Photochemistry of Cyanoacetylene at 193.3 nm

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Cyanoacetylene (CA) is an important minor constituent in the Titan atmosphere and is present in the interstellar medium. The absorption cross section of CA has been measured in the region from 190 to 255 nm with a resolution of 1 nm. The photochemistry of CA at 193.3 nm has been studied using a quadrupole mass spectrometer and a Fourier transform infrared spectrometer for product analysis. From the photolysis of HC_3N-D_2 and HC_3N-CD_4 mixtures and a plateau value of 0.3 for the quantum yield (QY) of DC_3N ($C_3N + D_2 \rightarrow DC_3N + D$), it is concluded that the main dissociation process is $HC_3N + h\nu \rightarrow H + C_3N$ with a QY of 0.30 ± 0.05 and a minor process is $HC_3N + h\nu \rightarrow C_2H + CN$ with a QY equal to or less than 0.02. The remaining process is the formation of metastable CA (a triplet or carbene). The photolysis of CA induces a noticeable pressure decrease and a concomitant formation of a mist. The QY of CA disappearance is 4.5 ± 0.5 , which is much higher than that of diacetylene (QY = 2.0 ± 0.5) and of acetylene (QY = 2.3). The rapid mist formation in CA may explain a haze observed in the Titan atmosphere. A detailed mist formation process is not known. The C₃N radical disappears partially by $C_3N + HC_3N \rightarrow C_6N_2 + H$ and $2C_3N \rightarrow C_6N_2$. To explain the formation of minor products, HCN, C_2H_2 , HC₅N, and C_4N_2 , two processes involving an unspecified CA metastable state or states may be proposed: $HC_3N* + HC_3N \rightarrow HC_5N + HCN$ and $C_4N_2 + C_2H_2$.

Introduction

The atmosphere of Titan, the largest moon of Saturn, consists mainly of N₂ and CH₄, while substantial amounts of H₂ have escaped from the atmosphere because of the low gravitational field of Titan. Titan is the only solar system object besides the Earth to have a substantial nitrogen atmosphere. The minor constituents are C₂H₆, C₃H₈, C₂H₂, HCN, CH₃C₂H, C₄H₂, HC₃N, and C₂N₂. These products are most likely formed as a result of complex reactions initiated by the photolysis of methane and dissociation of N₂ by cosmic rays.^{1,2a}

Similar photochemical processes may have occurred in the prebiotic Earth atmosphere.

The surface of Titan is covered by orange-colored haze which is a polymer formed probably by chemical reactions involving unsaturated hydrocarbons and nitriles. The photochemistry of unsaturated hydrocarbons and nitriles has been studied by many workers and is summerized in ref 1. Recently, the photochemistry of diacetylene, another constituent in the Titan atmosphere, has been studied by Glicker and Okabe³ and by Bandy et al.⁴ It has been shown tht the quantum yield (QY) of primary dissociation is much less than 1, and reaction of metastable diacetylene is important. Similar results have been found for acetylene photolysis at 193 nm, where the QY of dissociation is only 0.3 and the reaction of metastable acetylene to form diacetylene is $0.6.^{5a}$ On the other hand, the QY of dissociation of unity is obtained for methylacetylene at 193 nm,⁶ in which the most important process is $CH_3C_2H + h\nu \rightarrow CH_3C_2 + H$.

Cyanoacetylene (CA) and its radical, C_3N , have been found in the interstellar medium^{1,2,7,8} by radioastronomy. Cherchneff and Glassgold^{7a,b} have postulated that the C_3N radical reacts rapidly with C_2H_2 , $C_3N + C_2H_2 \rightarrow HC_5N + H$, similar to the reaction $CN + C_2H_2 \rightarrow HC_3N + H$.

Halpern et al.⁹ conclude that the QY of HC₃N + $h\nu \rightarrow$ C₂H + CN is about 0.05, and HC₃N + $h\nu \rightarrow$ H + C₃N is the main

dissociation process. Apparently, the reaction rate of C₃N with hydrocarbons has not been measured before. Kolos et al.¹⁰ have not found the UV absorption of C₃N in the 377–580 nm region. Sadlej and Roos¹¹ conclude from quantum mechanical calculations that transition intensities to the excited states, B²II (3.9 eV) and C² Σ (5.7 eV), may be too weak. Nevertheless, Cherchneff and Glassgold⁷ believe that the reactions of the C₃N radical with cyanopolyynes and acetylenes proceed with almost every collision. The UV absorption spectrum of CA has been measured and analyzed by Job and King.^{12a,b} The spectrum in the region 230–270 nm has been assigned to the transition from the ground state ¹ Σ ⁺ to a nonlinear planar excited state, ¹A". The stronger absorption in the region 200–230 nm is ascribed to the transition from the ground state to the linear excited state ¹ Σ ⁻ (or ¹ Δ).

Fluorescence from CA was observed from absorption in both the A-X (${}^{1}A'' \leftarrow {}^{1}\Sigma^{+}$) and B-X (${}^{1}\Delta \leftarrow {}^{1}\Sigma^{+}$) region.^{5b} The fluorescence yield excited in the A-X region is 150 times stronger than that in the B-X region. The fluorescence spectrum excited in the A region lies in the 300 nm region with a lifetime of 1.6 ns and has no structure, while the fluorescence produced in the B region has a double-exponential decay of 1 and 20 ns in the 300-400 nm region.

The purpose of this study is to find the QY of the photochemical primary process of CA at 193.3 nm and the QY of disappearance of CA. The QY measurements are based on reactant and product analysis by a quadrupole mass spectrometer and the Fourier transform infrared (FT-IR) method. Because of a rapid buildup of deposit on the window surface and of mist inside the reaction cell, the number of photons absorbed in the cell by CA has to be corrected accordingly.

Experimental Details

The reaction cell was directly connected with the mass spectrometer leak into the ionization chamber. It was found that the intensity of the parent peak of CA in the mass spectrometer was linearly proportional to the cell pressure of

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CA in Torr. The yield of a product is expressed as the ratio of the peak intensity of the product to that of CA (which was about 20% less after photolysis), using a commercial quadrupole mass spectrometer (AMETEK, MA200M, mass range 1-200, 30 eV). A light source was a 193.3 nm ArF excimer laser (AQX-150, MPB Technologies). Mass spectrometric intensities of CA and hydrogen are calibrated using pure samples. FT-IR intensities of HCN and C_2H_2 are calibrated at 712 and 730 cm⁻¹, respectively, with pure samples by a Perkin-Elmer Model 1600 spectrometer. The QY of products is given as the ratio of product yield (the number of molecules produced by photolysis) to the number of photons absorbed by CA. The absorbed photon number is obtained from the yield of CO (=0.95) produced from the photolysis of acetone at 193.3 nm¹³ contained in the cell (15 cm path, 3.8 cm diameter) placed behind the reaction cell. The 193 nm laser beam was simultaneously directed to one acetone cell to measure the integrated incident light intensity and to another placed behind the sample cell (30 cm, 3.8 cm diameter) using a beam splitter as described before.^{5a,6} Acetone pressures of 7 Torr or more absorbed 99.9% of the 193 nm light in the 15 cm pass. The pressure of CO produced was measured by a capacitance manometer (MKS Baratron 220C). Typically 300 laser shots of about 3 mJ cm⁻² (3 \times 10¹⁵ photons cm⁻²) or less were used to decompose 20% of CA at a typical pressure of 1.5 Torr. The decomposition was accompanied by a decrease of gas pressure from 1.5 to 1.3 Torr and a concomitant formation of films on windows and the mist in the gas phase, suggesting a rapid polymerization of CA gas. To obtain the correct number of photons absorbed by CA, it was necessary to consider the transmission decrease by the windows (about 20%) and the decrease of transmission by the scattering of the beam by the mist formed in the gas phase. It was found that while the absorption cross section was constant below a pulse rate of 0.25 Hz, it started to increase almost linearly above 0.25 Hz. The concomitant gas phase mist formation was observed. It is likely that the increase is caused by the scattering of the laser beam by the mist. It takes longer than 4 s before the mist diffuses out of the laser beam. Thus, the QY obtained is based on pulse intervals longer than 4 s.

The CA sample, obtained commercially, was purified by bulbto-bulb distillation at about -77 °C to remove impurities (mostly acetone^{2b}) which contribute to lines at 195 nm and those above 200 nm in the UV and 1247 and 1776 cm⁻¹ in the IR region.

Results and Discussion

Absorption Cross Section. The absorption of CA was measured by a Cary 2390 (Varian) spectrophotometer with a resolution of 0.2 nm over the range from 190 to 280 nm. The absorption cell (15 cm path) with two quartz windows attached was used. CA samples (~10 Torr) were employed. Figure 1 shows the absorption spectrum. Cross section values are given in Table 1. The cross section of CA at 193.3 nm was measured by use of both the spectrophotometer with 1 nm resolution and the ArF light source and an acetone actinometer. The average cross section is $(3.3 \pm 0.2) \times 10^{-19}$ cm² molecule⁻¹.

Photochemical Processes in Cyanoacetylene. *Photodissociation Processes.* Two dissociation processes may be considered at 193.3 nm photolysis

$$HC_3N + h\nu \rightarrow H + C_3N \tag{1}$$

$$HC_3N + h\nu \rightarrow C_2H + CN \tag{2}$$

Bond dissociation energies in CA have not been accurately known. Fransisco and Richardson¹⁴ have recently calculated



Figure 1. Absorption cross sections of HC_3N In the 190–250 nm region (resolution, 1 nm). The peak assignments and values of the absorption cross section are given in Table 1.

 TABLE 1: Absorption Cross Section^a of Cyanoacetylene in the 190–260 nm Region

λ (nm)	cross section $(10^{-19} \text{ cm}^2 \text{ peak (P)})$ molecules ⁻¹ base e) or valley () peak assignt ^b	
240.0	0.077		peur ussigne	
248.0	0.067	D	-1	
227.4	1.0	Р	5_{1}^{1}	
226.4	0.6	V	1	
224.3	4.6	Р	5_0^1	
222.9	0.6	V		
221.6	1.6	Р	$6_0^1, 7_0^2$	
220.1	0.9	V		
217.2	1.6	Р	$2_0^1, 5_1^1$	
216.1	1.0	V	0. 1	
214.2	8.6	Р	$2_0^1, 5_0^1$	
212.9	1.0	V	0, 0	
211.8	3.5	Р	$2_0^1, 6_0^1, 7_0^2$	
210.5	1.6	V	0, 0, 0	
209.8	2.3	Р	$2_0^2, 5_1^1$	
207.9	1.8	V	0, - 1	
205.1	7.5	Р	$2_0^2, 5_0^1$	
203.6	2.0	V	0, 0	
203.1	3.4	Р	$2_{0}^{2}, 6_{0}^{1}, 7_{0}^{2}$	
201.4	1.8	V	-0, -0, -0	
201.1	2.3	Р	2^{3}_{2} $5^{1}_{1}(d)$	
199.0	1.8	V	- 0, b (d)	
196.6	4.5	Р	2^{3}_{2} $5^{1}_{2}(d)$	
194.4	25	V	20, 50(d)	
194.1	3.7	P	2^{3} 6^{1} 7^{2}	
193.3¢	3 3	v	$z_0, 0_0, 7_0$	
190.6	21	v		
170.0	<i>2</i> .1	•		

^{*a*} Error limit = ± 0.2 nm. ^{*b*} Reference 12b unless otherwise noted. ^{*c*} (3.3 ± 0.2) × 10⁻¹⁹ at 193.3 nm laser line; see text. ^{*d*} Reference 2a.

the bond energies by ab initio molecular orbital theory and obtained $D_0(H-C_3N) = 138 \pm 2$ and $D_0(HC_2-CN) = 146.9 \pm 2$, both in kcal mol⁻¹.¹⁴ On the other hand, Mains¹⁵ calculated $D_0(H-C_3N) = 119.9$ kcal mol⁻¹, in agreement with an experimental threshold of 240 nm or 119 kcal mol⁻¹ for the H + C₃N production.¹⁶ From the heats of formation of CN (101), HCC (127), HC₃N (85) in kcal mol⁻¹, $D_0(HC_2-CN) = 143$ kcal mol⁻¹ can be calculated,¹⁷ in good agreement with ref 14. Since process 2 requires more energy than process 1, it is likely that process 1 is the main dissociation process.

To show that process 1 is more important, we used $CA-D_2$ and $CA-CD_4$ mixtures to find products DC_3N (from process 1) nd C_2HD and DCN (from process 2).

Photolysis of $CA-D_2$ and $CA-CD_4$ Mixtures. The QY of process 1, $HC_3N + h\nu \rightarrow H + C_3N$, may be obtained from the yield of HCl in the photolysis of $HC_3N + Cl_2$ mixtures, similar to the case of methylacetylene photolysis.⁶ However, CA disappears rapidly in the FT-IR spectrum, as soon as Cl_2 is added, probably because of the formation of an addition product.

TABLE 2: Photolysis of HC₃N at 193.3 nm and Mass Spectrometric Analsysi of Products without and with Added D₂ (HC₃N Pressure, 1.5 Torr; Ionization Voltage, 30 eV; Laser Intensity, \leq 3 mJ cm⁻²; Total Shots, 300)

		pea	k ratio of product to CA (%)					
mass to	type	before	after photolysis ^{a} at a D ₂ press. (Torr) of					
charge ratio	of peak	photolysis	0	100	200	400	600	
1	Н	2.2	2.8	3.4	2.9	2.8	2.8	
26	CN, C_2H_2	4.4	4.6	7.2	6.0	5.6	5.4	
27	HCN, C_2HD^b	0.53	0.86	5.8	7.5	7.1	6.3	
28	N ₂ , DCN	1.02	1.02	1.02	1.02	1.02	1.02	
50	C ₃ N	71.0	51.0	50.0	49.0	48.0	49.0	
51	HC ₃ N	100.0	78.0	78.0	78.0	78.0	78.0	
52	CA isotopes	5.0	5.0	5.0	5.0	5.0	5.0	
	DC ₃ N	0	0	4.0	5.7	5.4	4.6	
75	HC ₅ N	0	0.4	0.8	0.3	0.2	0.1	
76	$C_4 N_2^c$	0	0.5	1.9	0.5	0.4	0.3	
100	$C_6N_2^d$	0	0.5	0.1	0.05	0.1	0.04	

^{*a*} Peak intensity ratios of products to the remaining CA (78%). ^{*b*} C₂HD is detected by FT-IR, when D₂ is added; an estimated QY of C₂HD is less than 0.02. ^{*c*} Contribution of the parent peak, C₄N₂ (*m/e* = 76), to fragment peaks, C₃N, C₂N (*m/e* = 50, 38), is less than 20% (ref 18), that is, less than 0.1. Likewise, the contribution of C₆N₂ to fragment peaks (C₅N, C₃N, *m/e* = 74, 50) would be less than 0.1. ^{*d*} The addition of D₂ removes most C₆N₂ product.



Figure 2. QY of DC₃N from the photolysis of HC₃N-D₂ (or CD₄) mixtures at 193.3 nm as a function of added gas pressure of D₂ (or CD₄); HC₃N, 1.5 Torr. The QY of DC₃N increases and levels off at 0.3 ± 0.05 , as the D₂ pressure increases over 200 Torr. The QY increases to 0.3 above 50 Torr for CD₄.

Therefore, we use the reaction $C_3N + D_2 \rightarrow DC_3N + D$ to obtain the QY of process 1 from the yield of DC_3N .¹⁶

Table 2 presents the mass peak values of photolysis products of CA with and without D_2 additions, where the CA pressure is 1.5 Torr and D_2 pressures are 100, 200, 400, and 600 Torr. The peak values were measured after pumping out D_2 at -195 °C or CD₄ at -100 °C.

A large increase of DC₃N (m/e = 52) signal in the mass spectrometric analysis when D₂ is added (Table 2) shows that process 1, HC₃N + $h\nu \rightarrow$ H + C₃N, is the major process. We may obtain the QY of process 1 on the assumption that the DC₃N signal has the same intensity as the HC₃N signal. In the case of C₆H₆ and C₆H₅D the same peak sensitivity (111 vs 112) is observed,¹⁸ where the fragmentation of the parent peak is relatively small. Since HC₃N shows also a small fragmentation (Table 2), it may be justified to assume that DC₃N has approximately the same sensitivity as HC₃N.

Figure 2 shows the QY of DC₃N (m/e = 52) as a function of D₂ pressure. The QY of DC₃N increases with an increase of pressure and reaches a plateau of 0.30 ± 0.05 above 200 Torr of D₂ and for CD₄ above 50 Torr. The fraction of C₃N

converted to DC_3N in the presence of D_2 (or CD_4) may be complete above 200 Torr of D_2 (and 50 Torr of CD_4).

The DCN (m/e = 28) peak intensity does not change even in the presence of 600 Torr of D₂ and 50 Torr of CD₄ (Table 2). No DCN peak was produced in FT-IR at 569 cm⁻¹. If CN is produced in process 2, HC₃N + $h\nu \rightarrow$ C₂H + CN, a fraction of CN may be converted to DCN in the presence of D₂ by the reaction

$$CN + D_2 \rightarrow DCN + D$$
 (3)

In the presence of 600 Torr of D₂, the fraction of CN converted to DCN can be calculated to be 0.13 from $k_3 = 7.2 \times 10^{-15 \ 19a}$ and $k_4 = 1.7 \times 10^{-11} \text{ cm}^3$ molecule⁻¹ s^{-1 20}

$$CN + HC_3N \rightarrow C_4N_2 + H \tag{4}$$

while in 50 Torr of CD_4 , 0.24 of CN may be converted to DCN by

$$CN + CD_4 \rightarrow DCN + CD_3$$
 (5)

since $k_5 = 1.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.^{21}$

Little change in the DCN intensity (Table 2) shown by the addition of D_2 or CD_4 indicates that the QY of process 2 may be equal to or less than 0.02, the experimental error limit.

The FT-IR spectra of photolysis products at 193.3 nm of 1.5 Torr HC₃N and 300 Torr D₂ mixtures show a small C₂HD peak at 677 cm⁻¹ and much larger DC₃N peaks at 494 and 522 cm⁻¹ after 300 shots of the laser beam.

Table 2 shows that m/e = 27 (C₂HD) increases to a plateau value, when D₂ above 100 Torr is added. The estimated QY of C₂HD from a mass spectrometric analysis, assuming an equal sensitivity for C₂H₂ and C₂HD, is equal to or less than 0.02. The C₂HD (m/e = 27) contributes to the peak from the reaction

$$C_2H + D_2 \rightarrow C_2HD + D \tag{6}$$

Since k_6 is 2.3 × 10⁻¹³ cm³ molecule⁻¹ s⁻¹,^{19b} 600 Torr of D₂ should remove at least 50% of C₂H radicals, assuming that the C₂H radical reacts with 1.5 Torr of HC₃N in every collision.

In the photolysis of $CA-C_2D_6$ mixtures, the FT-IR spectrum shows the QY less than 0.03 for C₂HD (677 cm⁻¹) and for DCN (569 cm⁻¹).

Photolysis Products and Secondary Processes Involving Radicals and Metastable State. *Photolysis Products*. Peak values of photolysis products of CA at 193.3 nm obtained by the mass spectrometer are given in Table 2 with respect to that of the remaining CA in arbitrary units. They are HCN, C₂H₂, HC₅N (monocyanodiacetylene), C₄N₂ (dicyanoacetylene), and C₆N₂ (dicyanodiacetylene). Products observed by FT-IR are HCN (1712), C₂H₂ (730), and C₆N₂ (dicaynodiacetylene, 717), in cm⁻¹.²² C₆N₂ is also observed in the UV absorption at about 272, 289, and 309 nm.²³ The approximate QYs of 1.5 Torr CA photolysis products at 193.3 nm are H₂ \leq 0.01, HCN = 0.04, C₂H₂ = 0.03, and small yields (about 0.03) of HC₅N, C₄N₂, and C₆N₂, where the H₂ mass spectrometric yield is calibrated with pure H₂. The HCN and C₂H₂ FT-IR yields are calibrated with pure samples.

Figure 3 shows the QYs of two minor products, HCN and C_2H_2 , at 193.3 nm from the photolysis of 2.5 Torr of CA as a function of N_2 pressure. The yields of the products are obtained from calibrated FT-IR yields of HCN and C_2H_2 at 712 and 730 cm⁻¹, respectively. The QY without N_2 is 0.04 and 0.03 for HCN and C_2H_2 , respectively, with an error limit of ± 0.01 . The yield of HCN increases with an increase of N_2 , while C_2H_2 decreases slightly with an increase of N_2 .



Figure 3. QYs of products HCN and C_2H_2 from the photolysis of 2.5 Torr of CA, as a function of N_2 pressure. The yields of C_2H_2 and HCN are obtained from intensities of FT-IR (730 and 712 cm⁻¹, respectively) calibrated with standard samples.

Products at the 248 nm photolysis of 5 Torr of CA are also HCN and C_2H_2 in comparable amounts with those at 193.3 nm.

Secondary Processes by Radicals. The rate constants of reactions 7 and 8

$$C_3N + D_2(CD_4) \rightarrow DC_3N + D(CD_3)$$
(7)

$$C_3N + HC_3N \rightarrow C_6N_2 + H \tag{8}$$

have apparently not been measured before, because of the difficulty in detecting C₃N. The reaction rate of C₃N with CD₄ is several times faster than that with D₂ (Figure 2.). Subsequent reactions of C₃N formed in process 1, HC₃N + $h\nu \rightarrow$ H + C₃N, must be process 8 in analogy with CN + C₂H₂ \rightarrow HC₃N + H, proposed by Yang et al.,²⁴ and CN + HC₃N \rightarrow C₄N₂ + H, suggested by Halpern et al.²⁵

The H atoms formed by process 1, $HC_3N + h\nu \rightarrow H + C_3N$, may be consumed partially by the addition to CA, $H + HC_3N$ \rightarrow products. Dicyanodiacetylene is formed partially by the combination of C₃N, process 9

$$C_3 N + C_3 N \rightarrow C_6 N_2 \tag{9}$$

and mainly by process 8. By the addition of D_2 to CA, C_6N_2 molecules formed by processes 8 and 9 disappear, as shown in Table 2, indicating that C_6N_2 is formed from the C_3N radical.

Formation of Metastable State and Its Reactions. A large fraction (70%) of photoexcited CA do not dissociate immediately and remain in an unspecified metastable state (or in an isomeric form). Although the detailed mechanism is not clearly understood, an average of four molecules disappear per one photon absorbed to produce a polymer. Ferris and Guillemin²⁶ found that tricyanobenzenes are minor products of UV photolysis, and the major product is an unspecified polymer. Clarke and Ferris¹⁶ found that CA is more likely to form a polymer than to form acetylene.

A decrease of pressure from 1.5 to 1.2 Torr suggests the formation of a polymer rather than gas phase photochemical reactions. The QY of CA disappearance is on average 4.5 \pm 0.5, which is shown in Table 3. The QY of disappearance in the gas phase is about 0.9 (processes 1, 8, and H + HC₃N \rightarrow product), and the QY of mist formatioin process is 3.6. That is, for one photon absorbed about four molecules disappear by forming a polymer, and only one molecule of CA disappears in the gas phase. Since H₂ and C₂N₂ are not found in the products (see Table 2), processes such as HC₃N* + HC₃N \rightarrow C₆N₂ + H₂ and HC₃N* + HC₃N \rightarrow C₄H₂ + C₂N₂ may be excluded, where HC₃N* means an unspecified metastable state of CA. As shown in Table 3, the addition of D₂ does not change

cyanoacetylene at 193.3 nm^{*a*} 4.3, ^{*b*} 4.0, ^{*c*} 4.0, ^{*b*} 4.8, ^{*b*} 5.5, ^{*d*} 4.2^{*b*} average 4.5 \pm 0.5 diacetylene in the UV^{*e*} 2.0 \pm 0.5 acetylene at 193.3 nm^{*f*} 2.3

^{*a*} This work; 300 shots of 3 mJ laser pulse. ^{*b*} 1.5 Torr of CA. ^{*c*} 1.5 Torr of CA + 100 Torr of D₂. ^{*d*} 1.5 Torr of CA + 400 Torr of D₂. ^{*e*} Reference 3. ^{*f*} Reference 5a. The QY is obtained from the mechanism $C_2H_2+h\nu \rightarrow C_2H + H, C_2H_2 + h\nu \rightarrow C_2H_2^*, C_2H_2^* + C_2H_2 \rightarrow C_4H_2 + H_2, C_2H + C_2H_2 \rightarrow C_4H_2 + H, H + C_2H_2 \rightarrow C_2H_3, 2C_2H_3 \rightarrow C_4H_6.$

the QY of CA disappearance, indicating that the C₃N radical is not involved in polymer formation.

To explain the products HC₅N (m/e = 75), HCN (m/e = 27), C₄N₂ (m/e = 76), and C₂H₂ (m/e = 26, see Table 2), processes 10 and 11 are proposed,

$$HC_3N^* + HC_3N \rightarrow HC_5N + HCN$$
(10)

$$HC_3N^* + HC_3N \rightarrow C_4N_2 + C_2H_2$$
(11)

The products HCN and C_2H_2 are produced even from the 248 nm excitation, corresponding to 115 kcal mol⁻¹, which is much less than the dissociation limit of CA (about 138 kcal mol⁻¹), a finding which supports that processes 10 and 11 are molecular processes. As shown in Figure 3, the HCN yield increases with an increase of N₂, while C_2H_2 decreases with an increase of N₂. The result may indicate that HCN and C_2H_2 are produced from the metastable state with different vibrational energies or from different excited states. The QYs of these products are less than 5%, and a majority of HC₃N* leads to the formation of a polymer, process 12,

$$HC_3N^* + nHC_3N \rightarrow polymer$$
 (12)

where n is 4.

Conclusion

The photochemical processes of CA, an important minor constituent in the Titan atmosphere, have been studied at 193.3 nm. The major dissociation process is $HC_3N + h\nu \rightarrow H + C_3N$ with a QY of 0.30 ± 0.05 and a minor process, $HC_3N + h\nu \rightarrow C_2H + CN$, with a QY equal to or less than 0.02. The QY is obtained from the yield of DC₃N plateau or C₂HD as a function of D₂ pressure in the photolysis of HC_3N-D_2 mixtures.

Minor photolysis products are HCN, C_2H_2 , HC_5N , C_4N_2 , and C_6N_2 . Secondary processes involving radicals and metastable state to form these products are discussed.

The major photochemical process is the formation of a metastable CA, HC_3N^* , which leads to the formation of a polymer, resulting in a pressure decrease. The QY of CA disappearance is 4.5 ± 0.5 . The efficient formation of a polymer in CA is probably a source of haze observed in the Titan atmosphere. A similar study will be extended to the photolysis of dicyanoacetylene.

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