

27 August 1999

Chemical Physics Letters 310 (1999) 111-120



www.elsevier.nl/locate/cplett

Temperature dependence of the $Cl + HN_3$ reaction from 300 to 480 K

Gerald C. Manke II *, Thomas L. Henshaw, Timothy J. Madden, Gordon D. Hager

Air Force Research Laboratory, AFRL / DELC, 3550 Aberdeen Avenue SE, Kirtland AFB, NM 87117-5776, USA

Received 10 May 1999; in final form 28 June 1999

Abstract

The rate constant for Cl + HN₃ over the temperature range 300–480 K has been studied in a flow reactor. Based on the rate of loss of HN₃ and the rate of NCl(a¹ Δ) generation, the temperature dependence of this reaction is described by the collision theory expression $1.2 \pm 0.3 \times 10^{-11} T^{0.5} \exp(-1514 \pm 93/T)$, with $E_0 = 3.0 \pm 0.2 \text{ kcal mol}^{-1}$ or an Arrhenius fit $k(T) = 2.0 \pm 1.0 \times 10^{-10} \exp(-1452 \pm 150/T)$ with $E_a = 2.9 \pm 0.2 \text{ kcal mol}^{-1}$. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The recent report of a direct measurement of gain [1] on the $I({}^2P_{1/2} - {}^2P_{3/2})$ transition in the $NCl(a^{1}\Delta)/I$ chemical system has increased interest in the use of metastable nitrene halides (NX) as energy donors for iodine-based chemical lasers analogous to the chemical oxygen iodine laser (COIL) [2,3]. There are several important advantages and disadvantages to the use of these molecules, which are isovalent with O_2 . The most obvious advantage is generation of the $(a^{T}\Delta)$ states in the gas phase [4-10] rather than the mixed gas/aqueous chemistry that is necessary for COIL operation. On the other hand, the NX($a^{1}\Delta$) molecules are much more reactive than $O_2(a^{1}\Delta)$ [11–13], and the scaling issues for generating high concentrations of NCl($a^{1}\Delta$) have not yet been resolved. The Cl/HN₃ chemical system

used for the generation of NCl($a^{1}\Delta$) is summarized by reactions (1) and (2):

$$Cl + HN_3 \rightarrow HCl + N_3 \tag{1}$$

$$\operatorname{Cl} + \operatorname{N}_{3} \rightarrow \operatorname{NCl}(a^{1}\Delta, b^{1}\Sigma^{+}, X^{3}\Sigma^{-}) + \operatorname{N}_{2}$$
 (2)

The ΔH_0^0 value for reaction (1) is -9.3 kcal mol⁻¹, and the enthalpy for reaction (2) is -39, -22, and -65 kcal mol⁻¹ for generation of the (a¹ Δ), (b¹ Σ ⁺), and (X³ Σ ⁻) states, respectively, using ΔH_f^0 (NCl) = 77.4 kcal mol⁻¹ [14]. The rate determining step for this process is reaction (1), which has a room temperature rate coefficient [15] of $1.1 \pm 0.3 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. Gain on the I(²P_{3/2})–I*(²P_{1/2}) transition was achieved when a small flow of HI is added to a flow of NCl(a¹ Δ):

$$Cl + HI \rightarrow HCl + I(^2P_{3/2})$$
 (3)

$$\operatorname{NCl}(a^{1}\Delta) + I({}^{2}P_{3/2}) \to \operatorname{NCl}(X^{3}\Sigma^{-}) + I^{*}({}^{2}P_{1/2})$$
(4)

^{*} Corresponding author. Fax: +1-505-846-4807; e-mail: mankeg@plk.af.mil

^{0009-2614/99/\$ -} see front matter @ 1999 Elsevier Science B.V. All rights reserved. PII: \$0009-2614(99)00726-5

To date, only reaction (4) has been characterized at a temperature other than 300 K [16], and $k_{4}(T) = 1.1$ $\times 10^{-10} \exp(-519 + 143 \ K/T) \ cm^3 \ molecule^{-1} \ s^{-1}$. Due to the exothermicity of (1)–(3) and the mechanism used to generate Cl, the temperature dependence of reaction (1) is one of the most critical parameters in the development of the NCl($a^{1}\Delta$)/ $I({}^{2}P_{3/2})$ chemical system as a chemical laser source.

We have used two techniques to measure k(T) for $Cl + HN_3$ in a flow reactor. The first simply monitors the intensity of NCl($a^{1}\Delta$) at 1077 nm as a function of reaction time Δt for known [Cl]_o and [HN₃]₀ and at a variety of temperatures. A simple kinetic model and a least-squares fitting routine was used to extract k_1 . Table 1 summarizes the F/Cl/HN₃ kinetic model. The second method monitored [HN₃] by adding N₂(A³ Σ_{μ}^{+}) and observing the $NH(A^{3}\Pi)$ emission as a function of reaction time and temperature. The reaction $N_2(A^3\Sigma_{\mu}^+) + HN_3$

$$N_{2}(A^{3}\Sigma_{u}^{+}) + HN_{3} \rightarrow NH(X^{3}\Sigma^{-}) + 2N_{2}(X^{1}\Sigma_{g}^{+})$$
(5a)
$$\rightarrow NH(A^{3}\Pi) + 2N_{2}(X^{1}\Sigma_{g}^{+})$$
(5b)

has a rate constant [17,18] of $7.3 \pm 0.2 \times 10^{-11}$ cm^3 molecule⁻¹ s⁻¹ at room temperature, and the radiative lifetime of NH($A^{3}\Pi$) is 0.4 µs [19]. Even though the branching [17] to NH(A³ Π) is only 0.025 this combination permits (5) to be a convenient monitor of the relative concentration of HN₃. Under

Table 1

Rate	coefficients	for	F	/C1/	/HN ₃	reaction	system
------	--------------	-----	---	------	------------------	----------	--------

pseudo-first-order conditions, the slopes of ln Intensity (NH(A³ Π)) versus Δt plots are equal to $-k_1$ [Cl]. Under non-pseudo-first-order conditions or in the presence of a modest [F], the plots are analyzed by a simulation process to get k_1 .

2. Experimental methods

The high temperature flow reactor (HTFR) used for this experiment has been described in detail previously [13]. A few minor modifications to the HTFR have been made for this work. First, an indicator inlet was installed 5 cm upstream of the observation zone to allow the addition of $N_2(A^3\Sigma_n^+)$ or H₂S. Also, the quartz rods were removed and glass windows were installed. Time resolution was achieved by fixed point observation and addition of reagents through one of two sliding injectors. For this work, the inner injector was used to add HN₃ and could extend from the observation zone ($\Delta t = 0$) to 36 cm upstream. Chlorine atoms were generated in the 150 cm long pre-reactor via reaction (6) [20]. $F + HCI \rightarrow HF + CI$ (6)

In nearly all cases, excess HCl was added, and reaction (6) goes to completion, giving $[Cl]_0 = [F]_0$ before HN₃ was added. The initial F atom concentrations, [F]₀, were determined by chemiluminescent titration. A small flow of H₂S (Matheson, CP grade) was added through the indicator inlet and the HF $(\Delta v = -3)$ emission at 875 nm monitored as a function of added Cl_2 (3% in He, Matheson) or CF_3I

Rate coefficients for F/CI/HN ₃ feaction system					
Reaction	k, model input (cm ³ molecule ⁻¹ s ⁻¹)	Ref.			
$F + HN_3 \rightarrow HF + N_3$	$1.1 \pm 0.2 \times 10^{-10}$	[5]			
$F + N_3 \rightarrow NF(a^1\Delta, b^1\Sigma^+, X^3\Sigma^-) + N_2(X^1\Sigma_g)$	$5 \pm 2 \times 10^{-11}$	[4,5,10]			
$Cl + N_3 \rightarrow NCl(a^{1}\Delta) + N_2(X^{1}\Sigma_g^{1})$	$1.5 \pm 0.6 \times 10^{-11}$	[8,10,13]			
$Cl + N_3 \rightarrow NCl(b^1\Sigma^+, X^3\Sigma^-) + N_2(X^1\Sigma_g^1)$	$\approx 1.5 \pm 0.6 \times 10^{-11}$	[8,10,13]			
$N_2(A^3 \tilde{\Sigma}^+_u) + HN_3 \rightarrow NH(A^3 \Pi) + 2N_2(X^1 \tilde{\Sigma}^1_g)$	$7.3 \pm 0.2 \times 10^{-11}$	[17,18]			
$N_2(A^3\Sigma_u^+) + HCl \rightarrow N_2(X^1\Sigma_g^1) + H + Cl$	1.3×10^{-12}	[20]			
$NCl(a^{1}\Delta) + NCl(a^{1}\Delta) \rightarrow products$	$7.2 \pm 0.9 \times 10^{-12}$	[13]			
$NCl(a^{1}\Delta) + F \rightarrow F + NCl(X^{3}\Sigma^{-})$	$2.2 \pm 0.7 \times 10^{-11}$	[8]			
$NCl(a^{1}\Delta) + Cl \rightarrow Cl + NCl(X^{3}\Sigma^{-})$	$1.0^{+1.0}_{-0.5} \times 10^{-12}$	[8]			
$NCl(a^{1}\Delta) + HCl \rightarrow products$	$1.5 \pm 0.4 \times 10^{-14}$	[12]			
$F + HCl \rightarrow HF + Cl$	1.2×10^{-11}	[18]			

(Lancaster, 97%). The smoothly extrapolated, zerointensity intercept from plots of I(HF) versus [titrant] gives $[F]_0$.

The mechanical pump/blower combination produced linear flow velocities of $3400-1150 \text{ m s}^{-1}$ at 0.5-1.5 torr when throttled with a gate valve. Absolute capacitance manometers (Baratron, model 622), measured the reactor pressure, and all species except HCl were metered with calibrated MKS mass flow meters (Model 1179A). Several freeze pump-thawcycles were performed while preparing 20–30% mixtures of HCl (Scott Specialty Gas, 99.999%), and



Fig. 1. Upper panel: A representative spectrum from the $F/Cl/HN_3$ reaction system after a reaction time of 0.013 s. The $HF(\Delta v = -3)$ emission was insignificant 0.025 s downstream of the HN_3 inlet. The experimental conditions were $[F] = 4.4 \times 10^{12}$, $[Cl] = 3.8 \times 10^{12}$, and $[HN_3] = 1.0 \times 10^{13}$ cm⁻³. The intense NF(b¹ Σ^+) and NCl(b¹ Σ^+) emissions, not shown, were observed at 530 and 665 nm, respectively. Lower panel: The emission intensity of NH(A³II) is plotted as a function of $[HN_3]$. The intensity at 335 nm (see inset spectrum) is linear over a wide range of initial $[HN_3]$ and is easily observable for $[HN_3] = 1.0 \times 10^{11}$ molecule cm⁻³.



Fig. 2. Pseudo-first-order plots of $\ln I/I_0(NH(A^3\Pi))$ versus reaction time. The experimental conditions and results are as follows: (300 K) [CI] = 1.2×10^{13} , [HN₃] = 2.0×10^{12} cm⁻³, $k = 1.4 \pm 0.1 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹; (373 K) [CI] = 8.0×10^{12} , [HN₃] = 3.0×10^{12} cm⁻³, $k = 4.5 \pm 0.3 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹; (413 K) [CI] = 6.0×10^{12} , [HN₃] = 2.8×10^{12} cm⁻³, $k = 6.5 \pm 0.4 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹; (458 K) [CI] = 6.0×10^{12} , [HN₃] = 1.7×10^{12} cm⁻³, $k = 8.5 \pm 0.3 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹.

 CF_3I in 12 L bulbs. The flow rate of HCl was determined by diverting the stream to a vessel of known volume and measuring the rate of pressure rise. The bulk of the flow (typically 2.5 SLPM, 1850 μ m s⁻¹) consisted of Ar (Airgas, UHP grade). Two microwave discharges on a CF_4 (Airgas, 99.5%)/Ar mixture produced up to 1.5×10^{13} cm⁻³ F atoms at 1.5 torr. Pre-prepared mixtures of HN₃ and He were

stored in a stainless steel vessel. HN_3 was added to the reactor via one of two sliding Pyrex injectors.

The entire reactor was encased by resistive heating units, which consisted of Nichrome wire helically wound inside a ceramic jacket. The temperature was measured by inserting several type K thermocouples into the gas stream at various points along the reactor. A flexible thermocouple was inserted

Т	k(T)	Т	k(T)
(K)	$(\times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	(K)	$(\times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$
300	1.3 ± 0.4	388	5.3 ± 1.5
333	2.0 ± 0.2	413	6.5 ± 1.5
348	2.2 ± 0.5	438	7.2 ± 1.9
368	3.4 ± 0.9	458	7.5 ± 0.7
373	4.4 ± 0.5	463	11 ± 1
378	4.5 ± 1.5	468	10 ± 4

Table 2 Summary of the k(T) measurements via loss of HN₃

into the one of the movable injectors to provide a temperature measurement at the center of the tube. The heaters were regulated with Omega controllers (Model CN76000) with an accuracy of $\pm 1^{\circ}$ at room temperature and $\pm 7^{\circ}$ at 480 K. All inner surfaces were coated with PTFE, which limited the temperature to 500 K.

A 0.3 m monochromator (Instruments S.A.) dispersed the chemiluminescence collected by a short focal length lens. Two different gratings (500 or 900 nm blaze, both with 1200 grooves mm⁻¹) were used, depending on the emission of interest. The emissions of HF ($\Delta v = -3$), NF(a¹ Δ), NCl(a¹ Δ), NF(b¹ Σ ⁺), and NCl(b¹ Σ ⁺) were monitored with a cooled



Fig. 3. Non-pseudo-first-order plots of $I(NH(A^3\Pi)$ versus reaction time. A least-squares fitting routine was used to extract k_1 from the data. The experimental conditions are as follows. Upper panel: T = 300 K, $[CI] = 1.1 \times 10^{13}$, $[F] = 2.0 \times 10^{12}$, $[HN_3] = 2.0 \times 10^{12}$ cm⁻³. Lower panel: T = 388 K, $[CI] = 6.5 \times 10^{12}$; $[F] = 1.5 \times 10^{12}$; $[HN_3] = 1.5 \times 10^{12}$ cm⁻³. Note that the data can be satisfactorily fit by several values for k_1 , and the relative error for this method is large.

 (-80°C) R1767 PMT (Hamamatsu) while the UV emission from NH(A³II) was detected with a R374 PMT (Hamamatsu) cooled to -50°C . When necessary, band pass or long pass filters were used to isolate signals of interest from unwanted background or second-order emissions. A representative spectrum (uncorrected for the relative response of the S-1 PMT) from the reaction of F and Cl atoms with HN_3 is shown in the upper panel of Fig. 1.

The relative concentration of HN_3 was monitored by adding $N_2(A^3\Sigma_u^+)$ via the indicator inlet and monitoring the resultant NH($A^3\Pi$) signal at 335 nm. The $N_2(A^3\Sigma_u^+)$ molecules were generated by energy transfer from metastable $Ar({}^3P_2, {}^3P_0)$ atoms using a



Fig. 4. Measurement of k_1 via generation of NCl(a¹ Δ). A least-squares model fit to [NCl(a¹ Δ)] versus Δt was used to determine $k(\text{Cl} + \text{HN}_3)$. The experimental conditions are as follows. Upper panel: T = 300 K, [Cl] = 1.8×10^{13} , [HN₃] = 2.0×10^{13} cm⁻³. Lower panel: T = 433 K, [Cl] = 8.0×10^{12} , [HN₃] = 1.4×10^{13} cm⁻³. Note that a wide range of values for k_1 can satisfactorily fit the data, and the relative error for this method is large ($\pm 30\%$).

rolled tantalum foil discharge design [21]. The NH(A³ Π) emission intensity increased linearly with the HN₃ flow rate (see the lower panel of Fig. 1). With optimization of the light collection and N₂(A³ Σ_{u}^{+}) generator, [HN₃] as low as 1×10^{11} molecule cm⁻³ could be routinely detected even though the branching ratio to (5b) is low.

3. Results and discussion

3.1. Monitoring the loss of $[HN_3]$

Under pseudo-first-order conditions ([Cl] \gg [HN₂]) the slope of a given $\ln(I(NH(A^3\Pi)))$ versus Δt plot is equal to k_1 [Cl], and the rate constant is given by simply dividing by the known [Cl]. Measurable decomposition of HN₃ does not occur below 560 K and reactive loss should be the only removal process [22]. Fig. 2 shows several such measurements taken at a variety of temperatures. In each case, the initial [Cl]₀ was determined by first measuring $[F]_0$ and then adding a slight excess of HCl. The intensity decreased with time, and a regression fit to the data gives the product k_1 [Cl]. At room temperature, the data is within the combined error bars of the established value for k_1 , $1.1 \pm 0.3 \times 10^{-12}$ cm^3 molecule⁻¹ s⁻¹. Several measurements were performed at each temperature and Table 2 lists the average and 2 standard deviations at each temperature. The value of k_1 increases up to $1.1 \pm 0.1 \times$ 10^{-11} cm³ molecule⁻¹ s⁻¹ for T = 460 K.

Because HCl quenches N₂(A³ Σ_{u}^{+}) ($k_{0} = 1.3 \times$ 10^{-12} cm³ molecule⁻¹ s⁻¹) [23], it was not always possible to add excess HCl and a few measurements of k_1 were performed with a mix of F and Cl atoms present with HN₃. A known flow of HCl is added to a measured $[F]_0$ and [F]'' and [Cl]' calculated from the bimolecular rate law. The temporal dependence of [HN₃], as monitored by $I(NH(A^{3}\Pi))$, is fit by the kinetic model listed in Table 1. In cases such as these, accurate measurement of k_1 requires [Cl] \gg [F], and $[F] \leq [HN_3]_0$. Otherwise, F removes nearly all of the HN₃ and it becomes impossible to accurately extract k_1 [5]. Several examples are shown in Fig. 3. In each case, the least-squares analysis produces a satisfactory fit to the data. This method, however, is inherently less sensitive than the method

described above and the error bars for k_1 are significantly larger. Table 2 summarizes the k(T) data for reaction (1) based on the loss of [HN₃].

3.2. Generation of NCl($a^{l}\Delta$)

The rate determining step for the generation of NCl($a^{1}\Delta$) is reaction (1). For nearly any set of conditions where no [F] is present, the rate of NCl($a^{1}\Delta$) growth is dependent upon k_{1} . Fig. 4 shows several examples of the growth of NCl($a^{1}\Delta$) versus Δt at a variety of temperatures. In each case the linear least-squares fit to the data is indicated by the solid line, while alternate values for k_1 are shown by broken lines. As expected, the established value for k_1 is reproduced at room temperature. However, the precision of this method is quite poor. As the plot shows, several values, up to $\pm 30\%$, also give reasonable fits to the data. This method is also susceptible to error in other ways. For example, as k_1 increases the value of $k_2(T)$ (which was fixed to the room temperature value) becomes more important because N₃ and HN₃ compete for reaction with [Cl]. Most importantly, it is difficult to generate observable $I(NCl(a^{1}\Delta))$ without high $[Cl]_{0}$ and $[HN_{3}]_{0}$, which may cause additional problems with quenching. Although this method is less satisfactory for the determination of k_1 , the results agree quite well with those obtained by monitoring $I(NH(A^3\Pi))$ (see Table 3).

All of the k(T) data for reaction (1) are summarized in Tables 2 and 3 and in Fig. 5. A least-squares

Table 3 Summary of the k(T) measurements via generation of NCl($a^{1}\Delta$)

$\frac{J}{T}$	k(T)	
(K)	$(\times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	
300	0.89 ± 0.27	
338	2.6 ± 0.8	
368	3.4 ± 1.0	
383	4.8 ± 1.4	
388	5.8 ± 1.7	
403	7.7 ± 2.3	
433	8.4 ± 2.5	
448	9.3 ± 2.8	
468	11 ± 3	



Fig. 5. Arrhenius and collision theory fits to the $k_1(T)$ data. Upper panel: The $k_1(T)$ data is fit by the Arrhenius expression. The best fit is achieved for $A = 2.0 \times 10^{-10}$ and $E_a = 2.9 \text{ kcal mol}^{-1}$. Lower panel: A collision theory expression is used and $A = 1.2 \times 10^{-11}$ and $E_0 = 3.0 \text{ kcal mol}^{-1}$. In both panels data from both the loss of HN₃ and generation of NCl($a^{1}\Delta$) techniques are shown.

analysis of the data using the collision theory expression, $AT^{0.5} \exp(-E_0/RT)$, results in a satisfactory fit with $A = 1.2 \pm 0.5 \times 10^{-11}$ and $E_0 = 3.0 \pm 0.3$ kcal mol⁻¹. The Arrhenius expression was also used to fit the data: $k(T) = 2.0 \pm 1.0 \times 10^{-10} \exp(-1452 \pm 150/T)$ with $E_a = 2.9 \pm 0.3$ kcal mol⁻¹. The data in Fig. 5 also includes an estimate for k_1 calculated from the data reported in Ref. [1], and excellent agreement is achieved.

4. Discussion

While several azide/atom (F, Cl, and H) reactions have been characterized at room temperature, (7b)

there have been few measurements for T > 300 K. For example, reaction (7)

$$2F + HN_3 \rightarrow HF + N_3 \rightarrow HF + NF(a^{1}\Delta) + N_2$$
(7a)
$$\rightarrow HNF + N_2 \rightarrow HF + NF(a^{1}\Delta) + N_2$$

is known to be an efficient source of the N₃ and NF(a¹ Δ) radicals. The room temperature rate constant [5] for (7a) is established as $1.1 \pm 0.2 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ and the nascent HF vibrational distribution from reaction (7a) is 0.36:0.36:0.22:0.06 for v = 1-4. Microscopic branching between direct abstraction and addition–elimination channels may account for the rather flat vibrational distribution. The branching to HNF (7b) has been established [24] as $0.03^{+0.02}_{-0.001}$. The rate coefficient for the reaction of H atoms with HN₃ has been measured [25] from 300 to 460 K and $k(T) = 2.5 \times 10^{-11} \exp(-2315/T)$ cm³ molecule⁻¹ s⁻¹. The reaction produces NH₂(²A₁, $\nu_2 \leq 20$) [26] and minor amounts of NH(A³\Pi) and NH(b¹ Σ).

$$H + HN_3 \rightarrow NH_2 + N_2 \tag{8a}$$

The mechanisms for NH($A^{3}\Pi$) and NH($b^{1}\Sigma$) production are not well established, but they are presumed to be generated by secondary reactions such as [26]:

$$H + HN_3 \rightarrow N_3 + H_2 \tag{8b}$$

$$H + N_3 \rightarrow NH(b^{1}\Sigma) + N_2 \tag{9}$$

$$2 \operatorname{NH}^*(b^1 \Sigma \vee a^1 \Delta) \to \operatorname{NH}(A^3 \Pi)$$
(10)

Prior to this report, the only halogen/azide reaction that had been characterized T > 300 K was Cl + ClN₃:

$$Cl + ClN_3 \rightarrow N_3 + Cl_2 \tag{11}$$

Combourieu et al. used mass spectrometric detection to measure the temperature-dependent rate constant between 300 and 657 K [27]. They reported a moderate temperature dependence of $k(T) = 2.3 \times 10^{-11} \exp(-554/T) \text{ cm}^3$ molecule⁻¹ s⁻¹.

The present results indicate a moderate temperature dependence for the reaction of $\text{Cl} + \text{HN}_3$, with $E_a \approx 3 \text{ kcal mol}^{-1}$. The pre-exponential factor is large and requires some comment. Hydrogen atom abstraction reactions such as F + HCl ($k = 4.4 + 1.5 \times$ $0^{-11} \exp(-400 \pm 100/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ 28] and Cl + HBr $(k = 4.8 \times 10^{-11} \exp(-454/T))$ cm^3 molecule⁻¹ s⁻¹) [29] have A factors which are $\sim 2-3$ smaller than the present result. Halogen atom addition reactions, on the other hand, typically have much larger pre-exponential factors. For example, a relevant comparison may be made with the fast reaction F + HN₃, A $\ge k_{300} = 1.1 \pm 0.2 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹. Chlorine atoms are known to add to olefins (e.g., C₂H₄ [30], C₂H₃Br [31], and C₂H₃Cl [32]) and these reactions are very fast at room temperature, $k(300) = 1.5 + 0.4 \times 10^{-10}$ cm^3 molecule⁻¹ s⁻¹. The Cl + olefin reactions also have very small activation energies, probably on the order of a few hundred cal mol^{-1} . For example, assuming $E_a = 0.3$ kcal mol⁻¹, and using $k_{298}(\tilde{Cl} +$ $C_2H_3Br) = 1.43 \pm 0.29 \times 10^{-10}$ cm³ molecule⁻¹ s^{-1} , the A factor is 2.4×10^{-10} cm³ molecule⁻¹ s⁻¹. Clearly, the large pre-exponential factor for $Cl + HN_3$ is consistent (i.e., within a factor of 2-3) with other Cl atom reactions and is suggestive of a Cl atom addition reaction rather than hydrogen abstraction.

The main products for reaction (1) are assumed to be HCl and N₃ even though vibrationally excited HCl has not been observed (only HCl(v = 1) is energetically possible) and the generation of HNCl cannot be ruled out. Independent confirmation of this could be accomplished in one of several ways: laser-induced fluorescence detection of N₃ or infrared absorption of HCl(v = 0, 1) generated by reaction (1) are the most easily implemented. Virtually nothing is known about the species HNCl. If one assumes that Cl + HNCl is sufficiently exothermic to give NCl(a¹ Δ), by analogy to the F + HN₃ system, both N₃ and HNCl should react rapidly with Cl atoms to give NCl(a¹ Δ).

5. Conclusions

The temperature dependence of the reaction Cl + HN_3 has been measured in a heated flow reactor. The rate coefficient was measured by monitoring the loss of HN_3 and the rate of generation of NCl(a $^{1}\Delta$) versus time for known starting concentrations. The

rate constant data was fit by an Arrhenius expression of $k(T) = 2.0 \pm 1.0 \times 10^{-10} \exp(-1452 \pm 150/T)$ with $E_a = 2.9 \pm 0.3$ kcal mol⁻¹. A collision theory fit to the data gave the expression $1.2 \pm 0.5 \times 10^{-11} T^{0.5} \exp(-1514 \pm 150/T)$, with $E_0 = 3.0 \pm 0.3$ kcal mol⁻¹.

Acknowledgements

The US Air Force Office of Scientific Research supported this work. G.C.M. also wishes to acknowledge the National Research Council for support. The authors are grateful for helpful discussions with Prof. R.D. Coombe, Prof. M.C. Heaven, and Prof. D.W. Setser.

References

- J.M. Herbelin, T.L. Henshaw, B.D. Rafferty, B.T. Anderson, R.F. Tate, T.J. Madden, G.C. Manke II, G.D. Hager, Chem. Phys. Lett. 299 (1999) 583.
- [2] W.E. McDermott, N.R. Pchelkin, D.J. Benard, R.R. Bousek, Appl. Phys. Lett. 32 (1978) 469.
- [3] D.J. Benard, W.E. McDermott, N.R. Pchelkin, R.R. Bousek, Appl. Phys. Lett. 34 (1979) 40.
- [4] X. Liu, M.A. MacDonald, R.D. Coombe, J. Phys. Chem. 96 (1992) 4907.
- [5] J. Habdas, S. Wategaonkar, D.W. Setser, J. Phys. Chem. 91 (1987) 451.
- [6] D.J. Benard, J. Phys. Chem. 100 (1996) 8316.
- [7] J.M. Herbelin, N. Cohen, Chem. Phys. Lett. 20 (1973) 605.
- [8] G.C. Manke II, D.W. Setser, J. Phys. Chem. A 102 (1998) 7257.
- [9] D.J. Benard, M.A. Chowdhury, B.K. Winker, T.A. Seder, H.H. Michels, J. Phys. Chem. 94 (1990) 7507.

- [10] K.B. Hewett, D.W. Setser, J. Phys. Chem. A 102 (1998) 6274.
- [11] K.Y. Du, D.W. Setser, J. Phys. Chem. 94 (1990) 2425.
- [12] K.B. Hewett, G.C. Manke II, D.W. Setser, G. Brewood, J. Phys. Chem. A (1999), submitted.
- [13] T.L. Henshaw, S.D. Herrerra, L.A. Schlie, J. Phys. Chem. A 101 (1997) 4048.
- [14] S.S. Xantheas, T.H. Dunning Jr., A. Mavridis, J. Chem. Phys. 106 (1997) 3280.
- [15] G.C. Manke II, D.W. Setser, J. Phys. Chem. A 102 (1998) 153.
- [16] T.L. Henshaw, S.D. Herrera, L.A. Schlie, J. Phys. Chem. A 102 (1998) 6239.
- [17] D.Z. Cao, D.W. Setser, J. Phys. Chem. 92 (1988) 1169.
- [18] T.L. Henshaw, Ph.D. Thesis, Denver University, 1987.
- [19] K.P. Huber, G. Herzberg, Molecular Spectra and Molecular Structure IV, Constants of Diatomic Molecules, Van Nostrand Reinhold, New York, 1979.
- [20] M.A.A. Clyne, W.S. Nip, Int. J. Chem. Kinet. 10 (1978) 367.
- [21] J.H. Kolts, D.W. Setser, in: D.W. Setser (Ed.), Reactive Intermediates in the Gas Phase, Academic Press, New York, 1979.
- [22] M.C. Sneed, R.C. Brasted, in: Comprehensive Inorganic Chemistry, vol. 5, Van Nostrad, Princeton, NJ, 1956, p. 42.
- [23] M.F. Golde, Int. J. Chem. Kinet. 20 (1988) 75.
- [24] K.B. Hewett, D.W. Setser, J. Phys. Chem. A 101 (1997) 9125.
- [25] G. LeBras, J. Combourieu, Int. J. Chem. Kinet. 5 (1973) 559.
- [26] O. Kajimoto, T. Kawajiri, T. Fueno, Chem. Phys. Lett. 76 (1980) 315.
- [27] J. Combourieu, G. Le Bras, G. Poulet, J.L. Jourdain, Proc. 16th Int. Combustion Symposium, The Combustion Institute, Pittsburgh, PA, 1976.
- [28] D.L. Baulch, J. Duxbury, S.J. Grant, D.C. Montague, J. Phys. Chem. Ref. Data 10 (1) (1981) 548.
- [29] R. Rubin, A. Persky, J. Chem. Phys. 79 (1983) 4310.
- [30] R.S. Iyer, P.J. Rogers, F.S. Rowland, J. Phys. Chem. 87 (1983) 3799.
- [31] J.Y. Park, I.R. Slagle, D. Gutman, J. Phys. Chem. 87 (1983) 1812.
- [32] R.S. Iyer, F.S. Rowland, J. Phys. Chem. 89 (1985) 3730.