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Reaction rates of the CN radical with diacetylene and dicyanoacetylene

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Abstract

Rates of CN reactions with diacetylene (DA) and dicyanoacetylene (DCA) have been measured at room temperature from the decay of the CN radical at various sample pressures by laser induced fluorescence. The rate constants are $(4.2 \pm 0.2) \times 10^{-10}$ and $(5.4 \pm 0.2) \times 10^{-13}$ in units of cm^3 $molec^{-1}$ s^{-1} for DA and DCA, respectively, which follow the general pattern of CN reactions with hydrocarbons and nitriles. In the lower temperature circumstellar envelopes and Titan's atmosphere, the CN reaction with C_4H_2 may be more important, while the reaction with C_4N_2 may become less important.

1. Introduction

Cyanoacetylene (HC_3N) has recently been discovered in interstellar clouds [1] and in Titan's atmosphere [2]. Other cyanopolyynes have been discovered in circumstellar envelopes of carbon rich stars [3–6]. Since then a photochemical model involving rapid reactions of CN and C_2H with acetylene and other hydrocarbons has been proposed by Cherchneff and coworkers [3,4] for the formation of cyanopolyynes and polyacetylenes. Early on it was suggested that the chain molecules were produced mainly by ion–molecule reactions because such reactions are usually extremely fast. However recent modelers [3–6], based on new kinetic experimental evidence, have suggested that the key processes may be rapid (neutral) radical–molecule reactions. Since the density of neutral species is 10 to 100 times larger than that of ions, the overall rate of neutral reactions may be larger than that of ion molecule reactions [3,4].

The reaction of CN with hydrocarbons and nitriles [7–9] may be divided into three categories: (a) Abstraction of hydrogen atom from saturated hydrocarbons, $CN + RH \rightarrow HCN + R$, where RH is saturated hydrocarbon. (b) An addition to an unsaturated C–C bond followed by the production of H atoms, $CN + C_2H_2 \rightarrow HC_3N + H$; The reaction is fast, on the order of 10^{-10} cm^3 $molec^{-1}$ s^{-1}, and has a small negative temperature dependency. (c) An addition to the CN bond followed by H elimination, $CN + HCN \rightarrow H(CN)_2 \rightarrow C_2N_2 + H$ or an addition followed by polymerization, $CN + C_2N_2 \rightarrow C_3N_3 \rightarrow nC_3N_3$. The reaction is slow, on the order of 10^{-14} cm^3 $molec^{-1}$ s^{-1} and is independent of the total pressure.

In this work we present results of the measurement of reaction rates of CN with C_4H_2 and C_4N_2 based on laser induced fluorescence (LIF) of CN and

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discuss the reaction mechanism for CN radicals with DA and DCA.

2. Experimental procedure

The detailed description of the experimental procedure is given [12–14]. The CN radical is produced by the photolysis of a small amount of BrCN mixed with 1 mTorr of C_4H_2 (or 10 to 300 mTorr of C_4N_2) and 30 Torr of N_2. The mixture flowed slowly through the reaction cell, which is made from stainless steel with CaF_2 windows and long baffle arms to reduce the scattered laser light. Nitrogen is used to slow diffusion to the walls and to relax the CN rotational excitations.

The photolysis light source is a weak (10^{-5} J cm^{-2} = 10^{13} photon cm^{-2}) unfocused ArF excimer laser (AQX-150, MPB Technologies) at 193.3 nm. The CN radical concentration is less than 10^{10} molec cm^{-3} estimated from the incident light intensity, absorption cross section (10^{-19} cm^2 $molec^{-1}$) [15] and pressure of BrCN (less than 100 mTorr). The partial pressure of DA in the cell ranged from 0.1 mTorr to 5 mTorr and that of DCA in the range from 10 to 300 mTorr. The partial pressure of BrCN was at least two orders of magnitude less than that of DCA. The total pressure ranged from 20 to 50 Torr. The CN concentration is much less than that of a reactant concentration and the CN decay satisfies the pseudo first order condition.

The P branch lines of the (0–0) vibrational band of the CN violet system were excited at about 388 nm. The excitation source was a Molectron UV-400 nitrogen laser pumped DL-14 dye laser using a solution of BBQ in P-dioxane. The 0.2 cm diameter dye laser beam was counter-propagated, collinear with the ArF laser. The diameter of the dye laser beam was set much smaller than that of the photolysis laser to minimize diffusion effects. LIF was observed in a direction perpendicular to the laser beam. Even at the lowest total pressure used in this work the nascent CN rotational distributions were relaxed after 5 μs. Since the distribution of CN radicals is always thermal during the interval in which the decay is measured, it is unimportant which rotational line is measured.

The CN decay rate was obtained by measuring the intensity of a given rotational line (usually $P = 8$) as a function of the delay time between the 193 nm laser and the dye laser. The delay time ranged from 5 to 250 μs depending on reaction rates. Even at the smallest total pressure used in this work, the CN rotational distribution was relaxed after 5 μs. The CN radical decay could be fitted to a single exponential decay. The data were fitted by a least squares analysis of

$$I = A\exp(-k_1 t) + B,$$

where I is the measured LIF intensity, k_1 is the pseudo first order decay rate constant arising from all removal processes, 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

$$k_1 = k_0 + k_2[\mathrm{R}],$$

where k_2 is the bimolecular rate constant for the reaction of CN with a reactant R, and k_0 is the removal rate constant for CN arising from the CN decay processes such as diffusion and recombination.

3. Sample preparation

Diacetylene was prepared from 1, 4-dichlorobutyne-2 in ethyl alcohol to which 40% aqueous sodium hydroxide solution was added dropwise [16,17]. The diacetylene evolved was carried away in a stream of nitrogen through 13% aqueous sodium hydroxide solution, dried over calcium chloride and condensed in a liquid nitrogen until use.

Dicyanoacetylene was synthesized [18] from thoroughly ground 5 g of acetylene dicarboxamide mixed with 30 g of sand, to which 15 g of P_2O_5 was added. The flask was evacuated and heated to 220°C in a silicone bath. The resulting C_4N_2 was collected by a tube at liquid nitrogen temperature. Major detected impurities by the mass spectrometer were CO_2 which was removed by a fractional distillation from −50°C to liquid nitrogen. C_4N_2 is 35 Torr at 0°C.

BrCN, obtained commercially, was purified by bulb to bulb distillation to liquid nitrogen temperature. Nitrogen gas has a stated purity of 99.9999% and was used directly from the cylinder.

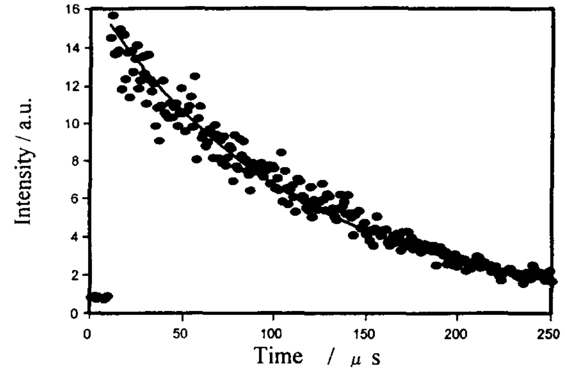

Fig. 1. Decay of CN LIF signal in mixtures of C_4H_2 = 0.7 mTorr, BrCN = 0.05 mTorr and N_2 = 30 Torr.

DA and DCA were purified by repeated bulb to bulb fractional distillation. The purity was checked by IR and mass spectrometry.

4. Results and discussion

4.1. The reaction of CN with C_4H_2

Fig. 1 shows a plot of typical CN LIF intensity as a function of decay time in μs, when mixtures of 0.05 mTorr BrCN, 0.5 mTorr C_4H_2 and 30 Torr of N_2 are irradiated by the 193.3 nm laser line.

The pseudo first order decay rates of CN, k_1, as a function of DA concentration are plotted in Fig. 2.

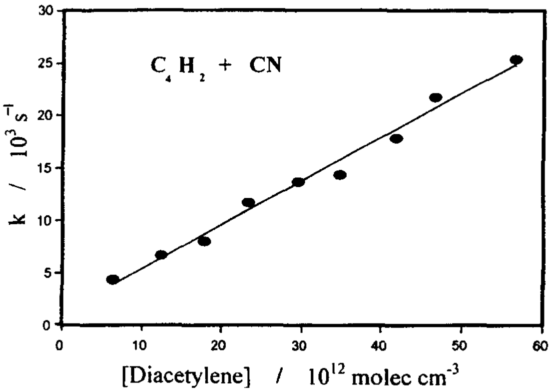

Fig. 2. A plot of pseudo first order decay rates of CN as a function of diacetylene concentration. The least squares analysis of the plot gives a bimolecular rate constant of $(4.2 \pm 0.2) \times 10^{-10}$ cm^3 $molec^{-1}$ s^{-1}.

Table 1
The bimolecular rate constant of CN with C_4H_2, and C_4N_2

Compounds	Pressure range (10^{13} molec cm^3)	Rate constant 10^{-13} cm^3 $molec^{-1}$ s^{-1}
C_4H_2	0-6	4200 ± 100
C_4N_2	0-2000	5.4 ± 0.2

The bimolecular rate constant obtained from a linear least-squares analysis of the slope is $(4.2 \pm 0.2) \times 10^{-10}$ cm^3 $molec^{-1}$ s^{-1} and is listed in Table 1.

There are three possible channels for the reactions with diacetylene.

$$\mathrm{CN} + \mathrm{C_4H_2} \rightarrow \mathrm{H} + \mathrm{HC_5N}, \quad \Delta H_f = -19\,\mathrm{kcal\,mol^{-1}}, \tag{1a}$$

$$\mathrm{CN} + \mathrm{C_4H_2} \rightarrow \mathrm{HCN} + \mathrm{C_4H}, \quad \Delta H_f = -3\,\mathrm{kcal\,mol^{-1}}, \tag{1b}$$

$$\mathrm{CN} + \mathrm{C_4H_2} \rightarrow \mathrm{HC_3N} + \mathrm{C_2H}, \quad \Delta H_f = +10\,\mathrm{kcal\,mol^{-1}}. \tag{1c}$$

The heat of formation values are taken from Glicker and Okabe [17], Benson [19] and Lias et al. [20] or calculated using group additivity for HC_5N [19]. Only reaction (1a) is highly exothermic and other reactions can be neglected.

The CN reaction with DA follows the general pattern of CN reactions with unsaturated hydrocarbons, that is, the CN addition to an unsaturated C–C bond followed by H atom elimination [7–11,21,22]. Reaction (1a), the CN addition to the unsaturated C–C bond followed by the H atom elimination, is the predominant reaction and reaction (1b), the HCN abstraction, is not important. Similar reactions have been studied between CN and many unsaturated hydrocarbons [7–11,21–23]. In general the CN reactions occur almost in every collision and have small negative temperature dependencies.

4.2. The reaction of CN with C_4N_2

The reaction of CN with C_4N_2 is about 10^3 times slower than that with C_4H_2 as shown in Table 1 and Fig. 3. The reaction with C_4N_2 may be the CN addition to the triple bond forming the stable C_5N_3 adduct, which may return to the reactants or be

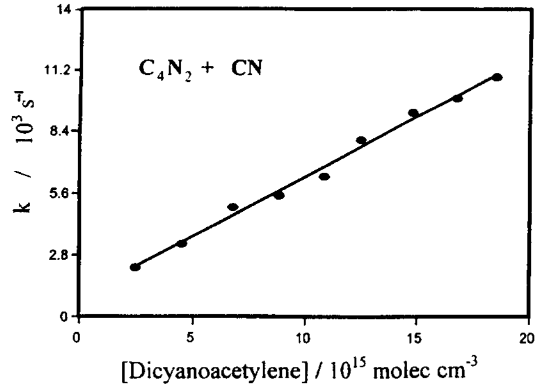

Fig. 3. A plot of pseudo first order decay rates of CN as a function of dicyanoacetylene concentration; the least squares analysis of the plots gives a bimolecular rate constant of $(5.4 \pm 0.2) \times 10^{-13}$ cm^3 $molec^{-1}$ s^{-1}.

stabilized by collisions, followed by polymerization. The observed CN decay may be attributed to the reaction with BrCN. The decay time of CN with BrCN is, however, about a second calculated from 0.1 mTorr of BrCN and the rate constant of 3×10^{-13} cm^3 $molec^{-1}$ s^{-1} [11], while the observed decay time is about 0.1 ms.

The CN reaction with DCA is about 500 times slower than the reaction with acetylene as shown in Table 2. The CN reaction with DCA may be similar to those with HCN and cyanogen. It is reported [7–11] that the mechanism for CN reaction with HCN and C_2N_2 can be schematically represented by

$$\mathrm{CN} + \mathrm{HCN} \rightleftharpoons \mathrm{H(CN)}_2^* \rightleftharpoons \mathrm{H} + \mathrm{C_2N_2}, \tag{2a}$$

$$+M \rightarrow \mathrm{HC(N)CN}, \tag{2b}$$

$$\mathrm{CN} + \mathrm{C_2N_2} \rightleftharpoons \mathrm{C_3N_3^*} \rightarrow \mathrm{N{=}C(CN)_2}, \tag{2c}$$

where * means the vibrationally excited adducts. Similarly, the mechanism for DCA can be expressed by

$$\mathrm{CN} + \mathrm{C_4N_2} \rightleftharpoons \mathrm{C_5N_3^*} \rightarrow \mathrm{C_2N_2} + \mathrm{C_3N}, \tag{2d}$$

$$+M \rightarrow \mathrm{C_5N_3}. \tag{2e}$$

Reaction (2d), endothermic by 19 kcal mol^{-1}, does not occur. The rate of CN with C_4N_2 is 20 times faster than the rate with HCN [10], as shown in Table 2. The result may indicate that the back process, $C_5N_3^* \rightarrow CN + C_4N_2$, has a higher potential barrier or that the C_5N_3 adduct is more stable than $H(CN)_2^*$.

Table 2
The rate constant for the reaction of CN radicals with acetylene, diacetylene, and some nitriles at room temperature

Reactant	Rate constant 10^{-13} cm^3 $molec^{-1}$ s^{-1}	Ref.
C_2H_2	2500	[7]
C_4H_2	4200 ± 100	this work
HC_3N	170	[12]
C_4N_2	5.4	this work
HCN	0.24	[10,11]
C_2N_2	0.031	[10]

4.3. The formation process of CA and DCA in the Titan atmosphere and that of nitriles in the circumstellar envelope of carbon-rich stars

Cherchneff and coworkers [3–6] have proposed a mechanism for the formation of cyanopolyynes based on the rapid CN radical reactions with unsaturated hydrocarbons.

$$\mathrm{CN} + \mathrm{C_2H_2} \rightarrow \mathrm{HC_3N} + \mathrm{H}, \quad \Delta H_f = -22\,\mathrm{kcal\,mol^{-1}} \tag{3}$$

In analogy with reactions (1a–c), the main channel of CN reaction with cyanoacetylene may be the CN addition to the unsaturated bond followed by H elimination,

$$\mathrm{CN} + \mathrm{HC_3N} \rightarrow \mathrm{C_4N_2} + \mathrm{H}, \quad \Delta H_f = -8\,\mathrm{kcal\,mol^{-1}}. \tag{4}$$

Both reactions (3) and (4) are rapid (see Table 2) and the product by process (3), CA, would further react with CN to form DCA by process (4).

The rate constant of process (4) is $(170 \pm 4) \times 10^{-13}$ cm^3 $molec^{-1}$ s^{-1}, which is 25 times slower than the reaction with C_4H_2 (Table 2). If the H elimination from the adduct is as fast as the reaction (1a), the rate constant for HC_3N must be half as much as the rate for C_4H_2, because HC_3N has only one H atom. Therefore the slower rate indicates that the barrier for the H elimination increases with CN substitution of C_2H and the adduct becomes more stable.

Table 3
The rate constant for the reaction of CN radicals with unsaturated hydrocarbons at room temperature

Reactant	Rate constant 10^{-10} cm^3 molec^{-1} s^{-1}	Ref.
C_2H_4	2.5	[7-11]
C_2H_2	2.5	[7-11]
CH_3C_2H	2.1	[21]
C_3H_6	3.4	[7-11]
$C_2H_3C_2H$	4.4	[7-11]
$C_2H_3C_2H_3$	4.5	[23]
C_4H_2	4.2	this work

The CN additions to the unsaturated C–C bonds [7–10,21–23] have been studied. Rate constants at room temperature are listed in Table 3. It is common for these reactions to have a negative temperature dependence [7–10,21–23]. Table 3 shows that the reaction rate does not depend on the C–H bond energy. For example the bond energy (BE) in C_2H–H is 133 kcal mol^{-1}, while the BE in C_2H_3–H is 102 kcal mol^{-1} [20]. The CN reactions with C_2H_2 and C_2H_4 have comparable rates. Hence Lin et al. [7–11] suggest the CN insertion to the C–C unsaturated bond followed by the H elimination, and not an abstraction by CN to form HCN product. The rate of CN with diacetylene observed in this study is almost equal to the other unsaturated C_4 compounds. The results indicate that the mechanism of CN reaction with diacetylene is the CN insertion–H atom elimination process. The slight increase of CN reaction rate on the chain length may indicate that the induced dipole moment by CN radicals is directly proportional to the carbon chain length.

5. Conclusions

We have directly measured the rates of CN with DA and DCA at room temperature using LIF technique. The reaction of CN with DA is extremely fast, $k = 4.2 \times 10^{-10}$ cm^3 molec^{-1} s^{-1}, and in analogy with other CN reactions with unsaturated hydrocarbons, the CN radical is added to C–C bond followed by H atom elimination. The reaction rate is comparable to that of typical ion–molecule reactions. Therefore it is concluded that the reaction of CN with DA may form HC_5N in interstellar clouds. The HC_5N may also be formed from

$$C_3N + C_2H_2 \rightarrow HC_5N + H, \qquad (5)$$

as suggested by Cherchneff et al. [3], although the reaction rate has apparently not been measured before.

The reaction of CN with DCA is relatively slow, $k = 5.4 \times 10^{-13}$ cm^3 molec^{-1} s^{-1}. If C_4N_2 is produced near carbon-rich stars, C_4N_2 would be a final product.

Since CN reaction rates with unsaturated hydrocarbons increase with a decrease in temperature, the reaction with C_4H_2 becomes more important at lower temperatures, while the reaction with C_4N_2 may be less important at lower temperatures in analogy with the CN reactions with HCN and C_2N_2.

We plan to measure the reaction rate at lower temperature regions down to −140°C.

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