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Abstract

The rate constant for Cl + HN_3 over the temperature range 300–480 K has been studied in a flow reactor. Based on the rate of loss of HN_3 and the rate of $NCl(a^1\Delta)$ 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 $E_0 = 3.0 \pm 0.2$ kcal mol^{-1} or an Arrhenius fit $k(T) = 2.0 \pm 1.0 \times 10^{-10} \exp(-1452 \pm 150/T)$ with $E_a = 2.9 \pm 0.2$ kcal mol^{-1}.

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 $(a^1\Delta)$ 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/HN_3 chemical system used for the generation of $NCl(a^1\Delta)$ is summarized by reactions (1) and (2):

$$Cl + HN_3 \rightarrow HCl + N_3 \quad (1)$$

$$Cl + N_3 \rightarrow NCl(a^1\Delta, b^1\Sigma^+, X^3\Sigma^-) + N_2 \quad (2)$$

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 $(a^1\Delta)$, $(b^1\Sigma^+)$, and $(X^3\Sigma^-)$ states, respectively, using $\Delta H_f^0(NCl) = 77.4$ kcal mol^{-1} [14]. The rate determining step for this process is reaction (1), which has a room temperature rate coefficient [15] of $1.1 \pm 0.3 \times 10^{-12}$ cm^3 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 $NCl(a^1\Delta)$:

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

$$NCl(a^1\Delta) + I\left(^2P_{3/2}\right) \rightarrow NCl(X^3\Sigma^-) + I^*\left(^2P_{1/2}\right) \quad (4)$$

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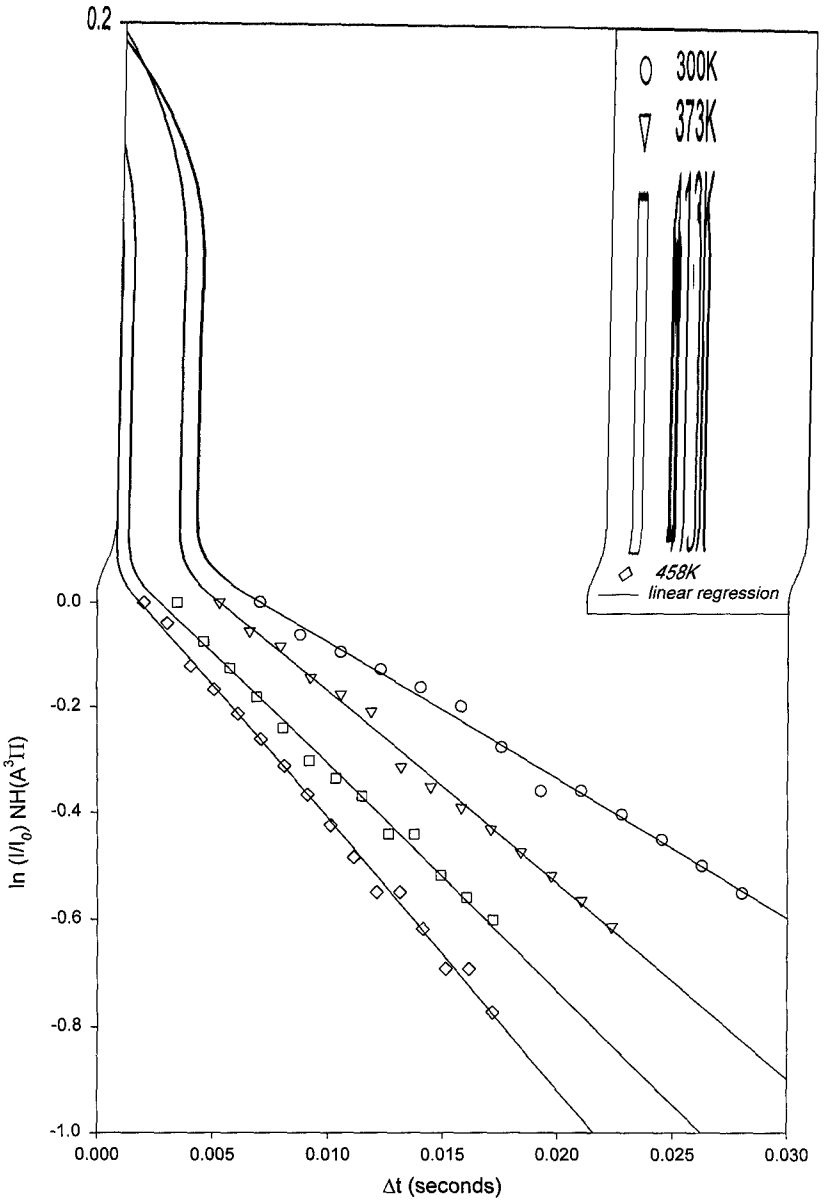

Fig. 2. Pseudo-first-order plots of ln I/I_0(NH($A^3\Pi$)) versus reaction time. The experimental conditions and results are as follows: (300 K) [Cl] = 1.2×10^{13}, [HN_3] = 2.0×10^{12} cm^{-3}, $k = 1.4 \pm 0.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}; (373 K) [Cl] = 8.0×10^{12}, [HN_3] = 3.0×10^{12} cm^{-3}, $k = 4.5 \pm 0.3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}; (413 K) [Cl] = 6.0×10^{12}, [HN_3] = 2.8×10^{12} cm^{-3}, $k = 6.5 \pm 0.4 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}; (458 K) [Cl] = 6.0×10^{12}, [HN_3] = 1.7×10^{12} cm^{-3}, $k = 8.5 \pm 0.3 \times 10^{-12}$ cm^3 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 $\mu m\,s^{-1}$) 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 HN_3 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

Table 2
Summary of the $k(T)$ measurements via loss of HN_3

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 $\pm 1°$ at room temperature and $\pm 7°$ 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($a\,^1\Delta$), NCl($a\,^1\Delta$), NF($b\,^1\Sigma^+$), and NCl($b\,^1\Sigma^+$) were monitored with a cooled

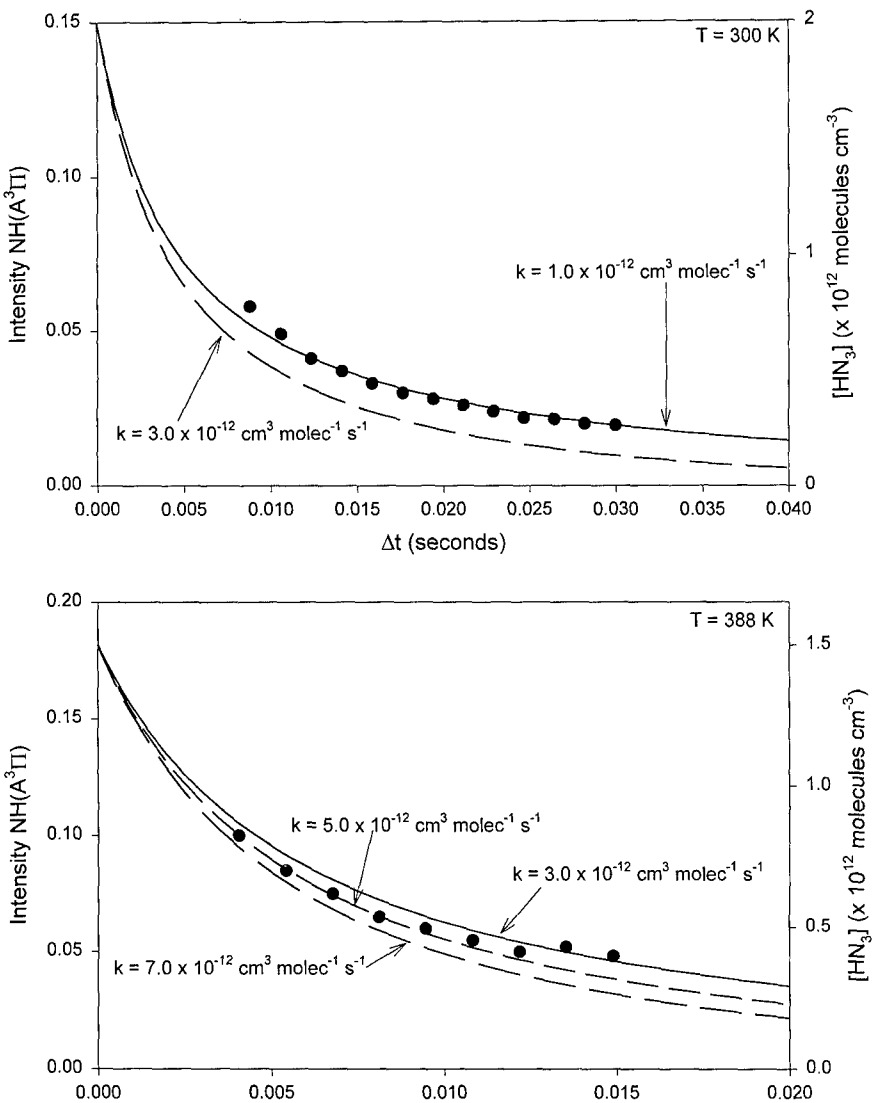

Fig. 3. Non-pseudo-first-order plots of I(NH($A\,^3\Pi$) versus reaction time. A least-squares fitting routine was used to extract k_1 from the data. The experimental conditions are as follows. Upper panel: $T = 300$ K, [Cl] = 1.1×10^{13}, [F] = 2.0×10^{12}, [HN_3] = 2.0×10^{12} cm^{-3}. Lower panel: $T = 388$ K, [Cl] = 6.5×10^{12}; [F] = 1.5×10^{12}; [HN_3] = 1.5×10^{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 $NH(A\,^3\Pi)$ 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

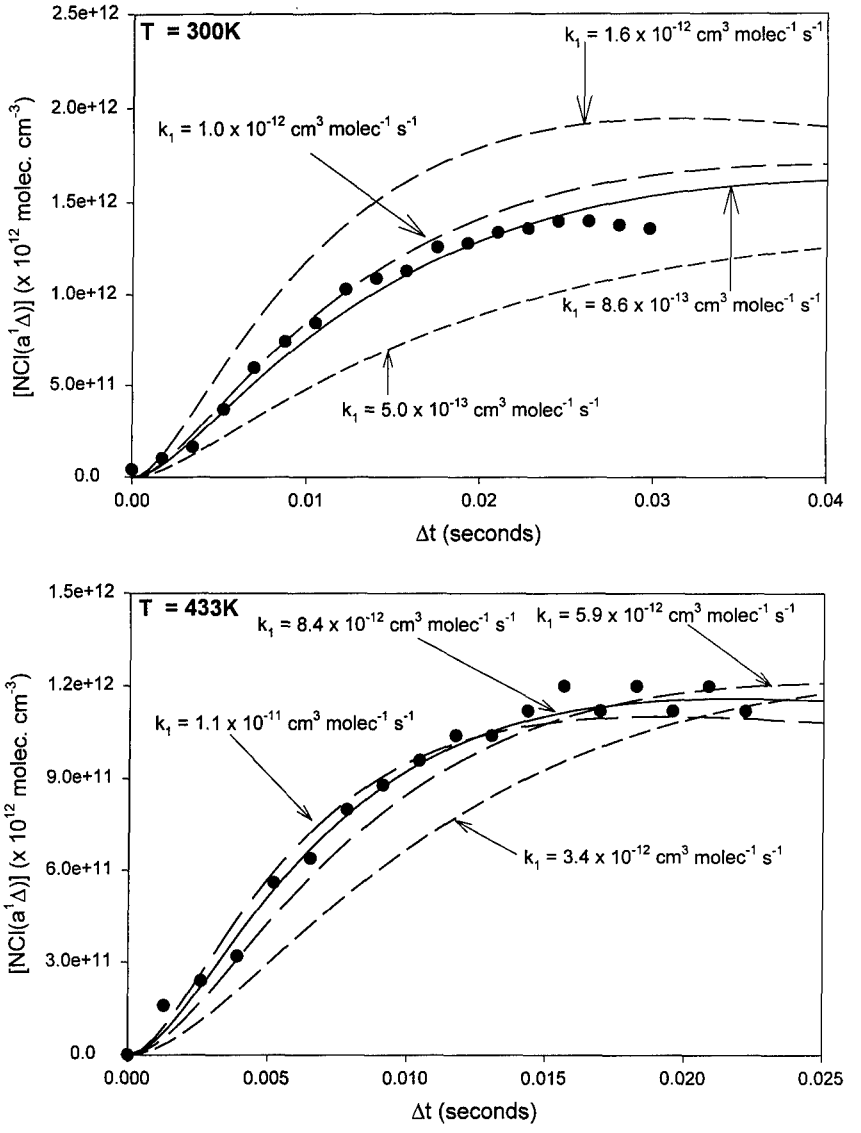

Fig. 4. Measurement of k_1 via generation of $NCl(a\,^1\Delta)$. A least-squares model fit to $[NCl(a\,^1\Delta)]$ versus Δt was used to determine $k(Cl + HN_3)$. The experimental conditions are as follows. Upper panel: $T = 300$ K, $[Cl] = 1.8 \times 10^{13}$, $[HN_3] = 2.0 \times 10^{13}$ cm^{-3}. Lower panel: $T = 433$ K, $[Cl] = 8.0 \times 10^{12}$, $[HN_3] = 1.4 \times 10^{13}$ 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 (±30%).

rolled tantalum foil discharge design [21]. The $NH(A^3\Pi)$ emission intensity increased linearly with the HN_3 flow rate (see the lower panel of Fig. 1). With optimization of the light collection and $N_2(A^3\Sigma_u^+)$ generator, $[HN_3]$ 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 ($[Cl] \gg [HN_3]$) 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 HN_3 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 $1.1 \pm 0.1 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} for $T = 460$ K.

Because HCl quenches $N_2(A^3\Sigma_u^+)$ ($k_Q = 1.3 \times 10^{-12}$ cm^3 $molecule^{-1}$ 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 HN_3. 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 $[HN_3]$, 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 $[F] \leqslant [HN_3]_0$. Otherwise, F removes nearly all of the HN_3 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 $[HN_3]$.

3.2. Generation of $NCl(a^1\Delta)$

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 $\pm30\%$, 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 N_3 and HN_3 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 $NCl(a^1\Delta)$

T (K)	$k(T)$ ($\times10^{-12}$ cm^3 $molecule^{-1}$ 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

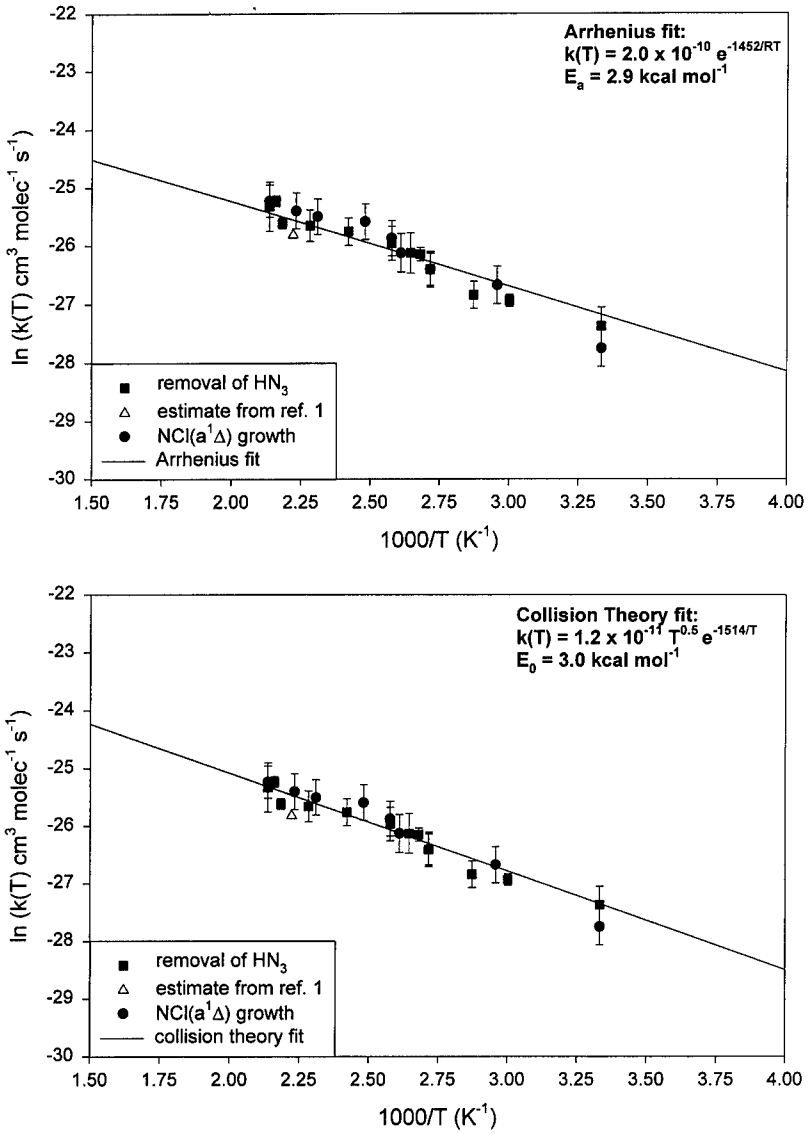

Fig. 5. Arrhenius and collision theory fits to the $k_1(T)$ data. Upper panel: The $k_1(T)$ data is fit by the Arrhenius expression. The best fit is achieved for $A = 2.0 \times 10^{-10}$ and $E_a = 2.9$ kcal mol^{-1}. Lower panel: A collision theory expression is used and $A = 1.2 \times 10^{-11}$ and $E_0 = 3.0$ kcal mol^{-1}. In both panels data from both the loss of HN_3 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,

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

$$2\,F + HN_3 \rightarrow HF + N_3 \rightarrow HF + NF(a\,^1\Delta) + N_2 \quad (7a)$$

$$\rightarrow HNF + N_2 \rightarrow HF + NF(a\,^1\Delta) + N_2 \quad (7b)$$

is known to be an efficient source of the N_3 and $NF(a\,^1\Delta)$ radicals. The room temperature rate constant [5] for (7a) is established as $1.1 \pm 0.2 \times 10^{-10}$ cm^3 $molecule^{-1}$ 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 HN_3 has been measured [25] from 300 to 460 K and $k(T) = 2.5 \times 10^{-11} \exp(-2315/T)$ cm^3 $molecule^{-1}$ s^{-1}. The reaction produces $NH_2(^2A_1,\ v_2 \leqslant 20)$ [26] and minor amounts of $NH(A\,^3\Pi)$ and $NH(b\,^1\Sigma)$.

$$H + HN_3 \rightarrow NH_2 + N_2 \quad (8a)$$

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]:

$$H + HN_3 \rightarrow N_3 + H_2 \quad (8b)$$

$$H + N_3 \rightarrow NH(b\,^1\Sigma) + N_2 \quad (9)$$

$$2\,NH^*(b\,^1\Sigma \vee a\,^1\Delta) \rightarrow NH(A\,^3\Pi) \quad (10)$$

Prior to this report, the only halogen/azide reaction that had been characterized $T > 300$ K was $Cl + ClN_3$:

$$Cl + ClN_3 \rightarrow N_3 + Cl_2 \quad (11)$$

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 $k(T) = 2.3 \times 10^{-11} \exp(-554/T)$ cm^3 $molecule^{-1}$ s^{-1}.

The present results indicate a moderate temperature dependence for the reaction of $Cl + HN_3$, with $E_a \approx 3$ kcal mol^{-1}. The pre-exponential factor is large and requires some comment. Hydrogen atom abstraction reactions such as $F + HCl$ ($k = 4.4 \pm 1.5 \times 0^{-11} \exp(-400 \pm 100/T)$ cm^3 $molecule^{-1}$ 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 ~ 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 $F + HN_3$, $A \geqslant k_{300} = 1.1 \pm 0.2 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. Chlorine atoms are known to add to olefins (e.g., C_2H_4 [30], C_2H_3Br [31], and C_2H_3Cl [32]) and these reactions are very fast at room temperature, $k(300) = 1.5 \pm 0.4 \times 10^{-10}$ 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 $k_{298}(Cl + C_2H_3Br) = 1.43 \pm 0.29 \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}, the A factor is 2.4×10^{-10} cm^3 $molecule^{-1}$ 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 N_3 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 N_3 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 $NCl(a\,^1\Delta)$, by analogy to the $F + HN_3$ system, both N_3 and HNCl should react rapidly with Cl atoms to give $NCl(a\,^1\Delta)$.

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}.

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References

[1] 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.

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