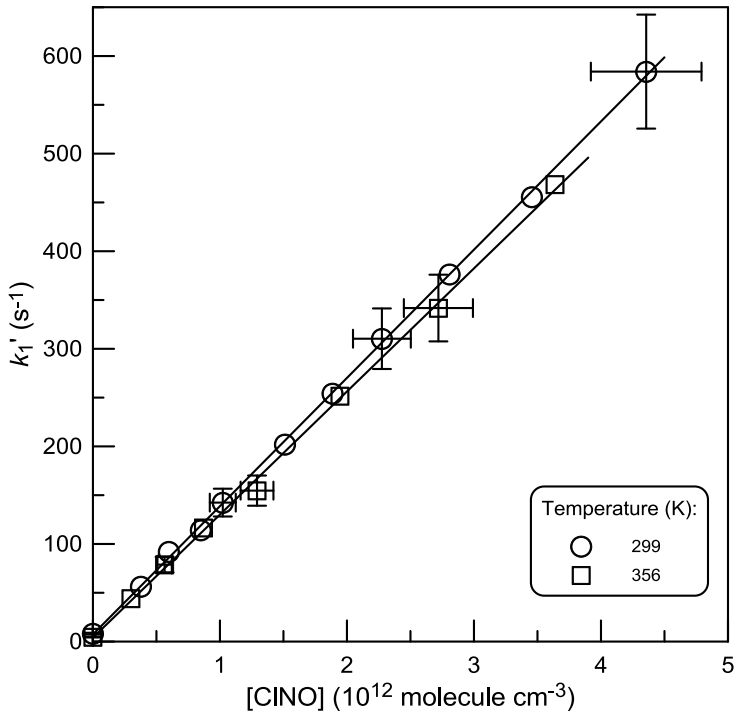

Figure 2. Reaction F + ClNO: example of pseudo-first order plots obtained from F-atom decay kinetics in excess of ClNO (T = 299 and 356 K). Error bars demonstrate estimated 10% maximum uncertainty on the measurements of k_1' and [ClNO].

All the measured values of k_1' were corrected for axial and radial diffusion of fluorine atoms.[11] The diffusion coefficient of F in He, $D_0 = 614 \times (T/298)^{1.75}$ Torr cm^{-2} s^{-1}, was calculated using Fuller's method.[12] Corrections were generally less than 10%. The slopes of the straight lines in Figures 2 and S2-S4 provide the values of k_1 at respective temperatures. The intercepts were in the range (1 - 10) s^{-1} in good agreement with F-atom loss rate measured in the absence of ClNO in the reactor.

All the results obtained for k_1 at different temperatures are shown in Table 1 and Figure 3. The combined uncertainty on the measurements of the rate constants was estimated to be ≤ 15 %, including statistical error (within a few percent) and those on the measurements of the flows (5%), pressure (3%), temperature (1%) and absolute concentration of ClNO (< 10%).

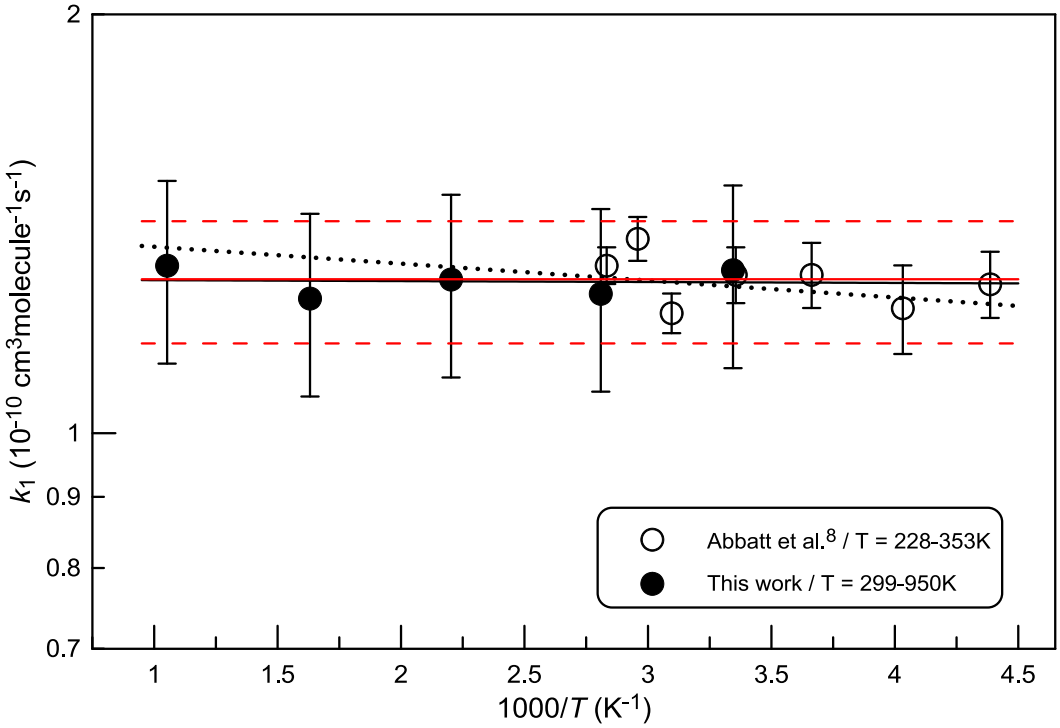

Figure 3. Reaction F + ClNO: temperature dependence of the rate constant. Solid black line, exponential fit to the present data; dotted line, exponential fit to the data from ref. 8; solid red line, mean of all the measurements from two studies; dashed red lines, mean value ± 10%. Error bars correspond to 15% for the present measurements and 1σ reported in ref. 8.

The unweighted exponential fit to the present data for k_1 (solid black line) yields the following Arrhenius expression:

$$k_1 = (1.29 \pm 0.10) \times 10^{-10} \exp(-(1.5 \pm 30)/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

where the cited uncertainties are 2σ statistical ones. The experimental data from the present study can also be well represented with temperature independent value of

$$k_1 (\pm 2\sigma) = (1.29 \pm 0.06) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

3.2. Products of reaction 1. Two series of experiments were carried out: products of reaction 1 were detected upon total consumption of F or ClNO in excess of ClNO or F, respectively. In the experiments in excess of ClNO, determination of the yields of the reaction products, FCl (channel 1a) and Cl (channel 1b), consisted in the measurements of the consumed concentration of F atoms and formed concentrations of the products. Reaction time was (0.01-0.02) s, initial concentrations of F atoms and ClNO are shown in Table 2.

Table 2. Experimental Conditions and Results of the Measurements of the Yields of FCl and Cl in Reaction F + ClNO.

T (K)	[F] (10^{12} molecule cm^{-3})	[ClNO] (10^{12} molecule cm^{-3})	k_{1a}/k_1	k_{1b}/k_1	total[a]
295	0.15-3.07	20-25	0.680	0.314	0.994
323	8-10	0.11-2.41	0.717	0.314	1.031
356	0.10-2.74	20-25	0.684	0.323	1.007
453	0.17-2.21	20-25	0.707	0.315	1.022
458	8-10	0.13-2.60	0.705	0.314	1.019
613	0.12-2.32	20-25	0.711	0.325	1.036
763	8-10	0.10-1.20	0.654	0.331	0.985
948	0.31-1.89	20-25	0.647	0.342	0.989

[a] Sum of the yields of the two reaction products.

Under these experimental conditions, F atoms were completely consumed in the reaction with ClNO. The formed concentrations of FCl were monitored at m/z = 54 (FCl^+). Let's note that absolute calibration of the mass-spectrometric signals for F and FCl was not required for the determination of FCl yield because the initial concentration of F atoms could be expressed as FCl upon titration of fluorine atoms with Cl_2 ([Cl_2] = (2-3)×10^{13} molecule cm^{-3}) through reaction 3. Cl atoms formed in reaction (1b) reacted rapidly with ClNO:

$$Cl + ClNO \rightarrow Cl_2 + NO \qquad (5)$$

and were detected as Cl_2 at m/z = 70 (Cl_2^+). It was verified that increase of the reaction time or concentration of ClNO had no impact on [Cl_2] formed. Example of the experimental data observed at T = 453 and 613 K is shown in Figure 4. Similar data observed at other temperatures of the study (T = 295, 356 and 948 K) are shown in Figures S5-S7 (Supplementary Information). It can be noted that detection of the co-products of FCl and Cl, NO and FNO, in these experiments was problematic because of the important contribution of ClNO at parent peaks of these species (m/z = 49 (NCl^+) and m/z = 30 (NO^+), respectively).

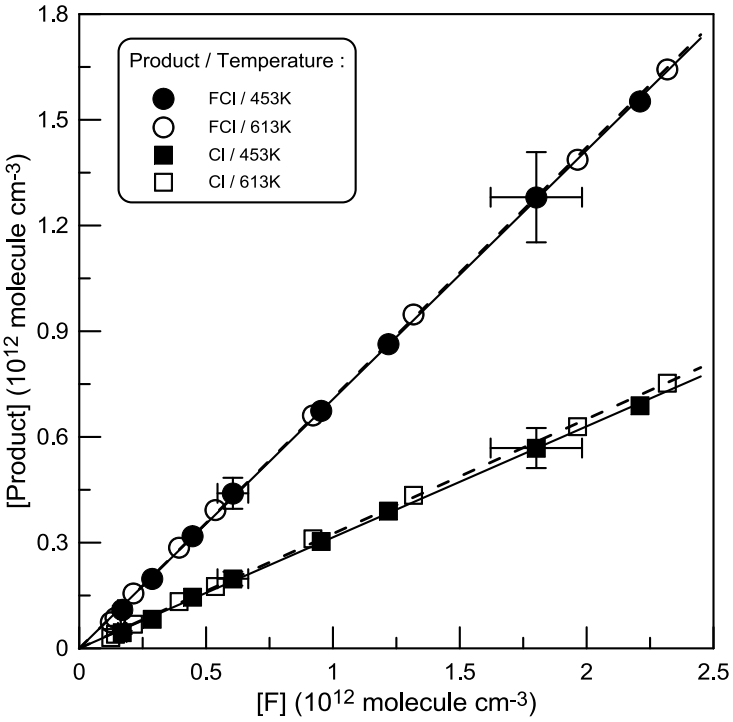

Figure 4. Reaction F + ClNO: concentrations of Cl and FCl formed in reaction (1) as a function of the consumed concentration of F atoms. Error bars correspond to typical 10% uncertainties on the determination of the absolute concentrations of the relevant species. Continuous and dashed lines represent linear through origin fit to the experimental data at T = 453 and 613 K, respectively.

In excess of F atoms over ClNO, the reaction products were monitored upon total consumption of ClNO (reaction time was approximately 0.01 s). FCl was detected directly, while Cl-atom was transformed to BrCl in reaction 4 with Br_2 (introduced 5 cm upstream of the sampling cone of the mass spectrometer, see Figure S1) and was detected at m/z = 114/116 ($BrCl^+$). No evidence for the possible secondary endothermic[9] reaction

$$F + FCl \rightarrow F_2 + Cl \qquad \Delta_r H° = 97.6 \text{ kJ mol}^{-1} \qquad (6)$$

was observed: variation of [F] or of the reaction time had no impact on the concentration of FCl. Figures 5 and S8 show the dependences of the concentrations of FCl and Cl formed in reaction (1) as a function of the consumed concentration of ClNO observed at different temperatures in the reactor.

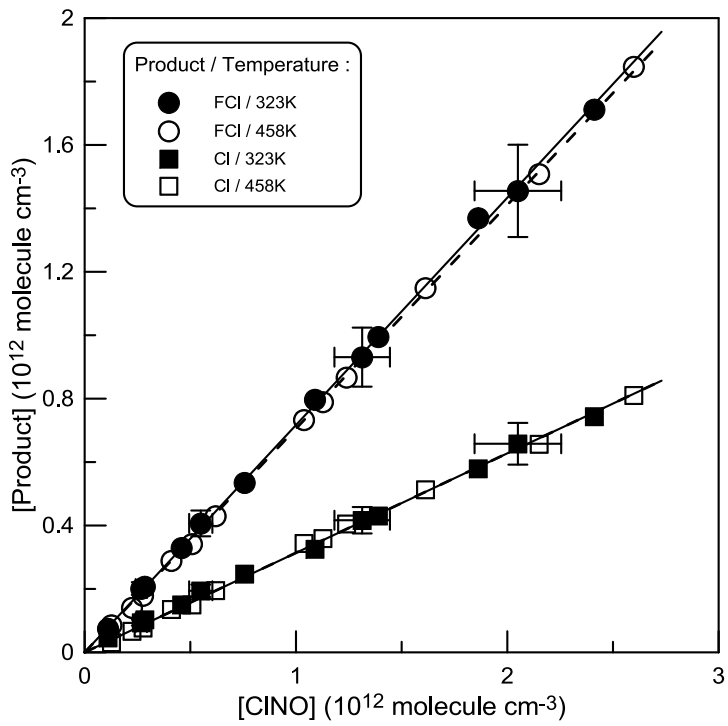

Figure 5. Reaction F + ClNO: concentrations of Cl and FCl formed in reaction (1) as a function of the consumed concentration of ClNO. Error bars correspond to typical 10% uncertainties on the determination of the absolute concentrations of the relevant species. Continuous and dashed lines represent linear through origin fit to the experimental data at T = 323 and 458 K, respectively.

The slopes of the straight lines in Figures 4, 5, S5-S8 provide the branching ratios for the chlorine atom and FCl forming pathways of reaction 1. All the results obtained in this way for k_{1a}/k_1 and k_{1b}/k_1 at different temperatures are shown in Table 2 and Figure 6. Estimated systematic uncertainty on the measurements of k_{1a}/k_1 and k_{1b}/k_1 is around 15% and is mainly due to the precision of the measurements of the absolute concentrations of the respective species. One can note an excellent agreement between the results obtained in two series of experiments under different experimental conditions, upon complete consumption of F-atom and ClNO in excess of ClNO and F, respectively.

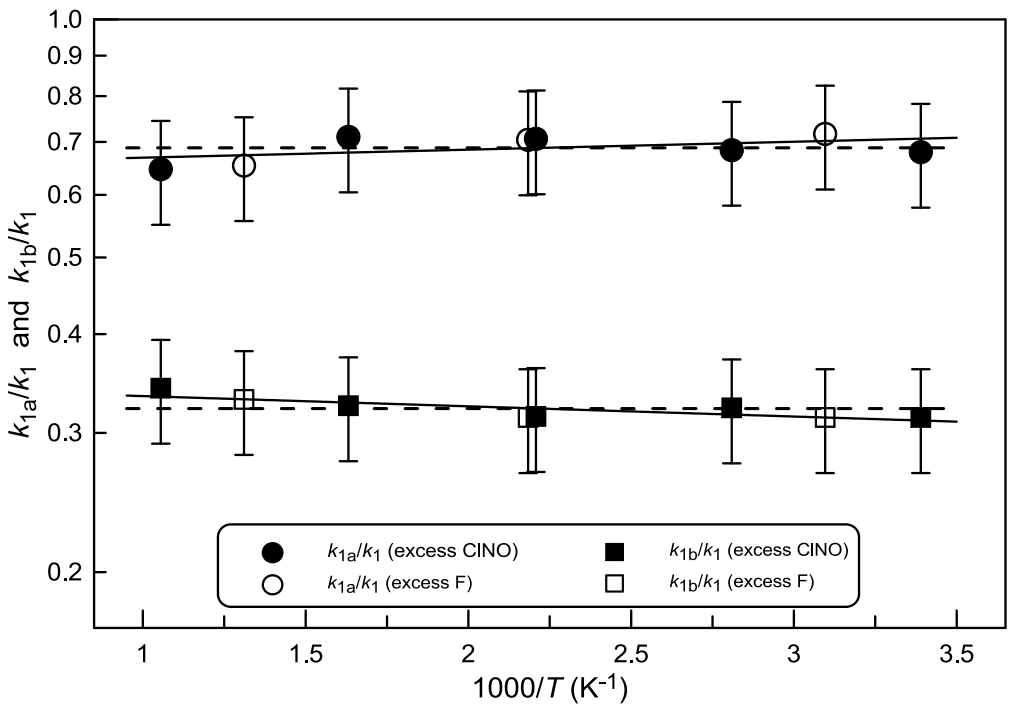

Figure 6. Reaction F + ClNO: branching ratios for two channels of reaction 1 as a function of temperature. The error bars represent estimated 15 % uncertainty of the measurements.

A slight trend of increase of k_{1b}/k_1 and decrease of k_{1a}/k_1 with increasing temperature is observed corresponding to the following Arrhenius expressions (solid lines in Figure 6):

$k_{1a}/k_1 = (0.653 \pm 0.048)\ \exp((23.2 \pm 32.6)/T)$

$k_{1b}/k_1 = (0.344 \pm 0.014)\ \exp(-(29.7 \pm 18.0)/T)$

with 2σ statistical uncertainties. On the other hand, the k_{1a}/k_1 and k_{1b}/k_1 ratios can be considered as independent of temperature between 295 and 948 K (dashed lines in Figure 6). Finally, from this study we recommend the independent of temperature values of

$k_{1a}/k_1 = 0.68 \pm 0.10$,

$k_{1b}/k_1 = 0.32 \pm 0.05$.

3.3. Rate Constant of Reaction 2. The rate constant of the reaction F + Br_2 was determined using three different approaches: monitoring the kinetics of F-atom or Br_2 consumption in excess of Br_2 or F, respectively, and with the relative rate method using the reaction of F-atom with Cl_2 as the reference one.

3.3.1. Kinetics of F-atom consumption in excess of Br_2. In experiments carried out in excess of Br_2, the initial concentration of F atoms was in the range (0.5-1.5) × 10^{11} molecule cm^{-3}, the concentrations of Br_2 are shown in Table 3.

Table 3. Reaction F + Br_2: Summary of the Absolute Measurements of the Rate Constant.

T (K)	number of kinetic runs	[excess reactant] [a] (10^{12} molecule cm^{-3})	k_2 [b] (10^{-10} cm^3 $molecule^{-1}$ s^{-1})
299	8	0.26-3.96	1.28
330	8	0.34-4.97	1.26
373	8	0.25-4.98	1.25
429	10	0.37-6.45	1.28
504	8	0.34-5.17	1.24
656	8	0.40-4.39	1.27
940	9	0.29-4.95	1.34

[a] excess reactant: fluorine atom at T = 330 and 429K, Br_2 at all other temperatures
[b] typical uncertainty on k_1 is 15%

F atoms were converted to FCl (in reactions with Cl_2 or ClNO, added at the end of the reactor 5 cm upstream of the sampling cone of the mass spectrometer) and detected at m/z = 54 (FCl^+). The flow velocity in the reactor was (2200-4440) cm s^{-1}. Examples of the exponential F-atom decays are shown in Figure S9. The consumption of Br_2 was negligible in most cases due to its sufficient excess over F atoms; however in a few kinetic runs it was observable (up to 15%). In this case, the mean values of [Br_2] over the reaction time of the F kinetics were used for the rate constant calculations. Figure 7 demonstrates the pseudo-first order rate constants, $k_2' = k_2[Br_2] + k_w$, measured as a function of concentration of Br_2 at T = 504 and 940K. All the measured values of k_2' were corrected for axial and radial diffusion[11] of fluorine atoms. Corrections were less than 8%. The slopes of the straight lines in Figure 7 give the values of k_2 at respective temperatures. All the results obtained for k_2 within the described approach at different temperatures are shown in Table 3.

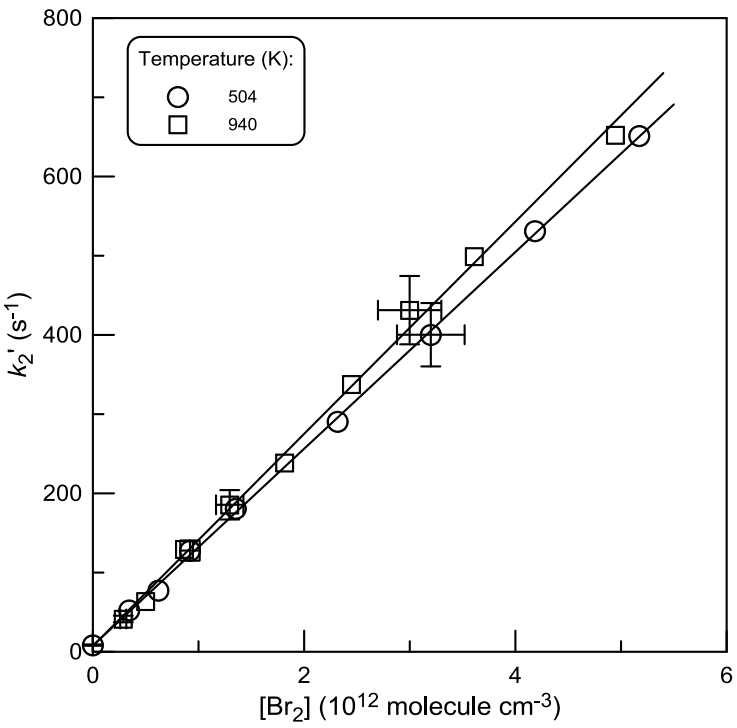

Figure 7. Reaction F + Br_2: example of pseudo-first order plots obtained from F-atom decay kinetics in excess of Br_2 (T = 504 and 940 K). Error bars demonstrate estimated 10% maximum uncertainty on the measurements of k_2' and [Br_2].

3.3.2. Kinetics of Br_2 consumption in excess of F-atoms. At two temperatures, 330 and 429K, the rate constant of reaction 2 was determined from the kinetics of Br_2 consumption in excess of F atoms. Experimental conditions in these experiments were as follows: $[Br_2]_0$ = (0.8-1.2) × 10^{11} molecule cm^{-3}, concentrations of F atoms are shown in Table 3, flow velocity in the reactor of (2700-3400) cm s^{-1}. Figure S10 shows temporal profiles of Br_2 observed with different excess concentrations of fluorine atoms at T = 429K. The concentration of F atoms was monitored simultaneously with the Br_2 decay kinetics. Consumption of the excess reactant, F-atom, was found to be always less than 20%, being insignificant in most of the experiments. Where necessary the mean concentration of F atoms along the reaction zone was used in calculations of k_2. The results of the measurements of $k_2' = k_2 \times [F]$ as a function of the concentration of fluorine atoms are shown in Figure 8. Corrections on axial and radial diffusion of Br_2[11] applied to k_2' and calculated with diffusion coefficient of Br_2 in He, D_0 = 276 × $(T/298)^{1.75}$ Torr cm^{-2} s^{-1} (estimated using Fuller's method)[12] were generally less than

10%. The slope of the linear through origin fit to the experimental data (solid and dashed lines in Figure 8) provides the values of k_2 at respective temperatures, which are shown in Table 3. The combined uncertainty on the measurements of k_2 was estimated to be of nearly 15 %, including statistical error and those on the measurements of the flows, pressure, temperature and the absolute concentrations of the relevant species.

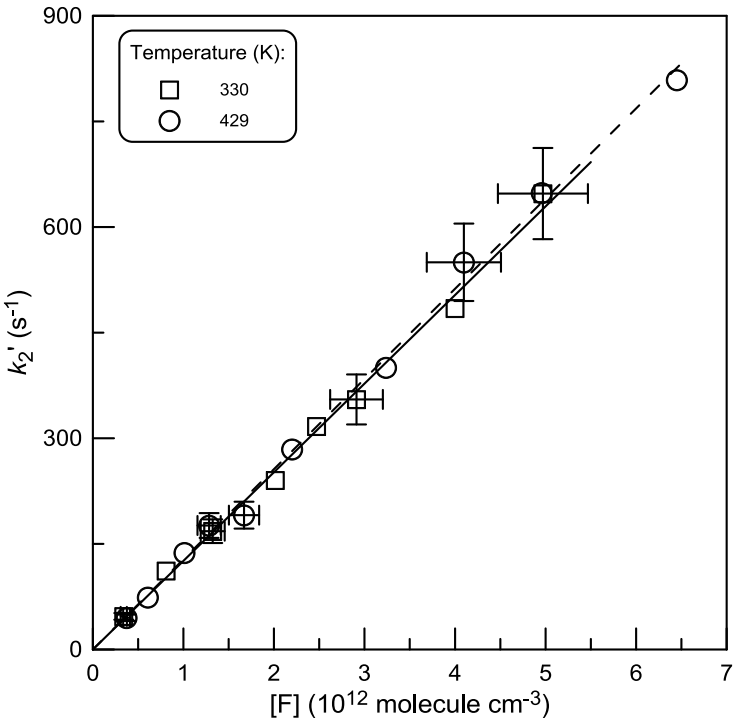

Figure 8. Reaction F + Br_2: example of pseudo-first order plots obtained from Br_2 decay kinetics in excess of F atoms. Solid and dashed lines represent linear through origin fit to the experimental data at T = 330 and 429 K, respectively. Error bars demonstrate estimated 10% uncertainty on the measurements of k_2' and [F].

3.3.3. Relative rate measurements. In these experiments the rate constant of reaction 2 was determined at T = 297 K using a relative rate method with reaction of F atoms with Cl_2 as a reference one:

$$F + Cl_2 \rightarrow FCl + Cl \qquad (3)$$

Fast titration of the initial concentration of F atoms, $[F]_0$, by a mixture of excess Cl_2 and Br_2 was performed, and the yields of FBr and FCl were measured as a function of the $[Br_2]/[Cl_2]$

ratio. The concentration of FBr formed is defined by the fraction of $[F]_0$ reacting with Br_2 in reaction 2:

$$[\mathrm{FBr}] = \frac{k_2[\mathrm{Br_2}]}{k_2[\mathrm{Br_2}]+k_3[\mathrm{Cl_2}]} \times [\mathrm{F}]_0$$

Rearrangement of this expression leads to:

$$\frac{[\mathrm{F}]_0}{[\mathrm{FBr}]} - 1 = \frac{k_3[\mathrm{Cl_2}]}{k_2[\mathrm{Br_2}]} \qquad \text{(I)}$$

Thus k_3/k_2 could be obtained by plotting ($[F]_0$/[FBr] - 1) as a function of the $[Cl_2]/[Br_2]$ ratio. It can be noted that this method did not need absolute calibration of the mass-spectrometric signals for F and FBr because the initial concentration of F atoms could be expressed as FBr signal in the absence of Cl_2 in the reactor, when F is titrated with an excess of Br_2. Thus, in the experiments, only the FBr signal was detected, first in Cl_2-free system, corresponding to $[F]_0$, and then in the Br_2 and Cl_2-containing system, corresponding to the fraction of $[F]_0$ reacted with Br_2. Initial concentration of F-atom in these experiments was $\approx 8 \times 10^{11}$ molecule cm^{-3}, concentration of Cl_2 was varied in the range $(0.26\text{-}5.63)\times10^{13}$ molecule cm^{-3}, concentration of Br_2 being nearly 1.2×10^{13} molecule cm^{-3} in all the experiments. The reaction time was around 0.015 s. The observed experimental data are shown in Figure 9. According to equation (I), the slope of the linear dependence in Figure 9 provides: k_3/k_2 ($\pm 2\sigma$) = 0.469 ± 0.013.

Similar procedure was applied for FCl formed in reaction 3. In this case the ratio of the rate constants, k_2/k_3, could be derived by plotting ($[F]_0$/[FCl] - 1) as a function of $[Br_2]/[Cl_2]$ according to the expression (II):

$$\frac{[\mathrm{F}]_0}{[\mathrm{FCl}]} - 1 = \frac{k_2[\mathrm{Br_2}]}{k_3[\mathrm{Cl_2}]} \qquad \text{(II)}$$

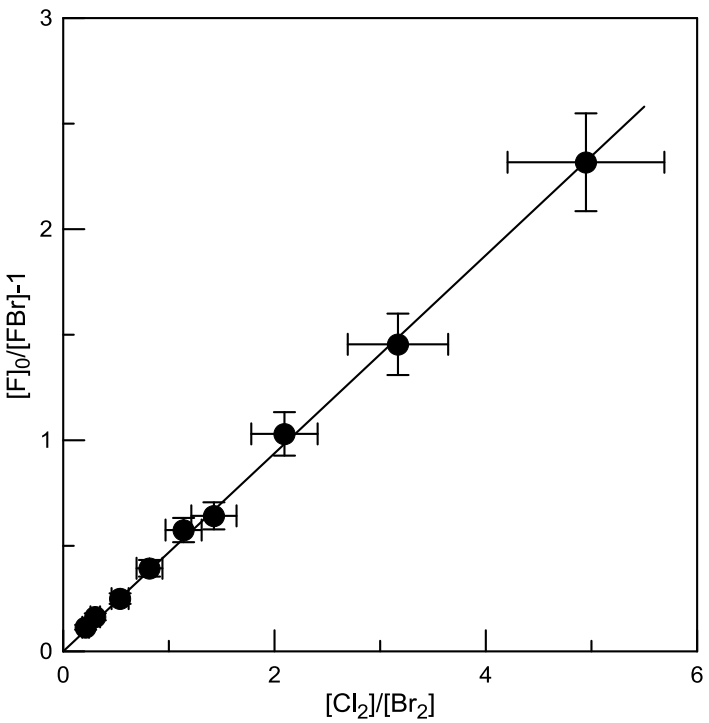

Figure 9. FBr yield from F-atom titration with Br_2 + Cl_2 mixtures at T = 297 K.

The experimental data obtained with monitoring of FCl and shown in Figure S11 (Supporting Information) provide, in accordance with equation (II), k_2/k_3 (± 2σ) = 2.10 ± 0.04, in excellent agreement with the results obtained by monitoring FBr. Using mean value of k_2/k_3 from two measurements and k_3 (297K) = (6.07 ± 1.10)×10^{-11} $cm^3molecule^{-1}s^{-1}$ (ref. 5), the value of k_2 (297K) = (1.28 ± 0.25)×10^{-11} $cm^3molecule^{-1}s^{-1}$ can be derived. This value is in good agreement with the absolute measurement of k_2 at room temperature (Table 3).

3.3.4. Temperature dependence of k_2. All the results obtained for k_2 are shown in Table 3 and Figure 10. One can note very good agreement between the results of the absolute, either in excess of Br_2 or F atoms, and relative measurements of k_2. The solid line in Figure 10 represents an unweighted exponential fit to all the data obtained in the present study and yields the following Arrhenius expression:

$k_2 = (1.31 \pm 0.07) \times 10^{-11} \exp(-(11.4 \pm 20.6)/T)$ cm^3 $molecule^{-1}$ s^{-1},

where the cited uncertainties are 2σ statistical ones. However, considering the extremely weak dependence of k_2 on temperature, the temperature independent value of

$k_2 = (1.28 \pm 0.20) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1},

is recommended from the present study for the rate constant of reaction 2 in the temperature range (299-940) K (dashed line in Figure 10).

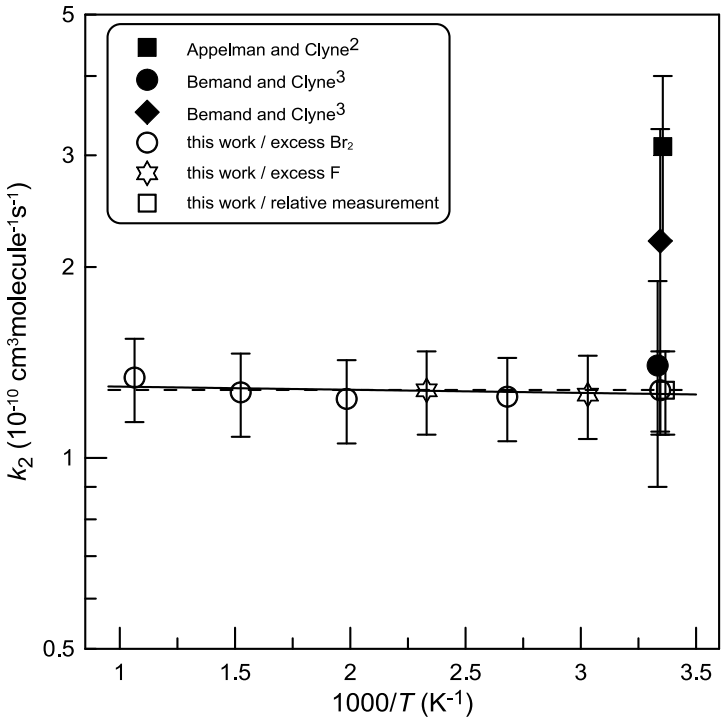

Figure 10. Reaction F + Br_2: summary of the experimental data for the reaction rate constant.

3.4. Comparison with previous data. Previously, reaction of fluorine atoms with Br_2 has been studied by Appelman and Clyne[2] in a discharge flow apparatus with mass spectrometric detection of the species. The reaction rate constant was determined from the kinetics of Br_2 consumption recorded in excess of F atoms: $k_2 = (3.1\pm0.9)\times10^{-10}$ cm^{3}molecule^{-1}s^{-1} at T = 298K and 1 Torr total pressure of helium. This value is significantly higher than that measured in the present work (see Figure 10). However, it should be emphasized that the authors noted that "no claim is made for high precision" of the reported results.[2] In another study from the same group, Bemand and Clyne[3] have used detection of F-atoms by resonance fluorescence to measure the rate of their reaction with molecular bromine and reported $k_2 = (1.4\pm0.5)\times10^{-10}$ cm^{3}molecule^{-1}s^{-1} at T = 300K. This value is in excellent agreement with that

measured in the present study at room temperature, although Bemand and Clyne[3] combining this value with previous mass spectrometric determination of k_2,[2] recommended the mean value from two studies $k_2 = (2.2\pm1.1)\times10^{-10}$ $cm^3molecule^{-1}s^{-1}$ at T = 298-300K. Temperature dependence of k_2, to our knowledge, has never been studied previously.

Rate constant of reaction 1 has been measured in only one study by Abbatt et al.[8] The measurements were realized in a discharge flow reactor at T = 228-353K and total pressure of 1.5-2 Torr using as a detection technique for F atoms their chemical conversion to D atoms in reaction F + D_2 with subsequent detection of D by resonance fluorescence. The results obtained for k_1 by Abbatt et al.[8] are shown in Figure 3 in line with those from the present study. Abbatt et al.[8] recommended the following Arrhenius expression for k_1, $(1.4\pm0.4) \times 10^{-10}$ exp $(28 \pm 84)/T)$ cm^3 $molecule^{-1}$ s^{-1} (dotted line in Figure 3), which is in good agreement with the present data. Finally, considering an excellent agreement between the results of two studies, we recommend a temperature independent value for the rate constant of reaction 1 (solid red line in Figure 3, mean of all the measurements from two studies) with 10% uncertainty (dashed red lines in Figure 3) and in an extended temperature range, T = 228-950K:

$k_1 = (1.29 \pm 0.13) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}

To our knowledge, the present study is the first one, analyzing the products of reaction (1). In only previous study of the reaction the channel (1b) was considered as negligible by analogy with reactions of ClNO with Cl, Br, O and N atoms.[8] Present results seem to clearly show that although Cl abstraction from ClNO by F-atom is the main channel of reaction 1 ($k_{1a}/k_1 = 0.68 \pm 0.10$), the second reaction pathway, leading to replacement of Cl-atom in ClNO with F-atom, is quite significant ($k_{1b}/k_1 = 0.32 \pm 0.05$) in the whole temperature range of the study (T = 295-948 K). Theoretical high level calculations would be very useful to better

understand the dynamics of this reaction leading to the observed distribution of the reaction products.

CONCLUSIONS

In this work, we investigated the kinetics and products of the reactions of F atoms with ClNO and Br_2 using a low pressure flow reactor coupled to an electron impact ionization mass spectrometer. Rate constant of the reaction F + Br_2 was determined, using both absolute and relative rate methods, as a function of temperature at T = (299 - 940) K: k = (1.28 ± 0.20) × 10^{-10} cm^3 $molecule^{-1}$ s^{-1}. The rate constant of F + ClNO reaction determined in the temperature range (299 – 950) K was found to be in excellent agreement with previous low temperature measurements, which allowed to recommend independent of temperature value of k_1 = (1.29 ± 0.13)×10^{-10} $cm^3 molecule^{-1} s^{-1}$ in an extended temperature range 228 – 950 K. Two major reaction pathways of the reaction F + ClNO, Cl-atom abstraction and Cl-atom replacement in ClNO with F-atom, were identified and the corresponding branching ratios were measured to be 0.68 ± 0.10 and 0.32 ± 0.05, respectively, independent of temperature between 295 and 948 K. Theoretical high level calculations would be very useful to better understand the dynamics of this reaction leading to the observed distribution of the reaction products.

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Supporting Information. Diagram of the flow reactor (Figure S1); pseudo-first order plots obtained from F-atom decay kinetics in excess of ClNO at T = 454, 613 and 950K (Figures S2-S4); concentrations of Cl and FCl formed in reaction F+ClNO as a function of the

consumed concentration of F at T = 295, 356 and 948K (Figures S5-S7); concentrations of Cl and FCl formed in reaction F+ClNO as a function of the consumed concentration of ClNO at T = 763 K (Figure S8); examples of F-atom (T = 504K) and Br_2 (T = 429K) consumption kinetics in reaction F+Br_2 (Figures S9 and S10, respectively); FCl yield from F-atom titration with Br_2 + Cl_2 mixtures at T = 297 K (Figure S11).

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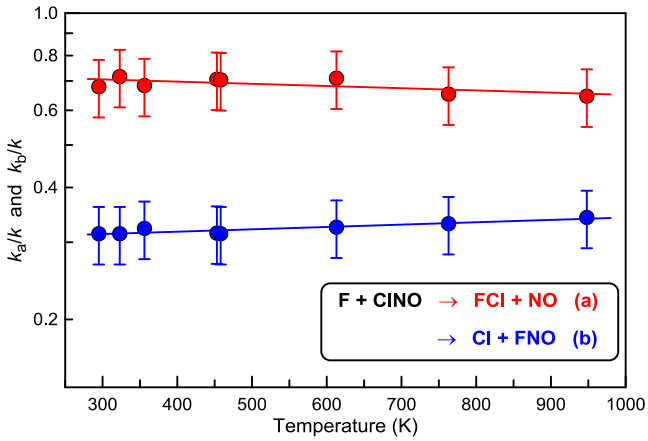
TOC Graphic


1.0
0.8
0.6
0.4
0.2
k_a/k and k_b/k
300
400
500
600
700
800
900
1000
Temperature (K)
F + ClNO → FCl + NO (a)
→ Cl + FNO (b)