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ABSTRACT

The kinetics of reactions of CN with the chlorinated methanes CH₃Cl, CH₂Cl₂, CHCl₃ and CCl₄ were investigated over the temperature range 298–573 K, using laser induced fluorescence (LIF) spectroscopy. At 298 K, rate constants of $9.0 \pm 0.3 \times 10^{-13}$, $8.8 \pm 0.4 \times 10^{-13}$, $9.0 \pm 0.5 \times 10^{-13}$ and $4.3 \pm 0.6 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ were measured, respectively. A small positive temperature dependence was observed, as well as kinetic isotope effects of $k_{\rm H}/k_{\rm D} \sim 2.14-2.25$. These data along with product detection experiments strongly suggest that hydrogen abstraction dominates these reactions.

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1. Introduction

Halogenated alkanes play an important role in stratospheric chemistry and combustion chemistry. Many groups have studied reaction kinetics of halogenated alkanes with different reactive species for example OH, Cl, etc. [1,2]. Reactions of CN radical are also important in combustion chemistry as it is an important intermediate in the formation of NO_x by oxidation of HCN with OH [3,4]. Reactions of CN with saturated and unsaturated hydrocarbons have been extensively studied [5–11]. CN radical reacts with saturated hydrocarbons by direct hydrogen abstraction, resulting in formation of HCN products [9].

In this work we report a study of the kinetics of CN radical reactions with chlorinated methanes. No previous literature exists on the kinetics of these reactions. Two different product channels are thermodynamically possible, hydrogen abstraction and chlorine atom abstraction

$$CN + CH_4 \rightarrow HCN + CH_3 \quad \Delta H^0_{298} = -87.34 \text{ kJ mol}^{-1}$$
(1)

$$CN + CH_3Cl \to HCN + CH_2Cl \quad \Delta H^0_{298} = -107.9 \ \text{kJ} \ \text{mol}^{-1} \eqno(2a)$$

$$\rightarrow$$
 ClCN + CH₃ Δ H⁰₂₉₈ = -71.36 kJ mol⁻¹ (2b)

$$CN+CH_2Cl_2 \rightarrow HCN+CHCl_2 \quad \Delta H^0_{298} = -124.36 \ \text{kJ} \ \text{mol}^{-1} \qquad (3a)$$

 $\rightarrow ClCN + CH_2Cl \quad \Delta H^0_{298} = -87.91 \text{ kJ mol}^{-1} \qquad (3b)$

$$\mathrm{CN} + \mathrm{CHCl}_3 \rightarrow \mathrm{HCN} + \mathrm{CCl}_3 \quad \Delta \mathrm{H}^0_{298} = -126.2 \ \mathrm{kJ} \ \mathrm{mol}^{-1} \eqno(4a)$$

$$- \text{CICN} + \text{CHCl}_2 \quad \Delta H^0_{298} = -108.55 \text{ kJ mol}^{-1}$$
 (4b)

 $CN+CCl_4 \rightarrow ClCN+CCl_3 \quad \Delta H^0_{298} = -126.25 \ \text{kJ} \ \text{mol}^{-1} \eqno(5)$

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Thermodynamic data were taken from JANAF tables [12], except for CICN [19]. A major goal of this study is to determine the dominant product channel in these reactions.

2. Experimental section

Rate constant measurements were performed using LIF (laser induced fluorescence) techniques. ICN was used as a photolytic precursor for CN radicals

$$ICN + hv(248 \text{ nm}) \rightarrow CN + I$$
 (6)

Details of the LIF apparatus used for kinetics measurements have been described in a previous publication [13]. The photolysis laser light was provided by an excimer laser (Lambda Physik COM-PEX 200) operating at 248 nm and a repetition rate of 4 Hz. Typical photolysis pulse energies were 2-6 mJ, resulting in typical initial $[CN]_0$ concentrations of $\sim 1-2 \times 10^{13}$ molecule-cm⁻³. CN radicals were detected by LIF, using 387.088 nm probe light (~0.5 mJ/ pulse), which was produced by frequency doubling 774.176 nm light from a dye laser (Continuum ND-6000) pumped by the second harmonic of a Nd:YAG laser (Continuum Surelite II-10). The probe laser was operated at a repetition rate of 8 Hz. The photolysis and probe beams were made collinear using a dichroic mirror and copropagated down a 88-cm Pyrex reaction cell. Fluorescence was detected 90° from the laser beams using an R508 photomultiplier tube. The unamplified PMT signal was recorded by a boxcar integrator (Stanford Instruments model 250) with a 10-60 ns delay and a 400 ns gate width, and averaged on a computer. A digital delay generator (Stanford DG535) was used to vary the delay between excimer and dye laser pulses in order to produce a LIF signal vs. time profile. The CN concentration was assumed to be proportional to the LIF signal. The static cell was resistively heated to collect data at elevated temperatures up to 573 K. Gases introduced into the reaction cell were allowed to mix for 5 min to ensure complete mixing and thermal equilibration.



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In some experiments, FTIR spectra of reactants and products were recorded by transferring the contents of the reaction cell into a shorter 12-cm cell, and collecting spectra using a Thermo Nicolet NEXUS 470 FTIR spectrometer. Also, some experiments used a high resolution infrared diode laser spectrometer as described previously [14].

ICN (Aldrich) was purified by vacuum sublimation to remove dissolved air. SF_6 and CH_3Cl (Matheson) were purified by repeated freeze-pump-thaw cycles at 77 K. CH_2Cl_2 (Alfa Acer), $CHCl_3$ and CCl_4 (Aldrich) were purified by repeated freeze-pump-thaw cycles at 77 K to remove dissolved air.

Typical experimental conditions were $P_{ICN} = 0.05-0.2$ Torr, $P_{Chlorinated Methane} = 0-0.9$ Torr and $P_{SF6} = 0.5-1.0$ Torr. The reaction cell was evacuated and refilled after every kinetic run.

3. Results and discussion

3.1. Total rate constant measurements

The decay of CN was measured in the absence of chlorinated methane reagent; a very small decay rate was observed, as shown in Fig. 1. This decay is attributed to reactions of CN radical with itself or with traces of oxygen present in the system. When a reagent such as CH₃Cl was added to the reaction mixture the decay rate of CN was observed to increase substantially as shown in Fig. 2. Above about 10 mTorr of CH₃Cl, pseudo-first-order conditions apply, leading to an exponentially decay function:

$$[CN] = [CN]_0 \exp(-k't) \tag{7}$$

$$k' = k[CN] + k_D \tag{8}$$

where k' is the observed pseudo-first-order rate constant, k is the desired bimolecular rate constant for the CN + chlorinated methane reaction, and k_D is the decay rate of CN in the absence of added reagent. Several processes contribute to k_D , including diffusion of CN radicals out of the probed volume, self-reaction of CN radicals, and reaction with trace amounts of O₂. Fig. 2 shows a plot of k' vs. CH₃Cl pressure at different temperature (298, 373, 473 and 573 K). The slope of this plot gives the bimolecular rate constants (k) for CN + CH₃Cl reaction at different temperatures. These values are summarized in Table 1.



Fig. 1. Laser-induced fluorescence signals of CN as a function of excimer-dye delay time. Reaction conditions: P_{ICN} = 100 mTorr, $P_{chloromethane}$ = variable, P_{SF6} = 900 mTorr at 298 K.



Fig. 2. Pseudo-first-order decay rates of CN LIF signals as a function of CH_3CI pressure at different temperatures.

Similar set of experiments were performed for CH_2Cl_2 , $CHCl_3$ and CCl_4 . Figs. 3–5 shows a plot of k' vs. reagent pressures at different temperatures for CH_2Cl_2 , $CHCl_3$ and CCl_4 , respectively. For reaction of CN with $CHCl_3$ and CCl_4 at high temperatures some saturation effect was observed, i.e. at higher pressures (≥ 400 mTorr) of reactant gas (CHCl_3 and CCl_4) no change in the k' value observed for these reactions. The LIF intensity was observed to decrease with increasing reactant gas pressure. This suggests that dark reactions, possibly involving ICN precursor molecules, are taking place at higher temperature. This effect was also observed with CH_2Cl_2 but only at higher pressures of ≥ 800 mTorr. We carried out some experiments to confirm the existence of dark reactions (described below). The result of the dark reaction was to limit reliable data collection to $T \leq 373$ K for CHCl₃ and to room temperature for CCl₄.

The rate constant values for all these reactions are summarized in Table 1. The rate constant values obtained for CN reaction with partially chlorinated methanes are higher than that obtained with methane at all temperatures [6]. Fig. 6 shows the Arrhenius plot for measured rate constants for CN reactions with CH₃Cl and CH₂Cl₂. The data can be fit to the following expressions for reactions (2) and (3), respectively (error bars represent one standard deviation):

$$k_2(\text{CN} + \text{CH}_3\text{Cl}) = (4.9 \pm 0.53) \times 10^{-11} \exp(-1213 \pm 45/T)$$

$$k_3(\text{CN} + \text{CH}_2\text{Cl}_2) = (6.8 \pm 1.6) \times 10^{-11} \exp(-1309 \pm 94/T)$$

The respective activation energy (E_a) values are listed in Table 1. The E_a value determined for reaction (4) is very approximate, as we could measure k values at only two temperatures for this reaction. Because of the presence of dark reactions at elevated temperatures, we were unable to determine an E_a value for reaction (5). The observation of positive activation energies of similar magnitude to that observed in the CN + CH₄ reaction is consistent with a direct H atom abstraction mechanism, channels (2a), (3a), and (4a).

3.2. Investigation of dark reactions

To monitor the dark reactions taking place in the presence of CHCl₃ and CCl₄, FTIR absorption measurements were carried out for the reaction mixture at room temperature and at 573 K. For these measurements the reaction mixtures were first filled in the LIF cell and allowed to mix and thermally equilibrate for 10 min

Table 1

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Rate constant and activation energy values for CN reaction with methane and chlorinated methanes at different temperatures						
Reagent	Rate constant (cm ³ molecule ⁻¹ s ⁻¹)					
	298 K	373 K	473 K	573 K		

	298 K	373 K	473 K	573 K		
CH4 ^a	$\textbf{7.28}\times 10^{-13}$	1.24×10^{-12}	2.12×10^{-12}	$3.27 imes 10^{-12}$	8.32	
CH₃Cl	$9.0\pm0.3 imes10^{-13}$	$1.9\pm0.2 imes 10^{-12}$	$3.5\pm0.5 imes10^{-12}$	$6.0\pm0.5 imes10^{-12}$	10.08	
CH ₂ Cl ₂	$8.8 \pm 0.4 imes 10^{-13}$	$1.9 \pm 0.5 \times 10^{-12}$	$4.0 \pm 0.2 \times 10^{-12}$	$7.5 \pm 0.5 \times 10^{-12}$	10.8	
CHCl₃	$9.0\pm0.5 imes10^{-13}$	$1.8 \pm 0.3 \times 10^{-12}$			~ 8.53	
CCl ₄	$4.3 \pm 0.6 \times 10^{-13}$					

^a Values taken from Ref. [8].



Fig. 3. Pseudo-first-order decay rates of CN LIF signals as a function of $\rm CH_2Cl_2$ pressure at different temperatures.



Fig. 4. Pseudo-first-order decay rates of CN LIF signals as a function of CHCl₃ pressure at different temperatures.

and then transferred to another cell for FTIR measurements. Two reaction mixtures used for recording FTIR spectra are (i) chlorinated methane and (ii) chlorinated methane + ICN. Spectra were recorded both before and after firing 100 photolysis laser shots. A similar set of experiments was performed at 573 K. Typical pressures of the gases in reaction mixtures used for these measurements are 300 mTorr of ICN and 4 Torr of chlorinated methanes. The following general features were observed:



 E_a (kJ/mol)

Fig. 5. Pseudo-first-order decay rates of CN LIF signals as a function of CCl₄ pressure at RT.



Fig. 6. Arrhenius plot of the CN + CH₃Cl and CN + CH₂Cl₂ reactions.

CN + CHCl₃: FTIR spectra of CHCl₃ were recorded at 298 K and at 573 K; no significant difference was observed in the spectral characteristics at these two temperatures. These spectra match well with the literature spectra. Similarly FTIR spectra of CHCl₃ in the presence of ICN were also recorded; this time we observed a difference in spectral characteristics at different temperatures. The 298 K CHCl₃ spectrum remained unchanged in the presence of ICN. At 573 K, however, the CHCl₃ spectrum in the presence of ICN shows an absorption at 3300 cm⁻¹, which is evidence of HCN

formation. $CHCl_3 + ICN$ spectra were also recorded at both temperatures after firing photolysis laser shots. In this case the characteristics absorption for HCN was observed at both the temperatures. These experimental observations demonstrate that HCN is a product (possibly the major product) of reaction (3), and that HCN is also formed at the high temperature without firing the photolysis laser, suggesting a dark reaction at high temperature which interferes with the rate constant measurements.

 $CN + CCl_4$: FTIR spectra of CCl_4 recorded at 298 K and 573 K matches with the literature CCl_4 spectrum at 298 K. $CCl_4 + ICN$ spectra were recorded after firing 100 shots of laser at both temperatures. These spectra have a weak absorption feature at 2000–2200 cm⁻¹ indicating formation of ClCN. This product was also formed at higher temperature without any photolysis laser firing, again suggesting a dark reaction at high temperature.

 $CN + CH_2Cl_2$: In the case of CH_2Cl_2 the recorded FTIR spectra at 298 K and 573 K matches with the reported spectrum at RT. At higher temperature CH_2Cl_2 + ICN spectrum recorded without firing laser shots shows only a trace of HCN, indicating only a slight amount of dark reaction.

3.3. Detection of ClCN products

High-resolution infrared diode laser absorption spectroscopy was used for the detection of CICN. (Unfortunately, diode laser detection of HCN products was not feasible because of the lack of available diode lasers with emission near 3300 cm⁻¹). Several groups have reported the infrared absorption spectrum of CICN [15-18]. Theoretical calculations of IR spectra have also been reported [19-21]. No high resolution IR absorption spectrum for CICN has been reported, but all previous studies have indicated that CICN has an absorption band in the 2000–2200 cm⁻¹ range. Using a high resolution diode laser, we have monitored the IR absorption near 2200–2210 cm⁻¹. Spectra of CCl₄, ICN and ICN + CCl₄ were monitored at room temperature. CCl₄ and ICN do not have any significant absorption in the monitored region: but upon extensive photolysis (~100 shots) of an ICN/CCl₄ mixture. several very weak absorption lines appeared near 2200 cm⁻¹. We attribute these absorptions to CICN formation via the slow reaction (5). The extremely small size of these signals precluded any measurement of the kinetics of product formation. The most significant result is that similar extended photolysis of ICN/CHCl₃ mixtures failed to produce those same absorptions, strongly suggesting that channel (4b) does not play a major role, and that hydrogen abstraction, channel (4a), dominates the reaction of CN with partially chlorinated methanes. We estimate an upper limit for φ_{4b} of <0.25.

3.4. Deuterium isotope effects

The rate constants of CN reacting with CD₃Cl, CD₂Cl₂ and CDCl₃ were measured at 298 K. Table 2 shows the resulting values of $k_{\rm H}/k_{\rm D}$. The ratio $k_{\rm H}/k_{\rm D}$ was found to be approximately 2.2 for all the three reagents. If CNCl formation (reactions (2b), (3b) and (4b)) were a major product channel we would expect only very small

Table 2

Rate constant values for CN reaction with deuterated methane and chlorohydrocarbons at 298 $\rm K$

Reagent	Rate constant (cm ³ molecule ⁻¹ s ⁻¹)	$k_{ m H}/k_{ m D}$
CD ₄ ^a	$1.74 imes 10^{-13}$	3.4
CD ₃ Cl	$4.0\pm0.2 imes10^{-13}$	2.25
CD_2Cl_2	$3.9 \pm 0.2 imes 10^{-13}$	2.25
CDCl ₃	$4.2\pm 0.3\times 10^{-13}$	2.14

^a Values taken from Ref. [6].

secondary isotope effects. Our results, however, are consistent with a primary isotope effect, nearly of the magnitude of the literature values for CH₄. This provides further evidence that these reactions proceed primarily via direct hydrogen abstraction, channels (2a), (3a), and (4a).

4. Conclusions

We have reported the first measurement of the kinetics of CN reaction with chlorinated methanes. These reactions are slightly faster than that of $CN + CH_4$. Several pieces of evidence, including the observation of positive activation energies, k_H/k_D ratios consistent with a primary isotope effect, and product detection experiments all indicate that the reaction of CN with partially chlorinated species CH_3Cl , CH_2Cl_2 and $CHCl_3$ are dominated by direct hydrogen atom abstraction and that CNCl formation is a minor or insignificant channel, except for the slower CN + CCl₄ reaction.

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