Formation of HCN and Acetylene Oligomers by Photolysis of Ammonia in the Presence of Acetylene: Applications to the Atmospheric Chemistry of Jupiter

James P. Ferris* and Yoji Ishikawa

Contribution from the Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180-3590. *Received October 14, 1987*

Abstract: HCN is formed by the photolysis of ammonia in the presence of acetylene at room temperature. There is a 70% decrease in the yield of HCN when the temperature is lowered to 178 K and two new reaction products, acetonitrile and acetaldehyde ethylidenehydrazone (**6**), are formed. Photolysis of **6** yields acetonitrile, and the hydrogen atom initiated decomposition of acetonitrile yields HCN. Aziridine, a predicted reaction intermediate, was not detected at 298 or 178 K. Oligomers of acetylene are also formed. Oligomers formed by the photolysis of ammonia in the presence of acetylene were shown by Fourier transform infrared spectroscopy to contain NH groupings and to differ from those produced by the direct photolysis of acetylene. The possible role of these photochemical processes on the formation of HCN and chromophores on Jupiter, Titan, and comets is discussed.

The observation of HCN on Jupiter was a surprising discovery because it was not expected that carbon at the oxidation level of a carboxylic acid would be present in its highly reduced atmosphere (89% H_2).[1] The detection of lightning on Jupiter provided support for the postulate that the HCN was formed as a consequence of shock waves and electric discharges.[2,3] The levels of HCN depend on where the lightning discharges are taking place in the atmosphere, and it is the conclusion of a recent theoretical study that the discharges occur in a water cloud beneath the ammonia clouds.[4] If this conclusion is correct, then lightning would not be a likely source of the HCN.[5] A second potential source of HCN is thermal synthesis at lower, hotter levels in the Jovian atmosphere and then rapid convection of the HCN to the region above the ammonia clouds. But it was calculated that this process could not account for the levels of HCN detected above the cloud deck.[6]

The photochemical formation of HCN is an attractive alternate to synthesis by discharges or thermal reactions because the HCN would be formed directly in the region of the atmosphere where it is detected. The photolysis of ammonia in the presence of methane yields HCN,[7] presumably via the formation of methylamine.[8,9] But HCN formation is inhibited by hydrogen and other inert gases, finding that strongly suggests that this is an unlikely synthetic route on Jupiter.[10] The photochemical dissociation of both methane and ammonia and the diffusion together of the radicals formed to yield methylamine and thus HCN[11] suffers from the low levels of HCN that will be formed by this pathway.[12] It was also calculated that the amount of methylamine formed in the upper stratosphere and lower trophosphere is not sufficient to account for the levels of HCN observed on Jupiter.[13]

A variation of the above proposal is the photochemical conversion of methane to a stable but reactive compound (acetylene), which then reacts with the radicals provided by ammonia photolysis to give intermediates that are photochemically converted to HCN (1-4).[12] The advantage of this proposal is that the formation of the HCN precursor is not limited to the narrow region of the Jovian atmosphere where both methane and ammonia absorb solar radiation.[11]

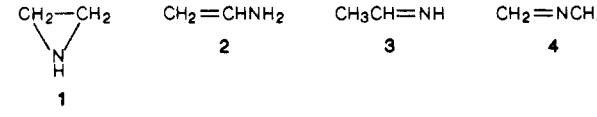
$$NH_3 \xrightarrow{h\nu} NH_2^{\bullet} + H^{\bullet} \quad (1)$$

$$H^{\bullet} + HC{\equiv}CH \xrightarrow{M} H_2C{=}CH^{\bullet} \quad (2)$$

$$H_2C{=}CH^{\bullet} + NH_2^{\bullet} \xrightarrow{M} C_2H_5N \quad (3)$$

$$C_2H_5N \xrightarrow{h\nu} HCN + CH_3^{\bullet} + H^{\bullet} \quad (4)$$

It was postulated that aziridine (**1**) was the most likely structure for C_2H_5N, the HCN precursor (3), but structures **2**-**4** were also suggested as likely possibilities.[12]



None of the proposed photoproducts[12] have been observed as products of the photolysis of ammonia in the presence of acetylene. Pyrrole is reported to be a product of the photolysis of ammonia-acetylene mixtures but no descriptions of the experiments was given.[14] Ethylamine, butyronitrile, and aniline are reported to be the products of the photolysis of 10:1 ammonia-acetylene mixtures with use of the 184.9-nm emission from a mercury lamp.[15]

Yellow, brown, and orange-brown chromophores were observed in the natural color Voyager photographs of Jupiter,[16] but the chemical structures responsible for the colors have not been identified. Initially, it was postulated that the red-brown, tarry materials formed by passing an electric discharge through methane-ammonia mixtures were the source of the colors.[17] But it appears unlikely that sporadic electric discharges will be able to form monomers and then cause the monomers to polymerize in an atmosphere that contains only 0.2% methane and 0.02% ammonia with the remainder being hydrogen and helium.[18] The constant flux of solar photons on the atmosphere above the cloud

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deck is a more plausible energy source for initiating chromophore formation.

Postulates that the Jovian chromophores are due to photochemically generated phosphorus[19] and sulfur[20] were initially convincing. Some doubt has been cast on the possible photochemical conversion of phosphine to phosphorus on Jupiter because the reaction intermediate, diphosphine, is a solid and it may condense from the Jovian atmosphere.[21-23] The possibility of the conversion of solid diphosphine to red phosphorus is a plausible alternative that has not been experimentally investigated. The phosphine mixing ratio over the Great Red Spot and the South Tropical Zone indicates that photochemically generated phosphorus is not responsible for the red color of the Great Red Spot.[24] The case for sulfur oligomers, formed by the photolysis of hydrogen sulfide, is weakened by the failure to detect hydrogen sulfide in the Jovian atmosphere.[25]

It was recently suggested that photochemically generated organic polymers should be considered as the source of the chromophores on Jupiter.[24] The photopolymerization of acetylene is one source of organic oligomers that absorb visible light (5–8).

$$HC{\equiv}CH \xrightarrow{h\nu} HC{\equiv}C^{\bullet} + H^{\bullet} \quad (5)$$

$$HC{\equiv}C^{\bullet} + HC{\equiv}CH \rightarrow HC{\equiv}CC{\equiv}CH + H^{\bullet} \quad (6)$$

$$HC{\equiv}CC{\equiv}CH \xrightarrow{h\nu} HC{\equiv}CC{\equiv}CH^{*} \quad (7)$$

$$HC{\equiv}CC{\equiv}CH^{*} + C_2H_2 \rightarrow C_6H_2 + H_2 \quad (8)$$

The extent of chromophore formation is decreased markedly by the addition of hydrogen.[26] This inhibition is probably due to the rapid rate of reaction of the acetylenic radical intermediates with hydrogen so that they do not react appreciably with the lower concentration of acetylene present. The photochemical condensation of any diacetylene formed by reaction 7 proceeds by excited state and not radical species to form oligomers,[27] so this route to chromophores may not be inhibited by hydrogen. This proposal for chromophore formation is only valid in the region of the Jovian atmosphere where the concentration of ammonia is much lower than that of acetylene. In the regions near the cloud tops the ammonia concentration is so high that it shields the acetylene from the solar flux and reaction 5 does not occur.

The experimental observation of the formation of HCN by the photochemical dissociation of ammonia in the presence of acetylene is reported herein. Brown oligomers of acetylene are also formed. Thus, photolysis of ammonia in the presence of acetylene provides a plausible solution to two previously intractable problems concerning the atmospheric chemistry of Jupiter. A preliminary report of some of these observations has been published.[28]

Experimental Section

General Procedures. UV spectra were measured on a Cary 219 spectrophotometer. Gas chromatography was performed on a Varian 2400 flame-ionization gas chromatograph. A 6-ft, 2 mm i.d. glass column packed with 4% Carbowax 20 M and 0.8% KOH on Carbopack B (60–80 mesh) was used. Temperature programming of 4°/min from 90 to 150 °C was used with a nitrogen carrier gas flow rate of 20 mL/min. A 6-ft, 2 mm i.d. glass column packed with Porapak QS 80–100 mesh was also used. It was operated isothermally for 7.5 min at 30 °C and then programmed at 8°/min to 170 °C with a nitrogen carrier gas flow rate of 20 mL/min. Both columns were obtained from Supelco. Comparable columns and operating conditions were used for GC/MS analysis with the exception that helium was used as the carrier gas on a HP 5987 spectrometer equipped with a glass jet separator. Gas mixtures were prepared on a mercury-free vacuum line equipped with a MKS 270B signal conditioner and 370HA sensor for pressure measurements. Fourier transform infrared (FT-IR) measurements were performed on Perkin-Elmer Model 1800 instrument. The spectra were recorded directly on photolysis reactions performed in cells with Supracil or calcium fluoride windows. Some spectra were also measured on the gaseous reaction products after they were transferred to a gas cell with sodium chloride windows. HCN was analyzed by the pyridine–pyrazolone method at 625 nm.[29] A linear correlation with cyanide concentration was observed in the 10^{-4}–10^{-6} M concentration range.

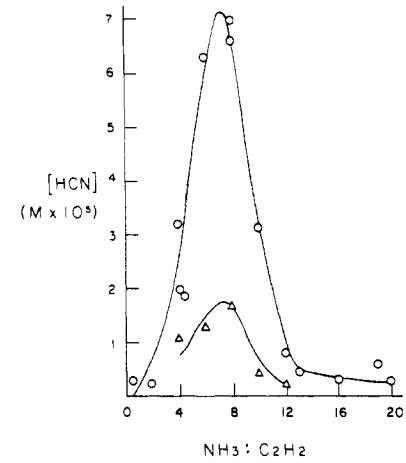

Figure 1. Variation in HCN yield with NH_3–C_2H_2 ratio: ○ 185-nm photolysis, (△) 206-nm photolysis.

Materials. Acetylene (Matheson, purified, 99.6%) was separated from acetone by bubbling through (1) concentrated sodium bisulfite and (2) concentrated sodium hydroxide and then dried by passing over anhydrous calcium chloride. It was then distilled at 178 K, condensed at 77 K, and stored on the vacuum line. The absence of acetone was ascertained by GC/MS. Ammonia (Linde, electronic grade, 99.999%) was degassed by three freeze–pump–thaw cycles and stored on the vacuum line. Sulfur hexafluoride (Matheson, instrument purity 99.999%) and hydrogen (Matheson ultrahigh purity, 99.999%) were used as received. Acetaldehyde ethylidenehydrazone was prepared by the method of Frederickson[30] and had a boiling point (92–93 °C) and mass spectrum identical with that of a literature spectrum.

Photochemistry. Most of the photolyses were performed with a low-pressure mercury lamp with principal emissions at 184.9 and 253.7 nm. The light emission at 184.9 nm is 5×10^{15} photons/s in our experimental set up.[31] An iodine discharge lamp with principal emission at 206.2 nm was also used.[32] A 150-W xenon lamp (Oriel 901-C1) together with a Bausch and Lomb 33-86-75 high-intensity monochromator was used for irradiation experiments at wavelengths other than emission lines of the mercury or iodine lamps. Photolyses were performed in 10 × 2.8-cm cylindrical quartz cells of volume about 70 cm^3 or in an 8 × 2.7-cm cylindrical cell with 6 mm thick CaF_2 windows and a volume of 52.8 cm^3. During photolyses, the window of the cell was located 3 cm from the bottom of the spiral coil of the mercury lamp.[33] The extinction coefficient of ammonia at 185 nm is reported in the 52–140-cm^{-1} range and 35–73 cm^{-1} at 206 nm.[34-37] Average values of 87 cm^{-1} at 185 nm and 47 cm^{-1} at 206 nm were used to calculate the percent light absorbed by ammonia. The reported values of the extinction coefficients of acetylene at 185 nm are 20 cm^{-1}[38] and 2 cm^{-1},[39] while the value of 0.2 cm^{-1} is

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Table I. Variation in NH_3, HCN, and Oligomers with Time on Irradiation of Ammonia–Acetylene Mixtures[a]

		time, h					
		0	1	2	4	8	26
A.	NH_3, Torr	20			19	17	17
	HCN, mol × 10^5	0			1.9	1.5	2.7
	oligomers, absorbance at 300 nm	0			0.18	0.22	0.34
B.	NH_3, Torr	0.5	0.1	0.05		0	
	HCN, mol × 10^{-5}	0	0.5	0.9		0	
	oligomers, absorbance at 300 nm	0	0.09	0.12		0.15	

[a] 2.5 Torr of acetylene was used.

Table II. Variation in Yield of HCN Oligomers and HCN Precursors on Irradiation of Ammonia–Acetylene Mixtures[a]

	temp, K	H_2, Torr	HCN, mol × 10^5	oligomers[b]	HCN precursors[c]
1.	298	0	10.1 (0.9)	0.24 (0.005)	0
2.[d]	298	0	12.5	0.16	0
3.[e]	298	0	4.5	0.13	0
4.	298	77.5	6.4 (2.7)	0.09 (0.04)	0
5.	178	0	2.9 (0.75)	0.14 (0.01)	0.12 (0.03)
6.	178	77.5	0.55 (0.13)	0.09 (0.04)	0.09 (0.12)
7.	178	700	0.39 (0.14)	0.05 (0.01)	0.27 (0.10)

[a] Irradiation of 5 Torr of NH_3 and 2.5 Torr of acetylene for 8 h; standard deviations given in parentheses. [b] Monitored by the absorbance at 300 nm. [c] Monitored by the absorbance at 220 nm. [d] Irradiation for 4 h. [e] Irradiation for 4 h with use of a cell with calcium fluoride windows.

reported at 206 nm.[39] An extinction coefficient of 0.59 cm^{-1} at 206 nm was measured in the present work. Average values of 11 cm^{-1} at 185 nm and 0.40 cm^{-1} at 206 nm were used to calculate the percentage of light absorbed by acetylene.

Results and Discussion

Formation of HCN. It was determined that HCN was formed by photolysis of ammonia–acetylene mixtures at room temperature by FT-IR analyses of the gaseous reaction products. HCN was detected by the C–H stretching frequencies in the 3300-cm^{-1} region and a weak C–H deformation band at 712 cm^{-1}.[40] HCN was observed when photolysis cells with Supracil or calcium fluoride windows were used. Its formation when such diverse materials are used in the cell windows indicates that surface catalysis has no role in HCN formation and is consistent with its formation in the gas phase. The presence of HCN was confirmed and measured quantitatively using the pyridine–pyrazolone color test.[29] Initial studies established that the yield of HCN is optimal with an 8:1 ammonia–acetylene ratio in experiments where the ammonia partial pressure is 20 Torr and the partial pressure of acetylene was varied (Figure 1). Ammonia is absorbing 98% of the incident 185-nm light when an 8:1 ammonia–acetylene ratio is used, so it is likely that HCN formation is initiated by ammonia photolysis. This conclusion was confirmed by photolysis at 206.2 nm where ammonia absorbs 99.9% of the photons. The same variation in HCN yield with the ammonia–acetylene ratio was observed at both 206 nm and 185 nm (Figure 1). The lower yield of HCN at 206 nm reflects the lower photon flux of the iodine lamp.[22,23] The HCN yield at 185 nm, based on ammonia consumed, is in the 1–7% range.

The formation of methane and ethane as reaction products was also established by FT-IR analysis. A characteristic series of methane C–H stretching frequencies were observed in the 3020-cm^{-1} region and additional bands at 3000–2900 cm^{-1} were superimposed on the absorption bands of other ethane and other hydrocarbons.[40] A C–H deformation band characteristic of methane was also detected at 1306 cm^{-1}. Nine of the vibrational bands of ethane, observed in the 3007–2970-cm^{-1} spectral region, were used to identify ethane. Other ethane bands may also have been present in this region, but they could not be distinguished from methane bands of the same frequency.[41]

A brown deposit forms on the cell window during the photochemical synthesis of HCN. The amount of this deposit, which is assumed to be a polymer of acetylene, increases with increasing partial pressure of acetylene. The amount of this deposit was monitored by its absorbance at 300 nm, which increases linearly with acetylene partial pressures up to 2.5 Torr (Figure 2). At acetylene partial pressures greater than 2.5 Torr, the oligomeric deposit absorbs so much ultraviolet light that its rate of formation decreases. This observation also explains why the maximum yield of HCN is at an 8:1 ammonia–acetylene ratio where the acetylene partial pressure is also 2.5 Torr. Thus, the optimum in the HCN yield (Figure 1) is due to a diminished photon flux and is not a consequence of a change in the reaction pathway resulting from the ammonia–acetylene ratio.

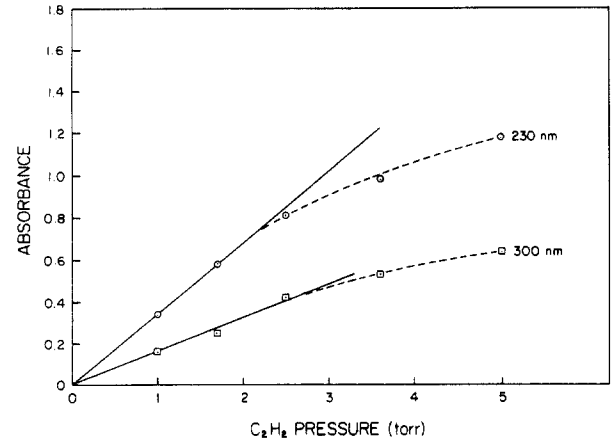

Figure 2. Variation oligomer yield with acetylene partial pressure.

The diminished flux due to the oligomeric deposit was confirmed by studies performed at short irradiation times (Table I, A). The yields of HCN and deposit after only 4 h of irradiation are more than half the yields observed after 26 h, indicative of a rapid initial synthesis. The UV absorption of the deposit after 4 h shows sharply increasing end absorption in the 220–200-nm region with an absorbance of 1.0 at 200 nm, corresponding to the absorption of 90% of the incident light. Thus, at the end of 4-h irradiation, the deposit is probably absorbing even more than 90% of the 185-nm photons.

Photolyses were also performed under optically thin conditions where the absorbance of the ammonia and acetylene at 185 nm was much less than 1 (Table I, B). The HCN and oligomer yield is of the same order of magnitude as under the optically thick conditions (Table I, A). This finding is consistent with our observation that HCN formation is independent of the cell window material and that the formation of the oligomers and HCN proceeds in the gas phase and not in a heterogeneous reaction on the cell window. Our failure to observe HCN after irradiation

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Table III. Formation of HCN by Irradiation of Ammonia–Acetylene Mixtures[a]

	irradn time, h	temp, K	HCN, mol × 10^5
1.	8	298	5.3
2.	1	298	0.5
3.	8	178	0.4
4.[b]	8	178	
	1	298	2.8
5.[c]	8	178	
	1	298	5.0

[a] NH_3–C_2H_2–H_2, 5:2.5:77.5 Torr. [b] Irradiation for 8 h at 178 K followed by 1 h at 298 K. [c] Irradiation for 8 h at 178 K and then most of the ammonia, acetylene and other volatile gases were separated and the HCN precursor fraction was irradiated for 1 h at room temperature.

of an optically thin sample for 8 h reflects its photochemical decomposition once the ammonia has been destroyed and HCN begins to absorb ultraviolet light.[42]

The photolyses were also performed in the presence of hydrogen and at a lower temperature to gain an understanding of the effect of reaction conditions closer to those present on Jupiter on the formation of HCN and the oligomeric deposit (Table II). An ammonia partial pressure of 5 Torr was used to be certain that all of the ammonia would be in the gas phase at 178 K, the lower temperature selected for the photochemical studies. The yield of HCN is decreased 70% when the temperature was lowered to 178 K (Table II, 5) and there is a further 80% decrease when 77.5 Torr of hydrogen was added to the photolysis mixture (Table II, 6). No further decrease was observed when 700 Torr of hydrogen was used instead of 77.5 Torr (compare 6 and 7, Table II).

A HCN precursor fraction that is not observed at room temperature is formed when the photolysis is performed at 178 K. These products were first detected by an increased UV absorption in the 200–270-nm region over that observed in photolytic reactions performed at room temperature. The HCN precursors present in this mixture are formed in the presence and absence of hydrogen (Table II). These compounds have a low vapor pressure at 178 K and condense from the gas phase on the cell wall where they are no longer subjected to UV radiation and so are not converted to HCN.

Precursors of HCN were shown to be present in this fraction by their rapid conversion to HCN. Photolysis of a mixture of ammonia–acetylene–hydrogen (5:2.5:77.5 Torr, respectively) for 8 h at 178 K resulted in the formation of 20% of the amount of HCN observed at room temperature (Table III). The enhanced UV absorption at 220 nm due to the HCN precursors was detected in this low-temperature photolysis. When this photolysate was warmed to room temperature and photolyzed for an additional hour, an HCN yield comparable to an 8-h photolysis at room temperature is observed (Table III, run 4). The UV absorption of the precursor fraction disappeared during the course of the 1-h photolysis. Furthermore, irradiation of the precursor fraction for 1 h after it had been separated from most of the unreacted ammonia and acetylene also gave an HCN yield comparable to an 8-h photolysis at room temperature (Table III, run 5). These experiments establish that precursors to HCN condense from the photolysis mixture at 178 K, thus explaining the low yield of HCN at that temperature.

The precursor fraction was partially characterized by investigation of its volatility and stability. The bulk of the fraction, as measured by its UV absorption, condenses at temperatures as high as 247 K. The UV spectrum of the fraction did not change after it was allowed to stand for 24 h at room temperature or for 1 h at 353 K. The observed thermal stability indicates that neither compounds **2** or **3** account for the rising UV end absorption of the precursor fraction. Both have been prepared previously and both have half-lives of only 20 min at room temperature.[43,44] Aziridine (**1**) is stable at 353 K and would be expected to condense at 247 K; additional studies were required to exclude it as a possible photoproduct.

Analysis of the HCN Precursor Fraction. Comparable traces were obtained when the HCN precursor fraction was analyzed by gas chromatography with Carbowax or Porapak columns. The major components were identified by using GC/MS with direct comparison of their mass spectra with published spectra. Acetonitrile and acetaldehyde ethylidenehydrazone (**6**) were found to be the main nitrogen-containing photoproducts. The structures of the other reaction products, which are believed to be hydrocarbons, are still under investigation.

A detailed search for aziridine (**1**) was performed, but none could be found. No peak was detected with the same retention time as aziridine with gas chromatography on Porapak. The total ion current from the mass spectrometer for the fractions eluted from both GC columns was scanned for peaks with mass 42, the strongest signal in the mass spectrum of aziridine. None of the compounds with a *m/e* 42 signal had a mass spectrum that corresponded with that of aziridine, so if it is present the amount is below the limit of detection ($\sim 10^{-7}$ mol) of our analytical methodology.

A reaction pathway to the HCN precursors and HCN can be proposed on the basis of this and other research. The initial step (1) is the dissociation of ammonia to hydrogen atoms and NH_2 radicals since ammonia is absorbing more than 98% of the 185-nm light. The addition of a hydrogen atom to acetylene (2) is proposed as the next step because the pseudo-first-order rate constant for the addition of a hydrogen atom[45] is 7×10^2 times greater than the addition of a NH_2 radical to acetylene at 298 K.[46] This rate difference increases to 3×10^3 at 178 K and 6×10^3 at 150 K. Vinylamine is formed by radical combination (9) and its isomerization to ethylideneamine (10) is a process characteristic of enamines.[47,48] Hydrogen abstraction from imines (11) and the subsequent formation of the nitrile from the resulting radical (12) finds precedent in the photochemistry of imines.[49] The formation of the allylic radical is postulated to be a second reaction pathway for vinylamine (13). Dimerization of the resulting radical yields a hydrazone (14). The azine derivatives of hydrazones are known to be more stable so the proposed rearrangement to acetaldehyde ethylidenehydrazone is a plausible reaction pathway (15).[50]

$$NH_3 \xrightarrow{h\nu} NH_2^{\bullet} + H^{\bullet} \quad (1)$$

$$H^{\bullet} + HC{\equiv}CH \xrightarrow{M} CH_2{=}CH^{\bullet} \quad (2)$$

$$NH_2^{\bullet} + CH_2{=}CH^{\bullet} \xrightarrow{M} CH_2{=}CHNH_2 \quad (9)$$

$$CH_2{=}CHNH_2 \xrightarrow{h\nu} CH_3CH{=}NH \quad (10)$$

$$CH_3CH{=}NH + H^{\bullet} \rightarrow CH_3C^{\bullet}{=}NH + H_2 \quad (11)$$

$$CH_3C^{\bullet}{=}NH \rightarrow CH_3C{\equiv}N + H^{\bullet} \quad (12)$$

$$CH_2{=}CHNH_2 + H^{\bullet} \rightarrow CH_2{=}CHNH^{\bullet} + H_2 \quad (13)$$

$$2CH_2{=}CHNH^{\bullet} \xrightarrow{M} CH_2{=}CHNHNHCH{=}CH_2 \quad (14)$$

$$CH_2{=}CHNHNHCH{=}CH_2 \xrightarrow{h\nu} \underset{\mathbf{6}}{CH_3CH{=}NN{=}CHCH_3} \quad (15)$$

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Photolysis of the HCN Precursors. Studies on the photolysis of acetaldehyde ethylidenehydrazone (**6**) and acetonitrile have both been reported previously. Acetaldehyde ethylidenehydrazone absorbs light at wavelengths below 340 nm, and its photochemistry has been studied in the 334–238 nm region.[51] One molecule of acetonitrile is formed per molecule of **6** with an initial quantum yield 0.5 in the 300 nm wavelength region (16). The stoichio-

$$\underset{\mathbf{6}}{CH_3CH{=}NN{=}CHCH_3} \xrightarrow{h\nu} CH_3C{\equiv}N + \underset{\mathbf{7}}{CH_3CH{=}NH} \quad (16)$$

metric yield and quantum yield decrease at shorter wavelengths (Φ = 0.18 at 238 nm) is indicative of the onset of other primary photochemical processes. Ammonia, methane, ethane, nitrogen, butane, and a polymeric solid were also observed as photoproducts in this study.[51] The first step in the mechanism proposed for the formation of acetonitrile is the dissociation of **6** to acetonitrile and ethylidenimine (**7**) (16). The ethylidenamine is converted to acetonitrile by reactions 11 and 12 as outlined above.

The FT-IR detection of methane and ethane as photoproducts at 25 °C is consistent with our proposal that CH_3CN is the precursor to HCN. No methane or ethane was detected in studies on the photolysis of acetylene alone described below. The photochemically initiated addition of ammonia to acetylene provides a route for the cleavage of the acetylene triple bond with the formation of cyanide triple bond and methane. It can be readily calculated from the enthalpies of formation of the reactants and products that the overall reaction (17) is thermodynamically favored at 25 °C (ΔH = −29.9 kcal/mol).[52]

$$HC{\equiv}CH + NH_3 \rightarrow HC{\equiv}N + CH_4 \quad (17)$$

At least two possible photochemical routes from acetonitrile to HCN are possible. One is the direct dissociation of acetonitrile to cyano radicals (18) followed by HCN formation (19). This

$$CH_3CN \xrightarrow{h\nu} CH_3^{\bullet} + {}^{\bullet}CN \quad (18)$$

$$CN^{\bullet} + RH \rightarrow R^{\bullet} + HCN \quad (19)$$

reaction pathway can be readily eliminated from further considerations since it is only operative at wavelengths below 185 nm, the onset of light absorption by acetonitrile.[53,54] Since acetonitrile has very weak light absorption in the 185-nm region, it would not be photodissociated in the presence of the more strongly absorbing ammonia and acetylene.

The hydrogen atom initiated conversion of acetonitrile to HCN proceeds independent of the light absorption by acetonitrile. The direct photolysis of acetonitrile at 185 nm, the reaction of acetonitrile with the hydrogen atoms formed by the mercury-sensitized decomposition of hydrogen, and the reaction of acetonitrile with the hydrogen atoms formed by the photolysis of hydrogen sulfide at 254 nm all result in the formation of HCN.[55] The quantum yield for the formation of HCN from acetonitrile is approximately 1. A reaction sequence (20, 21) was proposed to account for the

$$H^{\bullet} + CH_3CN \rightarrow CH_3C^{\bullet}{=}NH \quad (20)$$

$$CH_3C^{\bullet}{=}NH \rightarrow HC{\equiv}N + CH_3^{\bullet} \quad (21)$$

$$CH_3^{\bullet} + XH \rightarrow CH_4 + X^{\bullet} \quad (22)$$

$$2CH_3^{\bullet} \xrightarrow{m} CH_3CH_3 \quad (23)$$

formation of HCN by the reaction of acetonitrile resulting from the homolytic dissociation of acetonitrile, hydrogen, or hydrogen sulfide. Reaction 20 is the reverse of reaction 12, one of the steps in the proposed formation of acetonitrile. Reaction 12 is analogous to other photochemical routes to acetonitrile;[49] the acetonitrile condenses from the gas phase at 178 K and is protected from further reaction. The reverse process (20) proceeds in the gas phase at room temperature to produce HCN (21) as a result of the high flux of hydrogen atoms formed by the photolysis of ammonia (1). We have confirmed that HCN is formed by the photolysis of 5 Torr of ammonia in the presence of 0.3 Torr of acetonitrile. The formation of methane (22) and ethane (23) is consistent with the proposed formation of HCN from acetylene and ammonia via acetonitrile.

Table IV. Variation in the Yield of Oligomers on Photolysis of Acetylene[a]

	temp, K	H_2, Torr	He	oligomers[b]
1.	298	0	0	0.18 (0.01)
2.	298	77.5	0	0.09 (0.02)
3.	178	0	0	0.16
4.	178	77.5	0	0.19 (0.03)
5.	178	0	77.5	0.21 (0.01)

[a] Irradiation of 2.5 Torr of acetylene at 185 nm for 8 h; standard deviations given in parentheses. [b] Monitored by the absorbance at 300 nm.

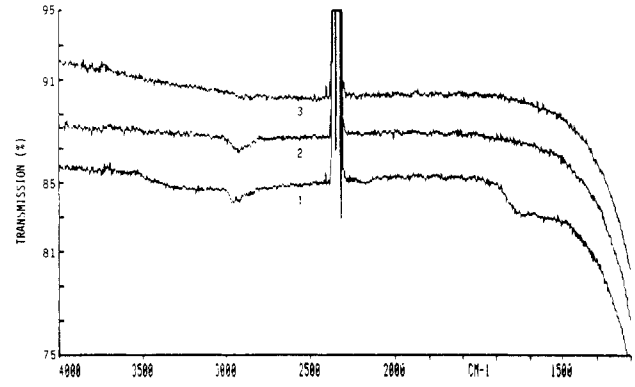

Figure 3. FT-IR spectra of the oligomers formed by (1) photolysis of 5 Torr of NH_3 in the presence of 2.5 Torr of acetylene, (2) photolysis of 2.5 Torr of acetylene and (3) empty CaF_2 cell. The irradiations were carried out for 4 h at room temperature in a cell with CaF_2 windows with a low-pressure mercury lamp. Spectra 1 and 2 are offset from 3 by 7% and 5%, respectively.

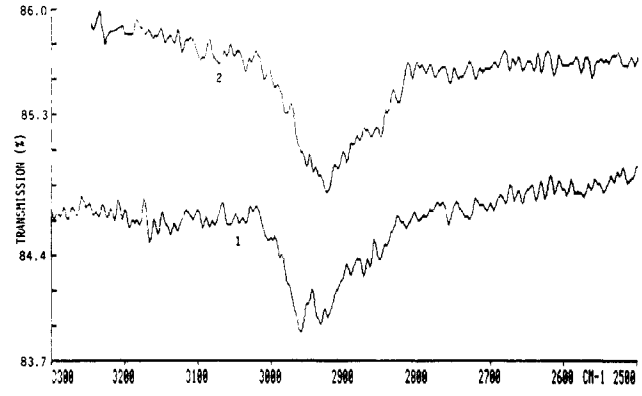

Figure 4. Expansion of the 3300–2500-cm^{-1} region in the FT-IR spectra in Figure 3 to illustrate the differences in the intensity of the C–H absorption at 2960 and 2870 cm^{-1}.

Photochemical Oligomerization of Acetylene. A tan deposit of oligomers forms on the cell window when acetylene is irradiated. A 50% decrease in the 300-nm light absorption of the oligomer fraction was observed when 77.5 Torr of hydrogen was added to the photolysis mixture at 298 K (entry 2, Table IV) but the effect of this 31-fold excess is not discernable at 178 K (entries 1 and 4, Table IV). Thus a 31-fold excess of hydrogen has a partial

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inhibitory effect at room temperature but no effect at 178 K. However, if the hydrogen–acetylene ratio is increased to 10^7, the marked inhibition of oligomer formation is observed.[26]

Diacetylene has been reported as a product of the photolysis of acetylene,[56–58] but we did not detect it by FT-IR analysis of the gaseous reaction products. The absence of diacetylene probably reflects its rapid conversion to oligomers by the 254-nm light emanating from the low-pressure mercury lamp.[27] When 2.5 Torr of acetylene is irradiated and the reaction is monitored by FT-IR, only the decrease in acetylene C–H absorption and the formation of a very weak bands in the 2850–2950-cm^{-1} region, due to acetylene oligomers, was observed (Figures 3 and 4). This IR absorption is consistent with the presence of CH_2 and possibly CH_3 groups in the oligomers.[59]

It was possible to obtain a more intense infrared spectrum from the tan oligomeric deposit formed by irradiating 25 Torr of acetylene. The infrared spectrum in the 4000–1200-cm^{-1} region (CaF_2 cell) was similar to that of the acetylene polymer formed by the action of 1 MeV electrons on acetylene.[60] The presence of CH_2 and possibly CH_3 groupings was supported by the observation of CH deformation bands at 1450 cm^{-1} along with stretching frequencies observed at 2850–2950 cm^{-1}.[59] The presence of unsaturation was deduced from the weak absorption observed at 3020 cm^{-1} and 1600–1720 cm^{-1}. The most intense bands at 2850–2950 cm^{-1} suggest that hydrogen atom additions, as well as cross-linking and cyclization reactions must occur to generate the aliphatic CH groups responsible for this absorption. The infrared spectrum of the photoproduct is very different from that of the conjugated polyacetylene formed by $Ti(OC_4H_9)_4$–$Al(C_2H_5)_3$ catalyzed polymerization of acetylene.[61] The weak IR absorption in the photoproduct due to unsaturation, and as a consequence the absence of extended conjugation, is consistent with its tan color. This is in marked contrast to the black color of the polymer formed by the metal complex catalyzed polymerization of acetylene, which contains a linear array of conjugated double bonds.[62]

Oligomerization of Acetylene Initiated by Ammonia Photolysis. The hydrogen atoms produced by ammonia photolysis (1) initiates photochemical oligomerization of acetylene. The oligomerization is not a surface-catalyzed process since the same yield of oligomer is obtained when either Supracil or calcium fluoride were used as cell windows. We proposed initially that a vinyl radical is produced first (2) and polymerization proceeds by the addition of the vinyl radicals to acetylene (24).[28] However, the sequence

$$CH_2{=}CH^{\bullet} + nHC{\equiv}CH \rightarrow H_2C{=}CH(CH{=}CH)_{n-1}CH{=}CH^{\bullet} \quad (24)$$

outlined by reactions 1, 2, and 24 is not consistent with the comparable partial inhibitory effect of hydrogen on the oligomerization of acetylene initiated by direct photolysis and by hydrogen atoms (compare runs 1 and 4 in Table II). A hydrogen atom initiated process should not be inhibited by hydrogen because vinyl radicals react with hydrogen 10^8 times more slowly than the ethynyl radicals that were proposed as intermediates in the direct photolysis of acetylene.[63] This inhibition by hydrogen indicates that the oligomerization reaction is more complicated than the simple sequence of events outlined by eq 1, 2, and 24.

The FT-IR spectrum of the oligomer formed by photolysis of ammonia in the presence of acetylene showed almost none of the similarity to the IR spectrum of the polyacetylene,[61] which would be expected if polymer formation proceeded as shown in eq 24 (Figures 3 and 4).[28] Instead, the polymer exhibited sharp bands at 2960 and 2870 cm^{-1} attributed to methyl groups and 2935, 2920, and 2820 cm^{-1} attributed to methylene groups (Figure 4).[59] The strong methyl absorption is believed to be due to the reduction of unsaturated groups by the hydrogen atoms generated by ammonia photolysis. This absorption is much weaker in the oligomer formed by the direct photolysis of acetylene because the flux of hydrogen atoms is expected to be much lower. The hydrogen atom initiated product also differs from the oligomers formed by the direct photolysis of acetylene by having a broad absorption band in the 3300-cm^{-1} region and overlapping broad bands that span the 1700–1500-cm^{-1} region (Figure 4). The 3300-cm^{-1} band is ascribed to NH stretching frequencies resulting from the incorporation of NH_2 and NH groups into the oligomers. N–H deformation, as well as imine stretching, accounts for the broad band centered at about 1620 cm^{-1}.[59] The 1620-cm^{-1} band is much more intense than the carbon–carbon double bond absorption observed in the polymer produced by the direct irradiation of acetylene.

Applications to Atmospheric Chemistry. HCN Formation. Experimental studies provide strong support for the hypothesis that both HCN and organic chromophores are formed on Jupiter by the photolysis of ammonia in the presence of acetylene. Acetonitrile is the direct precursor of HCN, and the acetonitrile may be formed from acetaldehyde ethylidenehydrazone (**6**). Acetonitrile may be converted to HCN by reaction with the hydrogen atoms formed by ammonia photolysis and, to a lesser extent, by the hydrogen atoms formed by the photolysis of other gases present in the atmosphere of Jupiter.

The gas-phase photolysis of acetonitrile will not occur if its vapor pressure is very low at the temperatures prevalent in the Jovian atmosphere. There are no published reports of the vapor pressure of acetonitrile in the 150–200 K range, but measurements have been performed on HCN in the 187–259 K range, and empirical mathematical expressions have been derived that correlate vapor pressure and temperature.[64,65] Since the vapor pressure of acetonitrile is about one-tenth that of HCN in the 220–273 K range,[66] the vapor pressure of acetonitrile can be estimated to be one-tenth the calculated value for HCN at 150 K. The calculated vapor pressure of HCN is 4×10^{-4} Torr, which corresponds to a mixing ratio of 5×10^{-7} at 1 bar, a value that is 250 times the observed mixing ratio of 2×10^{-9} on Jupiter.[1] Since the estimated vapor pressure of acetonitrile at 150 K is one-tenth that of HCN or 25 times greater than the observed HCN mixing ratio, there is little doubt that the vapor pressure of acetonitrile is sufficiently high for the photochemical generation of the amount of HCN observed in the atmosphere of Jupiter. It should be possible to detect low levels of acetonitrile on Jupiter by microwave spectroscopy.[67]

Acetaldehyde ethylidenehydrazone is also expected to undergo photolysis in the gas phase of Jupiter's atmosphere. The broad UV absorption of this hydrazone, which extends from below 200 nm out of 350 nm (Brinton, 1955), indicates that it will be rapidly photolyzed by longer wavelength UV light that penetrates through the atmosphere to the tops of the ammonia clouds. No vapor pressure data is available for this hydrazone, but its boiling point is only 15 °C higher than that of acetonitrile,[50] so its vapor pressure should be sufficiently high so that its photolysis will proceed on Jupiter before condensation takes place.

These findings suggest that acetonitrile may be the source of the cyano radicals and HCN formed on other bodies in our solar system and in the interstellar medium. The cyano radicals and smaller amounts of HCN observed when comets come near the Sun may be due to the hydrogen atom initiated decomposition of acetonitrile, a compound that has been detected on some comets.[68] The hydrogen atoms could be formed by the photochemical decomposition of the large amounts of water being ejected from the comet along with the much smaller amounts of acetonitrile. The direct photolysis of acetonitrile (18) does not appear to be the source of cometary nitrile radicals.[69] Photo-

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chemically generated hydrogen atoms on Titan may also account for the presence of HCN and absence of acetonitrile in its atmosphere.

Chromophore Formation. The hydrogen atom initiated oligomerization of acetylene appears to be a more plausible route to organic chromophores on Jupiter than the direct photolysis of acetylene. The latter process cannot proceed in the presence of ammonia because ammonia is a strong absorber of solar UV than acetylene. The hydrogen atom initiated reaction proceeds at low temperatures and is only partially inhibited by molecular hydrogen. The oligomer formed in the presence of ammonia incorporates hydrogen atoms and NH groupings. The incorporation of other radicals present in the Jovian atmosphere ($^{\bullet}PH_2$, $^{\bullet}CN$, and possibly $^{\bullet}OH$) may result in the generation of oligomers with different visible spectral properties than the one formed in our laboratory studies. For example, the chlorine atom initiated oligomerization of acetylene results in the formation of yellow to orange products instead of brown polymers.[70] These colors may reflect the incorporation of chromophoric chlorine groups into the oligomers.

Acknowledgment. This research was supported by Grant PR 10-38765 from NASA. The Model 1800 FT-IR was a gift to the Chemistry Department from Perkin-Elmer. Preliminary studies were performed by Dr. H. Khwaja, and we thank him for the design of the CaF_2 cell. We thank Dr. F. Raulin for bringing the abstract of Masanet et al. (1982) to our attention.

Registry No. 1, 151-56-4; **6**, 592-56-3; HCN, 74-90-8; NH_3, 7664-41-7; CH_3CN, 75-05-8; HC≡CH, 74-86-2; acetylene (homopolymer), 25067-58-7.

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Additions of Singlet Oxygen to Alkoxy-Substituted Dienes. The Mechanism of the Singlet Oxygen 1,2-Cycloaddition Reaction

Edward L. Clennan* and Krzysztof Nagraba[1]

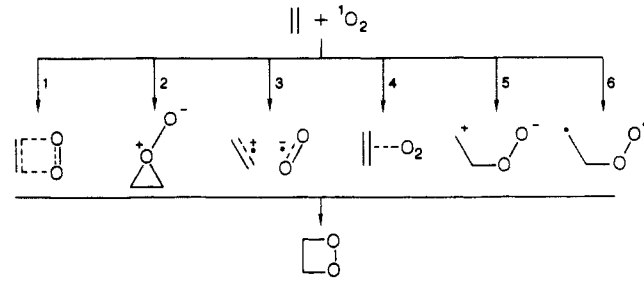
Contribution from the Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071. *Received November 5, 1987*

Abstract: The reactions of singlet oxygen with (*E*,*E*)-, (*E*,*Z*)-, and (*Z*,*Z*)-1,4-dimethoxy-1,3-butadienes are reported. These compounds react to give dioxetanes as the major oxidized products. All three compounds are suggested to react via zwitterions, which collapse to dioxetanes before rotational equilibrium is reached. The zwitterions are stabilized in the more polar solvents, and as a result their rotation competes more effectively than in less polar solvents with closure to the dioxetanes.

In 1969 Kopecky and Mumford[2] reported that the base cyclization of a bromo hydroperoxide allowed the first successful isolation of a 1,2-dioxetane. In 1970 Bartlett and Schaap[3] and Mazur and Foote[4] simultaneously reported the successful isolation of these strained peroxides from addition of singlet oxygen to an olefin. It soon became apparent[5] that this formal 2 + 2 cycloaddition of singlet oxygen was to take its place along with the ene[6] and 4 + 2 cycloaddition[7] as ubiquitous modes of singlet oxygen reactivity.

The mechanism of the singlet oxygen 1,2-cycloaddition reaction has been extensively debated in the literature.[8] The mechanisms

Scheme I



that have most often been considered are shown in Scheme I. Mechanism 1 is a concerted 2s + 2a cycloaddition and should be promoted by the small size of singlet oxygen.[5] Analysis of frontier orbital interactions in the favorable olefin–HOMO singlet oxygen–LUMO orbital arrangements, however, suggest that the olefin should act as the antarafacial component rather than as a suprafacial component as is experimentally observed.[8]

Mechanism 2 proceeds through a perepoxide intermediate. Perepoxides have received considerable support as intermediates in the singlet oxygen ene reaction.[9] Particularly persuasive

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