Kinetics of CCN Radical Reactions with a Series of Normal Alkanes

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The reactions of CCN($\tilde{X}^2\Pi_i$) radicals with normal alkanes have been studied at about 10 Torr total pressure and room temperature using the pulse laser photolysis/laser-induced fluorescence technique. CCN ($\tilde{X}^2\Pi_i$) radicals are generated by the fourth harmonic of a Nd:YAG laser photolysis of Cl_3CCN at 266 nm. The relative concentration of CCN ($\tilde{X}^2\Pi_i$) radicals was monitored in the (0−0) band of the CCN ($\tilde{A}^2\Delta \leftarrow \tilde{X}^2\Pi_i$) transition at 470.9 nm by laser induced fluorescence (LIF). From the analysis of the relative concentration−time behavior of CCN ($\tilde{X}^2\Pi_i$) under pseudo-first-order conditions, the rate constants for the reaction of CCN ($\tilde{X}^2\Pi_i$) with a series of normal alkanes (C_1−C_8) were determined for the first time. The new data establish that the gas-phase reactivity of small alkanes (C_1−C_8) towards the CCN radicals follows the linear free energy relationship typical of hydrogen abstraction. A comparison with the corresponding reactions of CN and OH radicals with a series of normal alkanes, leads us to suggest that the reaction of CCN ($\tilde{X}^2\Pi_i$) with small normal alkanes proceeds via the mechanism of hydrogen abstraction. The plausibility of the suggested reaction mechanism is strengthened by bond dissociation energy (BDE) correlations and linear free energy correlations.

Introduction

The cyanomethylidyne, CCN radical has attracted special interest in astrophysics and is important because a large number of linear carbon chain molecules have been observed in the interstellar medium.[1,2] For the nitrogen-bearing series, the CN[3], C_3N, and C_5N[4] radicals have been detected in interstellar clouds and in stellar envelopes, but CCN itself has not been observed to date. CCN is also thought to be involved in combustion processes in fuel-rich natural gas flames.[5] The first spectroscopic study of CCN was reported by Merer and Travis in 1965,[6] who performed flash photolysis of diazoacetonitrile, $HC(CN)N_2$, to generate the radical. They observed absorption spectra of the $\tilde{A}^2\Delta \leftarrow \tilde{X}^2\Pi_i$, $\tilde{B}^2\Sigma^- \leftarrow \tilde{X}^2\Pi_i$, and $\tilde{C}^2\Sigma^+ \leftarrow \tilde{X}^2\Pi_i$ band systems in the 350−470 nm region. Since the work by Merer and Travis, there have been several subsequent studies of the $\tilde{A}^2\Delta \leftarrow \tilde{X}^2\Pi_i$ transition.[7−12] Kakimoto et al.[7] studied laser-induced fluorescence (LIF) spectra of the $\tilde{A}^2\Delta(000) \leftarrow \tilde{X}^2\Pi_i(000)$ band using a cw dye laser with Doppler-limited resolution. Hakuta and Uehara[8] used an Ar^+ laser to pump the CCN radical into the $\tilde{A}^2\Delta$ state and observed the resulting LIF. The $\tilde{A}\Delta$ state spectra of the CCN radical are well studied. This is useful for the reaction kinetics study. In contrast to other carbon chain radicals, for example CN[13−15] and C_2H,[16,17] the study of the reaction kinetics of CCN is very poor. To our knowledge, there are no kinetics studies of the radical−molecule reactions involving the CCN radical. To understand fully the importance of the CCN radical in these drastically different environments, the rates of reaction of CCN with a wide range of compounds must be characterized.

Recently, we studied the reaction of CCN ($\tilde{X}^2\Pi_i$)with a series of normal alkanes. In this paper, we report the first determination of the bimolecular reaction rate constants for reactions of the CCN ($\tilde{X}^2\Pi_i$) radical with normal alkanes (C_1−C_8) in the presence of excess Ar buffer gas at about 10 Torr total pressure and room temperature using the pulsed laser photolysis/laser-induced fluorescence technique. The probable mechanism for these reactions is discussed, based on the bond dissociation energy (BDE) correlations and linear free energy correlations.

Experimental Section

The pulsed laser photolysis coupled with laser induced fluorescence (LP-LIF) detection of CCN was used to investigate the kinetics of CCN reactions with normal alkanes. The experimental setup has been described previously,[18,19] so only a brief summary of the main features is given here.

The CCN radicals were produced by photolysis of cyanotrichloromethane Cl_3CCN. The mixture of Cl_3CCN, Ar, and reactant normal alkanes flowed slowly through a stainless steel reaction cell, with long baffle arms to reduce the scattered laser light. Flows of all reagents and argon buffer gas are measured by calibrated mass flow controllers (D07-7A/2M, Beijing). All experiments were performed at room temperature and at total pressures near 10 Torr to maintain steady flow conditions. The volumetric flow rate and the laser pulse-repetition-frequency were such that there was no accumulation of products in the photolysis cell. The mixing ratios for Cl_3CCN and normal alkanes that were selected ensure pseudo-first-order conditions; typically the ratio was 10:1. Ar was used as a diluent gas to slow diffusion to the walls and to relax CCN ($\tilde{X}^2\Pi_i$) internal excitation

The photolysis laser light provided by a Nd:YAG laser (New wave) operating at 266 nm was used to generate the CCN($\tilde{X}^2\Pi_i$) radical. Typical photolysis pulse energies and time jitter of the photolysis laser are 6−9 mJ and 2 ns, respectively, and a repetition rate of 10 Hz was used. Rotational lines of the 0−0 vibrational band of the CCN ($\tilde{A}\Delta \leftarrow \tilde{X}^2\Pi_i$) transition were excited at 470.9 nm. The probe light source was a dye laser

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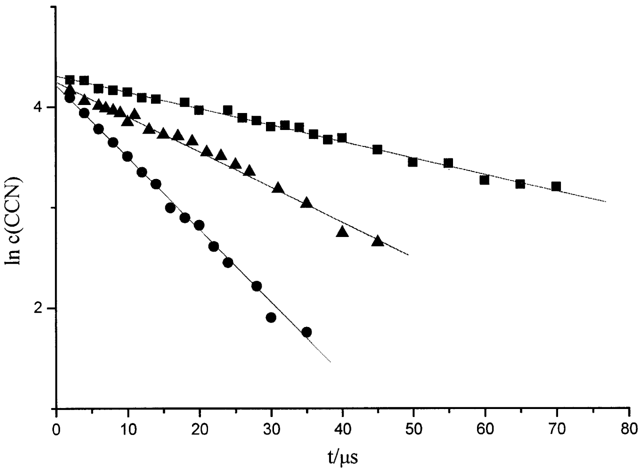

Figure 1. Typical semilogarithmic decay plots of relative CCN concentration measured in the reaction of CCN radicals with normal butane (C_4H_{10}) vs time between the photolysis laser and probe laser pulses at about 10 Torr total pressure and 298 K in different butane concentrations (10^{14} cm^{-3}): (●) 2.893; (▲) 10.12; (■)14.47. The solid lines are the results of exponential fits.

(Sirah) pumped by the third harmonic of a Nd:YAG laser (Spectra-Physics, GCR-170). The probe laser was also operated at a repetition rate of 10 Hz. The dye laser beam was collinear and counter propagating to the photolysis beam. The diameter of the dye laser beam was very small (about 0.2 mm in diameter) to minimize diffusion effects. Fluorescence signals were collected using a photomultiplier tube (R928, Hamamatsu) with the axis of the two laser beams and the fluorescence collection axis mutually perpendicular to minimize the collection of scattered laser light. The unamplified PMT signal was recorded by a digital storage oscilloscope (TDS380, Tektronix) or a transient digitizer and then averaged with a computer data acquisition system. A digital delay generator (Stanford DG535) was used to vary the delay between photolysis laser and dye laser pulses in order to produce a CCN ($\tilde{X}^2\Pi_i$) concentration vs time profile. In our experiments the fluorescence signals were averaged over 256 laser pulses.

Cl_3CCN (Aldrich, 99%), methane (Nanjing gas 99.9%), ethane (Nanjing gas 99.9%), propane (Nanjing gas 99.9%), butane (Nanjing gas 99.9%), pentane (Academic of army 99.9%), hexane (Yi Xing 99.9%), heptane (Han Zhou >97.5%), and octane (Shanghai >97.5%), obtained commercially, were purified by several standard freeze−pump−thaw cycles with liquid nitrogen. Argon of a stated purity of 99.999% (Nanjing gas 99.9999%) was used directly from a cylinder.

Results

LIF signals in the range between 460 and 475 nm with about 200 ns lifetime were observed upon 266 nm photolysis of Cl_3CCN. Based on previous spectroscopic data,[7,8] we could confidently assign these signals to the $\tilde{A}\Delta \leftarrow \tilde{X}^2\Pi_i$ transition of the CCN radical. We choose the (0−0) band of the CCN ($\tilde{A}\Delta \leftarrow \tilde{X}^2\Pi_i$) transition at 470.9 nm to detect the CCN ($\tilde{X}^2\Pi_i$) radical relative concentration. All experiments were performed under pseudo-first-order conditions. The CCN ($\tilde{X}^2\Pi_i$) radical concentration was about 5×10^{11} molecule cm^{-3}, estimated from the incident light intensity, the absorption cross-section, and the pressure of Cl_3CCN. The partial pressure of alkanes ranged from 0.5 to 40 mTorr ($1.5 \times 10^{14} \sim 1.8 \times 10^{15}$ molecule cm^{-3}). Figure 1 shows a plot of typical CCN LIF integrated signal amplitude as a function of delay time between the photolysis and probe laser. As shown, the CCN kinetic signals were found to be well approximated by single exponential decays over the range $t = 5-100$ μs. The decay rates were not significantly affected by the addition of Ar buffer gases. This observation suggests that vibrational relaxation effects are insignificant in these experiments. Either CCN was produced vibrationally cold, or vibrational relaxation was accomplished within 5 μs.

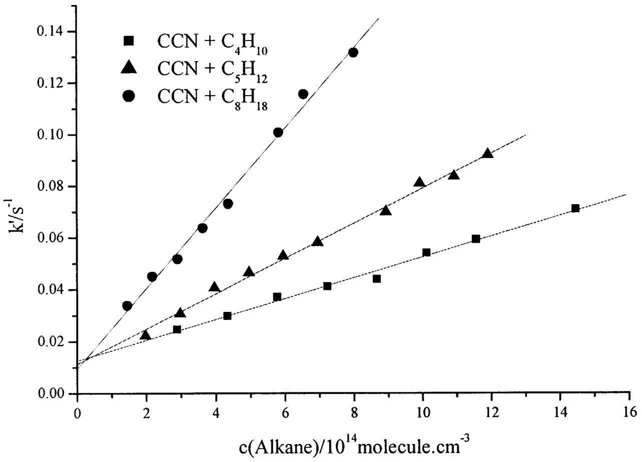

Figure 2. Plots of the pseudo-first-order decay constant k' vs the concentration of alkane in the presence of excess Ar buffer gas at 10 Torr total pressure and room temperature. The slopes give the bimolecular rate constant.

In the presence of significant alkane concentrations, under pseudo-first-order conditions, a standard kinetic analysis shows that

$$I = A \exp(-k_1 t)$$

where I is the measured LIF intensity, k_1 is the pseudo-first-order decay rate constant, and t is the delay time between the photolysis laser and the dye laser. The k_1 values are then obtained at various reactant concentrations and fitted by the equation

$$k_1 = k[R] + k_0$$

where k is the desired bimolecular rate constant for the reaction of CCN ($\tilde{X}^2\Pi_i$) with reactant R, and k_0 is the removal rate constant in the absence of added reactant. Contributions to k_0 include self-reaction, reaction with precursor molecules, and diffusion of detected species out of the probed volume. In the current experiments, the precursor molecule concentration was kept much lower than the alkane concentration and was fixed, so it will not affect the measurement. In fact, the signals were found to be reasonably fit to pseudo-first-order kinetics, even at low reactant concentrations. Figure 2 shows k_1 as a function of the concentration of several normal alkanes. The slope of these plots represents the bimolecular rate constant k. The rate constants of reactions of CCN ($\tilde{X}^2\Pi_i$) with the selected normal alkanes (C_1-C_8) at 298 K are summarized in Table 1. The reported uncertainty is one standard deviation from the uncertainty in the fit. Additional experimental errors are estimated to increase the error limits to 5%. To the best of our knowledge, the CCN radical reactions were investigated for the first time in the present study. Therefore, there are no literature rate constants for these reactions available for comparison.

Discussion

In general, electrophilic species such as CN and CCN are known to react with small hydrocarbons via two major

TABLE 1: Rate Constants for CCN, CN, and OH Reactions with Small Normal Alkanes and Bond Dissociation Energies (BDE) at 298 K

compound	K_{CCN}[a,c]	K_{CN}[a,[14]]	K_{OH}[a,[20]]	BDE[b]
methane	0.006 ± 0.002	0.056 ± 0.003	0.0008	104
ethane	0.29 ± 0.06	2.3 ± 0.2	0.028	98
propane	1.9 ± 0.06	8.1 ± 1	0.19	97.25
butane	4.2 ± 0.2	9[15]	0.3	96.8
pentane	7.6 ± 0.3	16 ± 2	0.5	96.5
hexane	11.5 ± 0.4		0.59	96.29
heptane	14.6 ± 1.2	23 ± 2	0.72[26]	96.13
octane	17.3 ± 1		0.84	96

[a] Rate constant in units of 10^{-11} cm^3 molecule^{-1} s^{-1}. [b] Bond dissociation energy, in units of kcal mol^{-1}, C−H bond. The bond dissociation energy is the average value of the C−H band dissociation energies for the primary and secondary hydrogen weighted by the number of the primary and secondary hydrogen of alkane. The C−H band dissociation energies for the primary and secondary hydrogen are 98 kcal mol^{-1} and 95 kcal mol^{-1}, respectively, (data from ref 27, 28). [c] This work.

pathways, addition and abstraction. Normally, the addition reaction occurs when the radical can form a bond with available π electrons, such as with unsaturated hydrocarbons, but abstraction reactions occur with saturated hydrocarbons. It is shown that the reaction rate constant of CCN ($\tilde{X}^2\Pi_i$) radicals with normal alkanes increases with increasing chain length of the normal alkane. For C3−C8 alkanes, the rate of reaction increases linearly with the increasing number of CH_2 groups. It is most pronounced in going from methane to ethane. This enhancement, which was also found in the hydrogen abstraction reactions of CN[14,15] and OH[20−22] radicals, corresponds to the decline in the ionization potential of the alkanes. It is helpful for us to determine the reaction mechanism. It is instructive to make a comparison with the related reactions of CN, since both CN and CCN radicals are similar in some of their chemical properties. The reaction of CN radicals with hydrocarbons has been investigated extensively, and the reactions with alkanes are supposed to be hydrogen abstractions leading to HCN or HNC as products.[14,15] Experimentally, the higher saturated hydrocarbons are more efficient at removing CCN ($\tilde{X}^2\Pi_i$) radicals, but the reaction rate is much slower with methane than with ethane. As can be seen from Table 1, a similar trend in the rate constants is apparent for the corresponding CN reactions. Therefore, we suggest that the reactions of the CCN ($\tilde{X}^2\Pi_i$) radical with normal alkanes occurs via the mechanism of hydrogen abstraction, which leads to HCCN as the main product, as observed in the corresponding reactions with CN[14,15] and OH[21,22] radicals. In current work, a series of rate constants for normal alkanes (C_1−C_8) is observed. It is possible to evaluate the reaction mechanism by linear free energy correlations between reactions having the same mechanisms. It is well known that there are linear free energy correlations between reactions having the same mechanism. On the other hand, the relationship between the observed rate constant and the ionization potential (IP) or the bond dissociation energy (BDE) of moleculae is also a useful tool to evaluate abstraction or addition reactions. In general, the reaction rate constants correlate with bond dissociation energies (BDE) for abstraction reactions or with ionization potentials (IP) for addition reactions. The suggested hydrogen abstraction mechanism for the reaction of CCN with normal alkanes is strengthened by the following analysis of the BDE correlation and linear free energy correlations with other reactions known to proceed via hydrogen abstraction.

(A) BDE Correlation. In the case of abstraction reactions, it is reasonable to anticipate that bond dissociation energies (BDE) should correlate with observed rate constants.[23,24] Under our experimental conditions, we cannot distinguish between primary and secondary hydrogens, and we only give the overall reaction rate constants for both primary and secondary hydrogen atoms. The rate constants should thus correlate with average bond dissociation energies. The average bond dissociation energies, weighted by the number of the primary and secondary hydrogens of the selected normal alkanes, are given in Table 1 and are qualitatively correlated with the CCN ($\tilde{X}^2\Pi_i$) abstraction rates. A least-squares fit was performed on these data and found to give a linear correlation, as shown Figure 3. The linear correlation between the natural logarithm of the reaction rate constant and the BDE means that hydrogen abstraction reactions are plausible mechanisms.

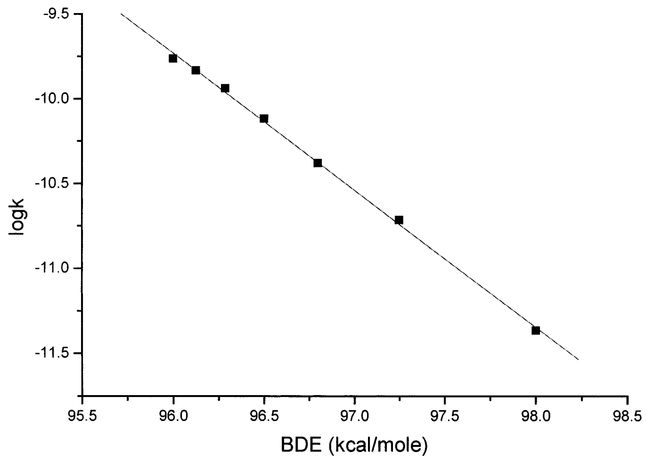

Figure 3. Bond dissociation energy (BDE) correlation for CCN hydrogen abstraction reactions. The line is the least-squares best fit of the data.

(B) Free Energy Correlation. Additional support is provided by a linear free energy correlation.[25] These reactions are analogous to CN[14,15] and OH[21,22] reaction mechanisms. It has been well established that CN and OH react with hydrogen and saturated hydrocarbons by hydrogen abstraction. The rate constants for CN and OH reacting with small normal alkanes have been measured by different methods[14,15,21,22] and are listed in Table 1. It is well known that there are linear free energy correlations between reactions having the same mechanism. Plots of log *k* (CN) and log *k* (OH) versus log *k* (CCN) are linear (Figure 4) as expected, which confirms the hydrogen abstraction mechanism for the reaction of CCN ($\tilde{X}^2\Pi_i$) radicals with normal alkanes.

On the basis of the bond dissociation energy (BDE) correlations and the linear free energy correlation analysis, we suggest that the reaction of CCN with saturated hydrocarbons occurs via the mechanism of hydrogen abstraction, which is similar to the reactions of CN and OH radicals with saturated hydrocarbons. Future theoretical calculations and experimental studies, for instance, the measurement of HCCN products, will be helpful to better understand the mechanism for reaction of CCN with saturated hydrocarbons.

Conclusion

For the first time, the CCN radical rate constants for gas-phase reactions with normal alkanes have been measured at room temperature from the decay of the CCN radical using the LP-LIF technique. The CCN radical was generated by the photolysis of Cl_3CCN with the focused output from the fourth harmonic of a Nd:YAG laser. The reaction rate increases with carbon chain length. A comparison with the corresponding

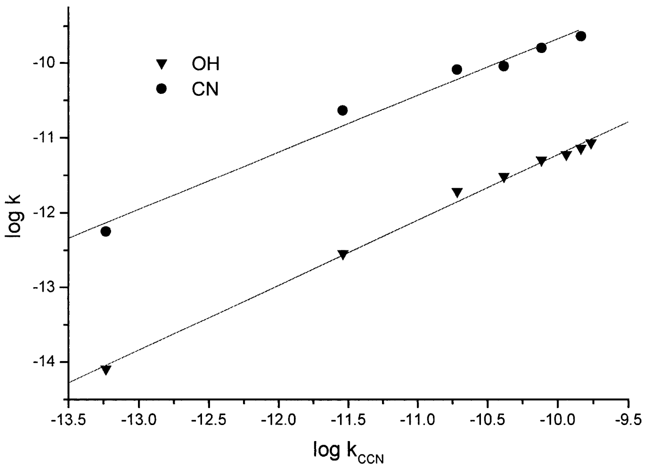

Figure 4. Linear free energy correlation of the rate constants for CCN reactions with CN (●) and OH (▼) radical reactions, which are known to proceed via hydrogen abstraction reaction. The solid lines are least-squares best fit.

reactions of CN and OH radicals with normal alkanes, suggests that the reaction of CCN with small normal alkanes proceeds via the mechanism of hydrogen abstraction. The plausibility of the suggested mechanism is strengthened by bond dissociation energy (BDE) correlations and linear free energy correlations. Future measurements, for instance, of the HCCN product, should provide valuable mechanistic information about the reaction of CCN radicals with alkanes.

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