



Mechanism for the Coupled Photochemistry of Ammonia and Acetylene: Implications for Giant Planets, Comets and Interstellar Organic Synthesis

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Abstract Laboratory studies provide a fundamental understanding of photochemical processes in planetary atmospheres. Photochemical reactions taking place on giant planets like Jupiter and possibly comets and the interstellar medium are the subject of this research. Reaction pathways are proposed for the coupled photochemistry of NH_3 (ammonia) and C_2H_2 (acetylene) within the context Jupiter's atmosphere. We then extend the discussion to the Great Red Spot, Extra-Solar Giant Planets, Comets and Interstellar Organic Synthesis. Reaction rates in the form of quantum yields were measured for the decomposition of reactants and the formation of products and stable intermediates: HCN (hydrogen cyanide), CH_3CN (acetonitrile), $\text{CH}_3\text{CH} = \text{N}-\text{N} = \text{CHCH}_3$ (acetaldazine), $\text{CH}_3\text{CH} = \text{N}-\text{NH}_2$ (acetaldehyde hydrazone), $\text{C}_2\text{H}_5\text{NH}_2$ (ethylamine), CH_3NH_2 (methylamine) and C_2H_4 (ethene) in the photolysis of $\text{NH}_3/\text{C}_2\text{H}_2$ mixtures. Some of these compounds, formed in our investigation of pathways for HCN synthesis, were not encountered previously in observational, theoretical or laboratory photochemical studies. The quantum yields obtained allowed for the formulation of a reaction mechanism that attempts to explain the observed results under varying experimental conditions. In general, the results of this work are consistent with the initial observations of Ferris and Ishikawa (1988). However, their proposed reaction pathway which centers on the photolysis of $\text{CH}_3\text{CH} = \text{N}-\text{N} = \text{CHCH}_3$ does not explain all of the results obtained in this study. The formation of $\text{CH}_3\text{CH} = \text{N}-\text{N} = \text{CHCH}_3$ by a radical combination reaction of $\text{CH}_3\text{CH} = \text{N}\cdot$ was shown in this work to be inconsistent with other experiments where the $\text{CH}_3\text{CH} = \text{N}\cdot$ radical is thought to form but where no $\text{CH}_3\text{CH} = \text{N}-\text{N} = \text{CHCH}_3$ was detected. The importance of the role of H atom abstraction reactions was demonstrated and an alternative pathway for $\text{CH}_3\text{CH} = \text{N}-\text{N} = \text{CHCH}_3$ formation involving nucleophilic reaction between N_2H_4 and $\text{CH}_3\text{CH} = \text{NH}$ is advanced.

Dedicated to the memory of Jim Ferris

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Introduction

I dedicate this paper in the heartfelt memory of my friend and mentor James P. Ferris, emeritus and research professor in the department of chemistry and chemical biology, at the Rensselaer Polytechnic Institute (RPI), whose encouragement and “you can do it” attitude helped guide me along a path of my dreams in space related research. Professor Ferris was the founding director of the NASA supported New York Center for Studies on the Origins of Life, later to become the New York Center for Astrobiology. While Jim is well known and highly respected for his seminal works on the terrestrial origins of life and potential for exobiology, it was his wonderful sense of humor and spirit which was equally inspiring. Through “Ferris”, doors opened into the fields of planetary and space science, where I met some of the coolest people on the planet.

<https://astrobiology.nasa.gov/news/in-memory-of-jim-ferris/>

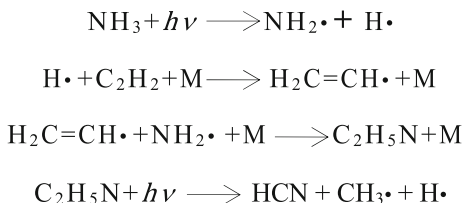
One of the more intriguing aspects of HCN is its potential role in prebiological organic synthesis (Ferris et al. 1978, 1979, Ferris and Chen 1975a, b; Ferris and Morimoto 1981; Ferris and Hagan 1984, Ferris 2006; Miller and Orgel 1974, Miller and Urey 1959; Oro 1961) on Earth and possibly elsewhere in the universe. The impetus for this work was to test a theoretical proposal of Kaye and Strobel (1983) that a non-cometary source for HCN on Jupiter could be the photolysis of NH_3 in the presence of C_2H_2 .

At the heart of the theoretical model is the photochemical conversion of CH_4 to the stable yet reactive molecule C_2H_2 . The C_2H_2 formed would then react with radicals formed upon NH_3 photolysis (Fig. 1) to yield intermediates that are photochemically converted to HCN (Kaye and Strobel 1983).

Four isomers with the molecular formula of $\text{C}_2\text{H}_5\text{N}$ were recognized as possible intermediates in HCN formation. They are aziridine, ethylideneimine, vinylamine and N-methyl methyleneimine (Fig. 2). The key intermediate in the Kaye and Strobel model is aziridine, the isomer chosen due to the availability of spectroscopic and photochemical data at the time.

In the case of $\text{C}_2\text{H}_5\text{N}$, the rate of reaction between $\text{NH}_2\cdot$ and $\text{C}_2\text{H}_3\cdot$, radicals produced in the coupled photochemistry of NH_3 and C_2H_2 , was not known. Kaye and Strobel (1983) equated this rate constant to that for the addition of $\text{NH}_2\cdot$ to $\text{C}_2\text{H}_5\cdot$. The reaction kinetics of all the possible photoproducts in this process were also not known. Increases in the rates of removal of HCN precursors and the possibility of other pathways involving the precursors would decrease the predicted HCN yield (Kaye and Strobel 1983).

Fig. 1 Summary of the Kaye and Strobel model for HCN formation on Jupiter (Kaye and Strobel 1983)



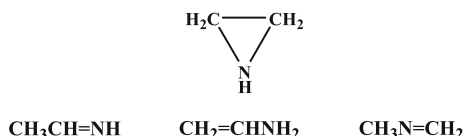


Fig. 2 Four isomers with the molecular formula $\text{C}_2\text{H}_3\text{N}$ recognized as possible intermediates in HCN formation (*top*) Aziridine, (*bottom*) ethylideneimine, vinylamine and N-methyl methyleneimine (Kaye and Strobel 1983)

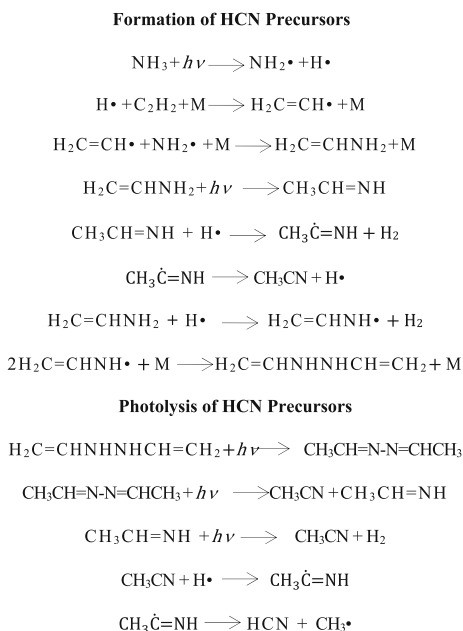
Earlier Studies on the Coupled Photochemistry of NH_3 and C_2H_2

The theoretical proposal of Kaye and Strobel was that NH_3 and C_2H_2 might occur together in the Jovian stratosphere so the reaction of the radicals formed by NH_3 photolysis with C_2H_2 was a plausible Jovian scenario. The results of laboratory experiments performed by Ferris and Ishikawa (1987, 1988) established that the photolysis of NH_3 in the presence of C_2H_2 could be a source for HCN.

HCN was formed by the photolysis of ammonia in the presence of C_2H_2 at 298 K and 178 K in the presence and absence of excess hydrogen. Their results indicated a ten-fold decrease in HCN formation by lowering the temperature to 178 K. This decrease in HCN formation was attributed to the condensation on the cell wall of acetonitrile and acetaldazine, reaction intermediates in the formation of HCN. The photolysis of acetaldazine ($\text{CH}_3\text{CH}=\text{N}-\text{N}=\text{CHCH}_3$) yields acetonitrile (CH_3CN) and the reaction of H atoms with CH_3CN yields HCN (Fig. 3). An earlier study by Tsukada et al. (1972) suggested that pyrrole ($\text{C}_4\text{H}_4\text{NH}$) was formed in photolysis of $\text{NH}_3/\text{C}_2\text{H}_2$ mixtures, however pyrrole was not detected by Ferris and Ishikawa (1987, 1988) or in this work.

Ferris and Ishikawa (1988) initially reported that the same process which results in HCN synthesis also forms a yellow-brown polymeric material which may have relevance to the chromophores found on Jupiter. This ultraviolet absorbing polymeric material

Fig. 3 Summary of proposed reaction pathway for HCN formation in the photolysis of $\text{NH}_3/\text{C}_2\text{H}_2$ (Ferris and Ishikawa 1988)



exhibited infrared spectral features consistent with CH stretch bands of methyl and methylene functional groups, thus indicating the presence of saturated aliphatic hydrocarbons, and the presence of $-NH$ and $-NH_2$ groups based on the NH stretch feature at 3300 cm^{-1} (Ferris and Ishikawa 1988).

The overall objectives of this research were (a) to obtain rate data, in the form of overall quantum yield measurements, for the decomposition and formation of reactants, intermediates and products formed in the photolysis of NH_3 in the presence of C_2H_2 and (b) to elucidate the reaction pathways involved in the formation of HCN as a result of the photolysis of NH_3 in the presence of C_2H_2 (Keane 1995).

This research is relevant to our understanding of astrophysical environments such as giant planets and comets because:

It will suggest which molecules are formed photochemically in regions where ammonia and acetylene are both present as a mixture and exposed to UV radiation. Knowledge of these potential molecular constituents will facilitate their identification by both ground based and spacecraft- probe observations. The data obtained on the rates of the photochemical synthesis and degradation of the reactants and intermediates may be of direct use to those modeling the atmospheric chemistry of giant planets, cometary comae and the interstellar medium.

Experimental

Materials

Commercial Acetylene (C_2H_2 , Matheson, purified, 99.6%) was separated from acetone by bubbling through two concentrated sodium bisulfite solutions and one saturated sodium hydroxide solution. It was then passed through a drying tube containing anhydrous calcium sulfate (drierite) and then over phosphorous pentoxide. The C_2H_2 was then distilled at 178 K and condensed at 77 K (dry ice to liquid nitrogen) and stored on the vacuum line after three freeze pump-thaw cycles. The absence of acetone was ascertained by NMR and FTIR spectroscopy. Ammonia (NH_3 , Linde, electronic grade, 99.999%) was degassed with three freeze-pump-thaw cycles and stored on the vacuum line. Hydrogen (H_2 , Matheson, ultrahigh purity, 99.999%) was passed through a cold trap at 77 K. Nitrogen (N_2 , Matheson, prepurified, 99.998%) was used as received. The bottle containing the ethylamine ($CH_3CH_2NH_2$, Eastman Kodak Co., 100 g) was precooled in an ice/water bath for about 1 h prior to opening, while an empty lecture cylinder bottle was evacuated on the vacuum line. After breaking the glass seal, the ethylamine was decanted into a large glass ampule which was previously flushed with argon and also cooled in an ice/water bath. The glass ampule containing the ethylamine was then placed into a large dewar of liq N_2 until all of the liquid had frozen. While still in liq N_2 this ampule was transferred to the vacuum line and pumped down. The ethylamine was then distilled at 203 K and condensed in the lecture cylinder at 77 K (dry ice/ethanol to liq N_2). Methylamine (CH_3NH_2 , Linde, 99%) was used as received. Acetonitrile (CH_3CN , Baker HPLC, 99.9%) was stored in a gas tight storage bulb after three freeze-pump-thaw cycles. Ethylene (C_2H_4 , Matheson C. P.) was degassed with three freeze-pump thaw cycles and stored on the vacuum line. Acetaldehyde (CH_3CHO , Aldrich, 99%) used as received. Anhydrous Hydrazine (N_2H_4 , Aldrich, 98%) used as received. Acetaldehyde ammonia trimer (hexahydro-2,4,6-trimethyl-1,3,5-triazine, $C_6H_{15}N_3$, Aldrich, 97%) was used as received. Potassium monophosphate (KH_2PO_4 , Fisher, 99.5%). Disodium phosphate hydrate ($Na_2HPO_4 \cdot 7H_2O$,

Fisher). Chloramine-T ($\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{-N}(\text{Cl})\text{Na}\cdot\text{H}_2\text{O}$, Aldrich). 3-Methyl-1-phenyl-2-pyrazolin-5-one ($\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}$, Aldrich). Bis 3-methyl-1-phenyl-5-pyrazolone -Previously synthesized by Dr. K. Rahman (Kruse and Mellon 1953). Pyridine ($\text{C}_5\text{H}_5\text{N}$, Fisher, 99.9%). Refer to Keane (1995) for further detail.

Synthesized Reaction Intermediates: Acetaldazine (Acetaldehyde ethylidenehydrazone) $\text{CH}_3\text{CH}=\text{N-N}=\text{CHCH}_3$, was synthesized by the reaction of acetaldehyde and hydrazine (Curtius and Zinkeisen 1898). Acetaldehyde Hydrazone $\text{CH}_3\text{CH}=\text{N-NH}_2$. The procedure of Friedrich et al. (1975) was used for the synthesis of acetaldehyde hydrazone since it gave a better yield than that of Karabatsos and Osborne (1968). Both procedures are outlined in detail by Keane 1995.

Photochemistry

Static Studies Gas mixtures used in static photolysis studies were prepared using standard gas-handling techniques (Keane 1995) on a mercury-free vacuum line which was evacuated with a Welch Model 1405 rough pump and an oil diffusion pump. Pressure measurements were made with an MKS Baratron Model 370-HA1000 and a Model 270B Signal Conditioner. Twelve quartz vacuum cells were used to provide both ultraviolet (UV) and infrared (IR) transparency for irradiation and spectral measurements. Each cell is constructed from cylindrical quartz tubing with optical quartz windows using Teflon stopcocks with FETFE-O ring seals.

Ultraviolet Light Sources A Hanovia low pressure mercury lamp was used to supply 184.9 nm and 253.7 nm light. When only the 254 nm line was desired a Corning 9–54 filter was placed between the lamp and the cell. An iodine plasma discharge lamp with principal emission at 206.2 nm is a convenient light source for NH_3 photolysis (Harteck et al. 1964). By the proper selection of a window and filter material, it is possible to prepare a source of virtually monochromatic 206.2 nm ultraviolet light (Harteck et al. 1964). In experiments designed to examine the direct photolysis of acetaldazine, which absorbs both the 187.6 nm and 206.2 nm lines, a 1 cm thick quartz water filter was used to remove the 187.6 nm iodine line. The cold finger on the lamp was kept at 284 K during operation in order to maintain an optimal iodine pressure for the maximum flux at 206.2 nm (Keane 1995).

Analytical

The majority of the qualitative, as well as the quantitative measurements were achieved using ^1H NMR spectroscopy, Varian XL-200 (200 MHz) or Unity 500 (500 MHz) spectrometers. Initial results were obtained on the Varian XL-200 spectrometer using long acquisition times while later analyses were performed on the Varian unity 500 MHz instrument. CDCl_3 (Isotec, 99.9% atom D) was the solvent used in all NMR spectral measurements. All quantitative measurements were performed in the following manner: The amount of residual CHCl_3 in a sample of CDCl_3 (~1 g) was determined by the addition of a known amount of CH_2Cl_2 (2–4 μl) and then comparing the relative peak areas (5.30 ppm for CH_2Cl_2 and 7.26 ppm for CHCl_3). The peak arising from CHCl_3 in the CDCl_3 was used as an internal standard. For less intense product signals appearing further upfield in the spectrum a secondary assayed standard of deuterated acetone was utilized. All products could then be quantitatively measured by

comparing product areas to the areas of these internal references. After the photolysis period, the cell was tared and a portion of CDCl_3 was added to the cell's neck, and using the vacuum of the cell, added to the cell. After a 1 h extraction period the cell was reweighed and the weight of the solvent in the cell (usually -1.5 g) was then used in the quantitative analysis. Ultraviolet/Visible spectra were measured on a Cary 219 Spectrophotometer. HCN was analyzed by the pyridine-pyrazolone method at 625 nm (Kruse and Mellon 1953; Epstein 1947) A linear correlation with cyanide concentration was observed in the 10^{-4} – 10^{-6} M concentration range. Infrared Spectra and C_2H_2 quantitative analyses were performed on a Perkin Elmer 1800 Fourier Transform Infrared (FTIR) spectrometer. A gas IR cell was used for the measurement of reference spectra. The cell, consisting of a pyrex body and sodium chloride windows, allowed spectra to be measured between 4000 and 450 cm^{-1} . A cold finger was used to trap gases in the cell for analysis. The IR spectra of the reactants and products were also obtained in the same quartz cells used for photolysis. The cells are transparent from 4000 cm^{-1} to 3750 cm^{-1} and from 3600 cm^{-1} to 2100 cm^{-1} . Refer to Keane (1995) for further detail.

Results and Discussion

The Low Temperature Photolysis of $\text{NH}_3/\text{C}_2\text{H}_2$

Three low temperatures were used in these experiments (208 K, 195 K and 180 K) and the results were compared to those obtained at 296 K. During the course of these experiments intermediates were identified that were not previously detected by Ferris and Ishikawa (1988). Quantum yields for all known products of the photolysis of $\text{NH}_3/\text{C}_2\text{H}_2$ mixtures at low temperature and room temperature were determined and the photochemistry of important stable intermediates identified in this process investigated. From the results of these experiments a revision of the Ferris and Ishikawa (1988) reaction mechanism is proposed.

Products of the Room Temperature and Low Temperature Photolysis of $\text{NH}_3/\text{C}_2\text{H}_2$

Gas mixtures of $\text{NH}_3/\text{C}_2\text{H}_2$ 40:5 Torr were irradiated for specific time intervals at 296 K, 208 K, 195 K and 180 K. The vapor pressures of NH_3 and C_2H_2 at 208 K and 195 K are high enough to insure that both the NH_3 and C_2H_2 remained in the gas phase during the irradiations except at 180 K where the NH_3 vapor pressure, 7.5 Torr, is exceeded and NH_3 condensation occurs. Thus about 7.5 Torr of NH_3 remains in the gas phase during photolysis at 180 K, still enough to insure 100% light absorption within the quartz cell. HCN yields were linear for the photolysis periods examined. An apparent steady state was reached for some of the reaction intermediates formed. The quantum yields for the formation of HCN, CH_3CN , $\text{CH}_3\text{CH}=\text{N}-\text{N}=\text{CHCH}_3$, $\text{CH}_3\text{CH}=\text{N}-\text{NH}_2$, $\text{C}_2\text{H}_5\text{NH}_2$, CH_3NH_2 and C_2H_4 in the low temperature photolysis of $\text{NH}_3/\text{C}_2\text{H}_2$ gas mixtures are summarized in Table 1.

The uncharacterized yellow-brown material initially reported by Ferris and Ishikawa (1988) and also observed in this work (Keane 1995), which was deposited on the cell window directly under the lamp, could also account for some of this leveling of product yields. During the course of irradiation this deposit begins to absorb an appreciable fraction of the incident light. Ferris and Ishikawa (1988) report an absorbance, due to the material, of 1.0 at 200 nm after 4 h of photolysis with 185 nm light. This corresponds to the absorption of 90% of the incident light. In this work, absorbances of 0.31, 0.45, 0.61 and 1.14 corresponding to the absorption of

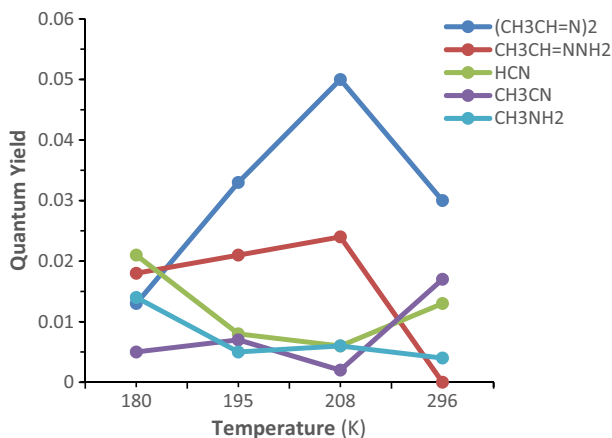
Table 1 Room temperature and low temperature photolysis of $\text{NH}_3/\text{C}_2\text{H}_2$ quantum yields for product formation

Molecule	180 K	195 K	208 K	296 K
HCN	0.021 (0.001)	0.008 (0.001)	0.006 (0.002)	0.013 (0.002)
$(\text{CH}_3\text{CH}=\text{N})_2$	0.013 (0.001)	0.033 (0.005)	0.050 (0.018)	0.030 (0.002)
CH_3CN	0.005 (0.001)	0.007 (0.002)	0.002 (0.0003)	0.017 (0.001)
$\text{C}_2\text{H}_5\text{NH}_2$	0.026 (0.008)	0.036 (0.006)	0.033 (0.010)	0.168 (NA)
CH_3NH_2	0.014 (0.001)	0.005 (0.001)	0.006 (0.001)	0.004 (0.003)
$\text{CH}_3\text{CH}=\text{NNH}_2$	0.018 (0.003)	0.021 (0.002)	0.024 (0.005)	0.000
C_2H_4	0.074 (0.014)	0.076 (0.022)	0.068 (0.024)	0.000

Errors are in brackets. NA = Quantum yield for $\text{C}_2\text{H}_5\text{NH}_2$ at 296 K estimated from first data point due to rapid steady state conditions and probably larger than those reported for multiple data points

51%, 64%, 75% and 93% of the incident light was determined after the irradiation of $\text{NH}_3/\text{C}_2\text{H}_2$ (40:5 Torr) with 206 nm light for 25 min, 45 min, 90 min and 8 h respectively. This polymer-like substance could be removed only by first washing with ethanolic NaOH and then aqua regia. No further characterization of this polymer-like material or deposit was pursued in this work.

The quantum yield for HCN formation increases from a minimum at 208 K as the temperature decreases to a maximum at 180 K. A similar trend of increasing quantum yield with decreasing temperature was found for CH_3NH_2 . The quantum yield for CH_3CN formation increased from 208 K and remained essentially constant at 195 K and 180 K. In contrast, the quantum yield for $\text{CH}_3\text{CH}=\text{N}-\text{N}=\text{CHCH}_3$ formation decreases from a maximum at 208 K to a minimum at 180 K. This trend in decreasing quantum yield with decreasing temperature was also found for $\text{CH}_3\text{CH}=\text{N}-\text{NH}_2$ (Fig. 4).

**Fig. 4** Variation of product quantum yields with temperature in the photolysis of $\text{NH}_3/\text{C}_2\text{H}_2$ 40:5 Torr

The quantum yield for C_2H_4 formation appears to remain independent of temperature within the low temperature region studied as does the quantum yield for $C_2H_5NH_2$ (Fig. 5).

In summary, quantum yields for both CH_3CN and CH_3NH_2 formation were generally observed to rise and fall with the quantum yield for HCN formation throughout the temperature range studied. Meanwhile the quantum yields for $CH_3CH = N-N = CHCH_3$ and $CH_3CH = NNH_2$ formation run opposite to that of HCN formation. The quantum yields for C_2H_4 and $C_2H_5NH_2$ appear to vary inversely with respect to each other.

It was generally observed that the initial rate of $CH_3CH = N-N = CHCH_3$ formation is faster than that of CH_3CN in all of the experimental studies whereas later CH_3CN formation outpaced $CH_3CH = N-N = CHCH_3$ formation at room temperature (296 K). In the 208 K and 195 K experiments $CH_3CH = N-N = CHCH_3$ formation remained greater than CH_3CN formation during the course of the reaction studied. At 180 K a dramatic shift again was observed with CH_3CN formation outpacing $CH_3CH = N-N = CHCH_3$ formation. The rate of $CH_3CH = N-N = CHCH_3$ decomposition was found to be proportional to the rate of CH_3CN formation (Keane 1995). Early studies on the direct photolysis of $CH_3CH = N-N = CHCH_3$ at 254 nm and 313 nm established CH_3CN as the predominant photoproduct (Horne and Norrish 1970; Brinton 1955). In this study it was found that the direct photolysis of $CH_3CH = N-N = CHCH_3$ with 206 nm results in a 39% conversion to CH_3CN . These results indicate that $CH_3CH = N-N = CHCH_3$ is an important source of the CH_3CN formed in the photolysis of NH_3/C_2H_2 mixtures.

The quantum yields obtained for the photolysis of NH_3/C_2H_2 mixtures at room temperature and low temperature in this work are in general agreement with the results of Ferris and Ishikawa (1988). The central intermediate formed in their proposed pathway is $CH_3CH = NH$ which results from the combination of $C_2H_3\cdot$ and $NH_2\cdot$ radicals. All the reaction products are derived from $CH_3CH = NH$. Hydrogen atom abstraction reactions lead to the formation of $CH_3\dot{C}=NH$ radicals. The $CH_3\dot{C}=NH$ radical decomposes to CH_3CN . The formation of $CH_3CH = N-N = CHCH_3$ was proposed to occur by the self reaction of $CH_2 = CHNH\cdot$ radicals formed by H atom abstraction from $CH_2 = CHNH_2$. However, the isomerization of enamine $CH_2 = CHNH_2$ to imine $CH_3CH = NH$ is a process characteristic of enamines (Granik 1984; Lovas et al. 1975) and theoretical studies indicate that the imine dominates the gas phase equilibrium in this enamine-imine tautomerism (Lammertsma and Prasad 1994; Bouchoux et al. 1993). It therefore seemed likely that the ethylideneiminyl radical ($CH_3CH = N\cdot$), also produced by H atom abstraction from $CH_3CH = NH$ self reacts to yield $CH_3CH = N-N = CHCH_3$. The initial data obtained in this work, with 40:5 Torr mixtures at 296 K and various low temperatures supported this recombination step for $CH_3CH = N-N = CHCH_3$ formation with the $CH_3CH = N\cdot$ radical having a central role in product formation (Fig. 6).

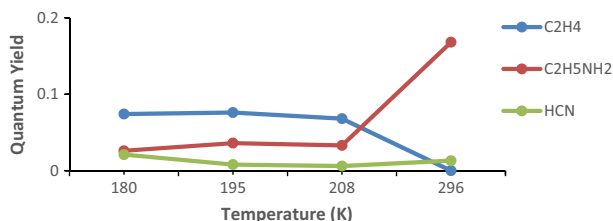


Fig. 5 Variation of product quantum yields with temperature in the photolysis of NH_3/C_2H_2 40:5 Torr (Note the change in verticle scale from Fig. 4 above)

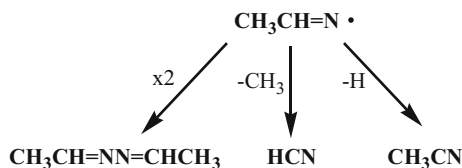


Fig. 6 The ethylideneiminy radical is a central intermediate within the proposed reaction pathway. Loss of a $\text{CH}_3\cdot$ yields HCN while loss of a H atom yields CH_3CN . Acetaldazine ($\text{CH}_3\text{CH}=\text{N}-\text{N}=\text{CHCH}_3$) would result from the self reaction of these radicals in this model

According to the Ferris and Ishikawa mechanism the photolysis of $\text{CH}_3\text{CH}=\text{N}-\text{N}=\text{CHCH}_3$ yields CH_3CN and the addition of H atoms to CH_3CN yields HCN. A decrease in the HCN yield was observed at low temperature. This was attributed to the condensation of $\text{CH}_3\text{CH}=\text{N}-\text{N}=\text{CHCH}_3$ and CH_3CN on the cell wall. This would remove the HCN precursor fraction from the gas phase where it is not subject to UV radiation and thus not converted to HCN. Again the results of the present work are in general agreement with those found by Ferris and Ishikawa.

In this study the quantum yield for HCN formation decreased while the quantum yield for $\text{CH}_3\text{CH}=\text{N}-\text{N}=\text{CHCH}_3$ formation increased as the temperature decreased to 208 K and 195 K. However, during this work it was found that the quantum yield for HCN formation increased at 180 K. This increase may be attributed to the different starting pressures of the reactant mixtures prepared at room temperature. Ferris and Ishikawa used 5 Torr of NH_3 and 2.5 Torr of C_2H_2 . Using this starting pressure for NH_3 insures that all of the NH_3 will remain in the gas phase at 178 K. In this work the starting pressures are 40:5 Torr $\text{NH}_3/\text{C}_2\text{H}_2$. Ammonia condensation will occur at 180 K leaving about 7.5 Torr in the gas phase, enough to insure complete light absorption. Therefore the experimental conditions change in going to 180 K in this work but remained constant in the experiments of Ferris and Ishikawa (1988). When NH_3 condensation occurs the partial pressure of NH_3 falls and the probability of a reactive encounter between a H atom and an HCN precursor increases thus increasing the rate of HCN formation. The increase observed for HCN formation at 180 K in this work was an interesting discovery because it suggested the possibility of a pressure related effect of NH_3 on HCN formation. Ferris and Ishikawa observed a decrease in the HCN yield with the addition of a high partial pressure of H_2 . However, Ferris and Ishikawa gave no explanation why the addition of H_2 resulted in a decrease in HCN yield.

Product Ratios at 195 K vs 180 K: Evidence for a Pressure Related Effect

Experiments were performed in order to investigate the relationship between the partial pressure of NH_3 and the changing photoproduct distributions observed between $\text{CH}_3\text{CH}=\text{N}-\text{N}=\text{CHCH}_3$ and CH_3CN at 195 K and 180 K. Mixtures of 40:5 Torr $\text{NH}_3/\text{C}_2\text{H}_2$ were photolyzed at 195 K. These photolysis results were then compared with irradiations performed at 180 K and 5:5 Torr mixtures irradiated at 195 K.

The product ratio for $\text{CH}_3\text{CH}=\text{N}-\text{N}=\text{CHCH}_3$ and CH_3CN obtained from the photolysis of $\text{NH}_3/\text{C}_2\text{H}_2$ at 195 K using 5:5 Torr was the reverse of that obtained at 195 K with a 40:5 Torr mixture. The results closely resemble what was obtained at 180 K where the partial pressure of NH_3 is 7.5 Torr. These results demonstrate that the distributions observed for $\text{CH}_3\text{CH}=\text{N}-\text{N}=\text{CHCH}_3$ and CH_3CN at 195 K and 180 K are not based on temperature dependent reaction kinetics but are dependent on the partial pressure of NH_3 . From these and previously reported

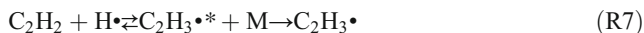
laboratory studies (Keane et al. 1996) a revised and expanded reaction pathway for the coupled photochemistry of ammonia and acetylene is proposed.

Ammonia is the principal light absorbing species, absorbing ~98% of the incident light in $\text{NH}_3/\text{C}_2\text{H}_2$ mixtures. The photolysis of NH_3 initiates all subsequent reactions and thus the factors controlling its photochemistry are considered as central to the interpretation of the observed results. The photochemistry of NH_3 has been studied in considerable detail and excellent discussions can be found in Groth and Rommel (1965), McDonald et al. (1954) and Noyes and Leighton (1941). The initial step is the dissociation of NH_3 to H atoms and NH_2 -radicals (R1). The quantum yield for NH_3 decomposition has been shown to be pressure dependent (Groth and Rommel 1965; McDonald et al. 1954; Noyes and Leighton 1941), the value increasing with decreasing pressure. The primary step is estimated to occur with a quantum yield close to unity at low pressures (Okabe 1978; Schurath et al. 1969; Calvert and Pitts 1966; Groth and Rommel 1965; McDonald et al. 1954; Noyes and Leighton 1941). This pressure dependency is attributed to collisional de-excitation (R2 - R4). The $\text{NH}_2\cdot$ radicals formed are removed rapidly by combination to N_2H_4 (R5). The homogeneous recombination of H atoms requires a three body collision and is therefore negligible. The N_2H_4 formed is subject to H atom abstraction which ultimately converts it to N_2 and H_2 (R6).



The addition of a H atom to C_2H_2 (R7) is proposed as the next step in the reaction mechanism after NH_3 photolysis because the pseudo-first-order rate constant for the addition of a H atom (Payne and Stief 1976) is 700 times greater than the addition of a $\text{NH}_2\cdot$ radical to C_2H_2 at 296 K (Bosco et al. 1984). The vinyl radical formed ($\text{C}_2\text{H}_3\cdot$) can react by different pathways. For example, addition of a H atom can result in C_2H_4 formation (R8). It has been determined that up to 2/3 of the $\text{C}_2\text{H}_3\cdot$ recycles back to C_2H_2 (R8a) upon reaction with H atoms (Monks et al. 1995). The rate constant for the reaction of $\text{C}_2\text{H}_3\cdot$ with H_2 (R8b) has recently been demonstrated to be 10^{10} times less than that for the reaction of $\text{C}_2\text{H}_3\cdot$ with $\text{H}\cdot$ and is therefore considered to be negligible (Fahr et al. 1995). Vinylamine ($\text{CH}_2 = \text{CHNH}_2$) is formed by radical combination (R9), another available reaction channel for $\text{C}_2\text{H}_3\cdot$. Support for the formation of vinylamine is found in the work of Guillemin et al. (1995a, b). They studied the photolysis of germane (GeH_4) and phosphine (PH_3) in the presence of C_2H_2 . Vinylgermane

($\text{H}_2\text{C} = \text{CHGeH}_3$) and vinylphosphine ($\text{H}_2\text{C} = \text{CHPH}_2$) were the major products detected. As discussed in Section 4.1 the isomerization of vinylamine to ethylideneimine (R10) is a process characteristic of enamines (Lammertsma and Prasad 1994; Bouchoux et al. 1993; Granik 1984; Lovas et al. 1975).

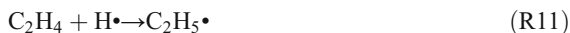


Photochemistry of Reaction Intermediates

In order to further elucidate the reaction pathways involved in the coupled photochemistry of $\text{NH}_3/\text{C}_2\text{H}_2$ a series of detailed laboratory studies of the photochemistry of various reaction intermediates were pursued. These studies included the direct photolysis and H atom initiated decomposition of ethene (C_2H_4), ethylamine ($\text{CH}_3\text{CH}_2\text{NH}_2$), Acetonitrile (CH_3CN) and acetaldazine ($\text{CH}_3\text{CH} = \text{N}-\text{N} = \text{CHCH}_3$).

C_2H_4

The photolysis of $\text{NH}_3/\text{C}_2\text{H}_4$ mixtures has been reported to yield $\text{C}_2\text{H}_5\text{NH}_2$ (Schurath et al. 1969). They examined the photolysis of 40/5 Torr mixtures of $\text{NH}_3/\text{C}_2\text{H}_4$ using the 206 nm line from an I_2 lamp at 296 K. The major products obtained were $\text{C}_2\text{H}_5\text{NH}_2$ (quantum yield = 0.35) and C_4H_{10} (butane: quantum yield = 0.20). They also detected C_2H_6 (ethane), $\text{C}_4\text{H}_9\text{NH}_2$ (butylamine), $\text{NH}_2\text{C}_2\text{H}_4\text{NH}_2$ (ethylenediamine), N_2H_4 (hydrazine) and N_2 and an unidentified product. The formation of $\text{C}_2\text{H}_5\text{NH}_2$ is proposed to occur through the addition of H atoms and $\text{NH}_2\cdot$ radicals to C_2H_4 (R11, R12) (Schurath et al. 1969).



The results of Schurath et al. (1969) agree favorably with the quantum yields for $\text{C}_2\text{H}_5\text{NH}_2$ formation and C_2H_4 loss at 296 K in this study. In this work the quantum yield for C_2H_4 loss

was experimentally determined to be 0.80. The quantum yield for $C_2H_5NH_2$ formation was 0.31 (Table 2).

Butane was also detected in these experiments as a major product, with a similar signal intensity as $C_2H_5NH_2$. No attempt was made to quantify its rate of formation. The N-ethyl derivative of ethylideneimine ($CH_3CH = N-C_2H_5$) was also detected with the next highest quantum yield. This may be the unidentified product referred to by Schurath et al. (1969). In addition to these major products trace amounts of CH_3NH_2 , CH_3CN , $CH_3CH = N-NH_2$ and $CH_3CH = N-N = CHCH_3$ were detected. None of the other products, C_2H_6 , $C_4H_9NH_2$, $NH_2C_2H_4NH_2$, N_2H_4 and N_2 , reported by Schurath et al. (1969) were immediately detected and no further search for them was conducted. The main differences between the room temperature and the low temperature photolysis of NH_3/C_2H_4 were the drop, to undetectable levels, in the quantum yields for $CH_3CH = N-C_2H_5$ and CH_3CN formation and the increases in the quantum yields for $CH_3CH = N-NH_2$, CH_3NH_2 and $CH_3CH = N-N = CHCH_3$. The quantum yield for C_2H_4 formation in the low temperature experiments remained constant with the exception of the 195 K result which is assumed due to indeterminate error (Keane 1995).

$CH_3CH_2NH_2$

The predominant product formed in the photolysis of $CH_3CH_2NH_2$ is N-ethylethylideneimine ($CH_3CH = N-C_2H_5$) which was identified in this work and the quantum yield for its formation measured. (Table 3) The quantum yield for $CH_3CH = N-C_2H_5$ formation is 0.43 molecules/photon. Acetaldazine ($CH_3CH = N-N = CHCH_3$) was detected in the H atom initiated experiments in addition to the products previously detected in the direct photolysis experiments (Keane 1995).

Previous studies of the similar aliphatic amine, methylamine (CH_3NH_2), demonstrated that this compound can be photolyzed to HCN ($\Phi = 0.08$), presumably via the imine intermediate methyleneimine ($CH_2 = NH_2$) (Gardner and McNesby 1982; Gardner 1981; Nishi et al. 1980). The reported quantum yield for CH_3NH_2 loss, roughly the same as that for ethylamine, ranges from 0.75 to 2.2 (Michaels and Noyes 1963; Emeleus and Jolley 1935; Emeleus and Taylor 1931). Previously detected intermediates in the photolysis of CH_3NH_2 include H_2 , NH_3 , CH_4 , N_2 , C_2H_6 , C_2H_4 and $CH_2 = N-CH_3$.

Table 2 Room temperature and low temperature photolysis of NH_3/C_2H_4 quantum yields for product formation and C_2H_4 consumption

Molecule ^a	296 K	208 K	195 K	180 K
HCN	N.D. ^b	N.D.	N.D.	N.D.
$(CH_3CH = N)_2$	0.002	0.003	0.003	0.002
CH_3CN	0.003	0.000	0.000	0.002
$C_2H_5NH_2$	0.305	0.194	0.315	0.324
CH_3NH_2	0.006	0.007	0.008	0.008
$CH_3CH = NNH_2$	0.003	0.013	0.008	0.006
C_2H_4	-0.79	-1.14	-5.69 ^c	-1.19
$CH_3CH = NC_2H_5$	0.010	0.000	0.000	0.000

^a Butane (C_4H_{10}) was also detected in these experiments. The quantum yield was not determined. However, the intensity of the signals in the NMR spectra suggests an efficient formation comparable to $C_2H_5NH_2$

^b N.D. = Not determined

^c The value of the quantum yield for C_2H_4 consumption at 195 K is due to indeterminate error

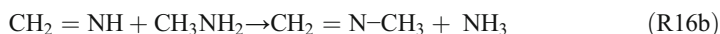
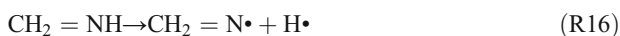
Table 3 The photolysis of C₂H₅NH₂ and NH₃/C₂H₅NH₂ quantum yields for product formation comparison of direct photolysis and h atom initiated decomposition

Molecule	Direct photolysis ^a	H Atom initiated ^b
HCN	0.005	0.004
CH ₃ CH = N-N = CHCH ₃	0.000	0.012
CH ₃ CN	0.018	0.014
CH ₃ CH = NC ₂ H ₅	0.43	0.55
C ₂ H ₅ NH ₂	-0.98	-0.66

^a Photolysis of C₂H₅NH₂ 5 Torr with 206 nm light at 296 K

^b Photolysis of NH₃/C₂H₅NH₂ 40:5 Torr with 206 nm light at 296 K. H atoms produced upon NH₃ photolysis

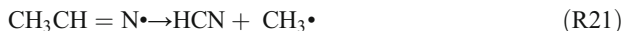
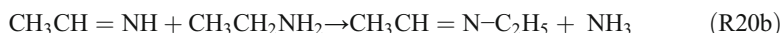
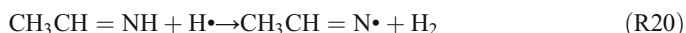
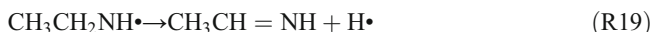
In the photolysis of CH₃NH₂ the primary process is thought to be cleavage of the N-H bond (R13). Quantum yields for CH₃NH₂ loss greater than unity were attributed to abstraction processes on CH₃NH₂ by the H atom produced upon CH₃NH₂ photolysis (R14). This would then be followed by dissociation or an abstraction of a hydrogen to form an imine (R15). The imine produced (methylideneimine) would then either be photolyzed or undergo another abstraction to yield HCN (R16 and R17). N-methylmethyleneimine (H₂C = N-CH₃) is thought to form by a nucleophilic addition reaction between CH₂ = NH and CH₃NH₂ (R16b) (Watson 1952; Wetmore and Taylor 1944).



In the photolysis of CH₃CH₂NH₂ the primary process (R18) is the same as that for CH₃NH₂ (Calvert and Pitts 1966) and this reaction is presumably followed by similar secondary reactions (R19-R22). However, the imine formed is ethylideneimine (R19) which can decompose (R20) to either HCN (R21) or CH₃CN (R22).

A precedent exists in the literature for the formation of the analogous imine in the photolysis of CH₃NH₂ (Watson 1952; Wetmore and Taylor 1944). The methylideneimine formed in the photolysis of CH₃NH₂ is thought to react with CH₃NH₂ to form the corresponding N-methyl derivative (CH₂ = N-CH₃) (R16b). Presumably, a similar nucleophilic addition occurs in the photolysis of CH₃CH₂NH₂ whereby the CH₃CH = NH formed reacts with CH₃CH₂NH₂ to give CH₃CH = N-C₂H₅ (R20b). Hydrogen atom

initiated decomposition of $C_2H_5NH_2$ (R18b) may be an important route for its decomposition in Jupiter's atmosphere.



The reaction pathway outlined above predicts the formation of CH_3CN in the photolysis of $CH_3CH_2NH_2$. The formation of CH_3CN was detected and the quantum yield for its formation measured and found to be 0.018 molecules/photon. A non-volatile liquid polymer was found on the cell window. Precedence for this type of polymer formation in the photolysis of CH_3NH_2 exists (Watson 1952; Wetmore and Taylor 1944).

CH_3CN

Previous studies suggested that CH_3CN was an important intermediate for HCN formation in the photolysis of NH_3/C_2H_2 mixtures (Ferris and Ishikawa 1988). Earlier experiments on the direct photolysis of CH_3CN (McElcheran et al. 1958) demonstrated the efficient photochemical conversion of CH_3CN to HCN. It was postulated that the addition of a H atom ($H\cdot$) to the π -bonds of CH_3CN (R23) would produce an unstable excited addition complex which can either split off the $CH_3\cdot$ group or back-dissociate (Svejda and Volman 1970; McElcheran et al. 1958). The forward reaction is exothermic by 10 kcal (McElcheran et al. 1958):



The addition product intermediate, which is an imine radical (ethylideneimino radical), apparently has a short lifetime, since no stable imine end product was detected (McElcheran et al. 1958).

The quantum yield for HCN formation was determined to be 0.14 molecules/photon. The quantum yield for CH_3CN loss in this system is 0.18 molecules/photon. The results of this work demonstrate that 78% of the CH_3CN reacted is converted to HCN, a very efficient process. These experiments establish CH_3CN as a key intermediate for HCN formation in the photolysis of NH_3/C_2H_2 . A visually similar, but not as dark, polymer

deposit was observed as in the photolysis of $\text{NH}_3/\text{C}_2\text{H}_2$ mixtures. The UV absorption of this polymer was not determined.

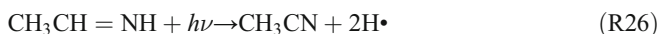
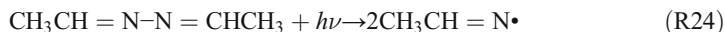


The results obtained in this study and in the initial work by Ferris and Ishikawa (1988) establish acetaldazine, $\text{CH}_3\text{CH} = \text{N-N} = \text{CHCH}_3$ as an important intermediate for CH_3CN formation and thus HCN formation in the photolysis of $\text{NH}_3/\text{C}_2\text{H}_2$ mixtures. Experiments were performed that would address three important questions about this important intermediate. First the quantum efficiency for CH_3CN formation resulting from the direct photolysis of $\text{CH}_3\text{CH} = \text{N-N} = \text{CHCH}_3$ with 206 nm light was determined. Second the possible role of H atom initiated decomposition reactions was explored. Finally the postulate of Ferris and Ishikawa (1988) that this intermediate would condense on the cell walls at low temperature, thus essentially removing it from further reaction, was investigated.

Direct Photolysis of Acetaldazine: CH_3CN Formation and Acetaldazine Loss

The quantum yield for CH_3CN formation is 0.58 molecules/photon. The quantum yield for $\text{CH}_3\text{CH} = \text{N-N} = \text{CHCH}_3$ loss was obtained from the same NMR spectra and was found to be 1.48 molecules/photon (Table 4). A non-volatile polymeric liquid was observed to form on the quartz window beneath the lamp.

Experimental studies on the photolysis of $\text{CH}_3\text{CH} = \text{N-N} = \text{CHCH}_3$ at 254 nm and 313 nm have been previously reported (Horne and Norrish 1970 and Brinton 1955). The predominant product was CH_3CN which was postulated to form through a disproportionation reaction between the ethylideneimino radicals produced in the primary process (R24-R26) (Horne and Norrish 1970):



No HCN was detected in the direct photolysis of $\text{CH}_3\text{CH} = \text{N-N} = \text{CHCH}_3$. However, these studies do suggest that $\text{CH}_3\text{CH} = \text{N-N} = \text{CHCH}_3$ may serve as a source of CH_3CN in the $\text{NH}_3/$

Table 4 Photolysis of $\text{CH}_3\text{CH} = \text{N-N} = \text{CHCH}_3$ and $\text{NH}_3/\text{CH}_3\text{CH} = \text{N-N} = \text{CHCH}_3$ quantum yields for $\text{CH}_3\text{CH} = \text{N-N} = \text{CHCH}_3$ loss and CH_3CN formation

Molecule	Direct photolysis ^a	H Atom abstraction ^b
$\text{CH}_3\text{CH} = \text{N-N} = \text{CHCH}_3$	-1.48	-0.49
CH_3CN	0.58	0.24

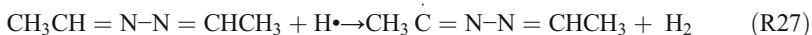
^a Photolysis of $\text{CH}_3\text{CH} = \text{N-N} = \text{CHCH}_3$ 10 Torr with 206 nm light at 296 K

^b Photolysis of $\text{NH}_3/\text{CH}_3\text{CH} = \text{N-N} = \text{CHCH}_3$ 600:1 Torr with 206 nm light at 296 K. H atoms produced upon NH_3 photolysis

C₂H₂ system. Hydrogen atoms, produced in NH₃ photolysis, would react with CH₃CN and yield HCN (Svejda and Volman 1970; McElcheran et al. 1958).

Quantum Yield for CH₃CH = N-N = CHCH₃ Loss and CH₃CN Formation Resulting from the H Atom Initiated Decomposition of CH₃CH = NN = CHCH₃

The objective of these experiments was to determine if direct photolysis or H atom abstraction is the predominant route of decomposition for CH₃CH = N-N = CHCH₃ on Jupiter. The H atom initiated decomposition of CH₃CH = N-N = CHCH₃ (R27 - R28) is a possible Jovian scenario. This reaction has not been reported in the literature but could result from H atom abstraction as outlined below:



Hydrogen atoms were generated by the photolysis of NH₃ with 206 nm light. The quantum yield for CH₃CH = N-N = CHCH₃ loss due to H atom abstraction was determined for NH₃/CH₃CH = N-N = CHCH₃ mixtures (600:1 Torr). The ratio of absorptivities for NH₃/CH₃CH = N-N = CHCH₃ is 47:260 at 206 nm, therefore a large excess of NH₃ was used in order to maximize the light absorption by NH₃ while minimizing absorption due to CH₃CH = N-N = CHCH₃. After allowing for the fraction of light directly absorbed by CH₃CH = N-N = CHCH₃ and its loss in that process, the quantum yield for CH₃CH = N-N = CHCH₃ loss due to H atom initiated decomposition was determined to be 0.49 molecules/photon (Table 4). No polymer formation was observed suggesting a different mechanism for CH₃CH = N-N = CHCH₃ decomposition by H atom as compared to that which occurs during direct photolysis.

The Reaction of N₂H₄ with CH₃CHO: a Model for an Alternative Pathway for CH₃CH = N-N = CHCH₃ and CH₃CH = N-NH₂ Formation

Acetaldazine (CH₃CH = N-N = CHCH₃) and ethylideneimine hydrazone (CH₃CH = N-NH₂) are products formed upon the photolysis of NH₃/C₂H₂ mixtures. The mechanism of their formation may be due to a gas phase radical recombination process. In the case of acetaldazine, a reactive encounter between two ethylideneiminyl radicals (CH₃CH = N•) would be necessary while the addition of NH₂• to CH₃CH = N• would yield the corresponding hydrazone. Another possible pathway for their formation could be by nucleophilic addition of hydrazine (N₂H₄), a combination product of NH₂•, to ethylideneimine (CH₃CH = NH). One way to test the feasibility of this mechanism is to mix hydrazine and the imine in the gas phase and look for the presence of the hydrazone and/or acetaldazine. Earlier attempts at a synthesis of this imine proved unsuccessful so it was decided to use CH₃CHO in place of the imine. The aldehyde and the imine are expected to have similar chemical properties. Furthermore, the aldehyde is known to react with hydrazine to yield both of the sought after products.

Immediately upon addition of the second reactant gas, excess CH₃CHO when forming CH₃CH = N-N = CHCH₃ and excess N₂H₄ when forming CH₃CH = NNH₂, a film of condensate appeared on the cell walls. The FTIR spectra obtained (Figs. 7 and 8) confirmed what would be expected if these reactions occurred as a homogeneous gas phase reaction or a

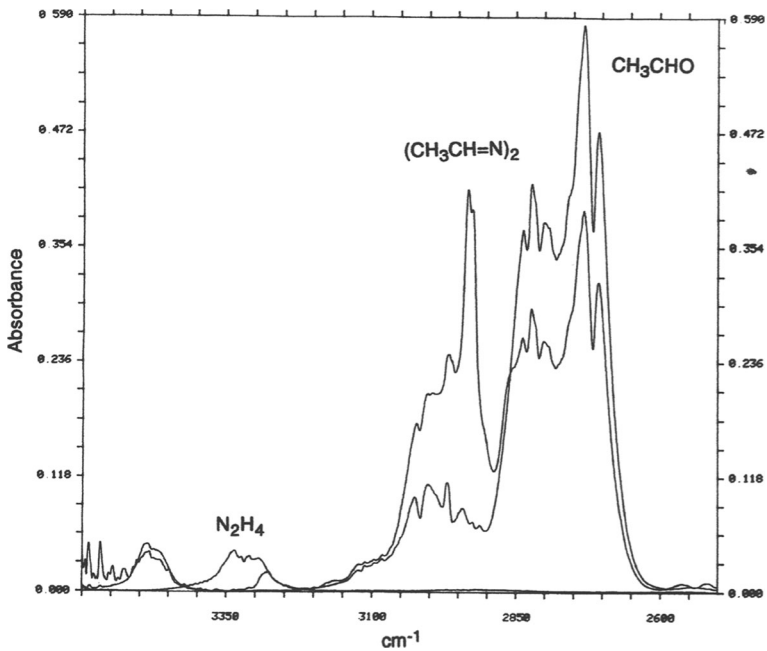


Fig. 7 FTIR spectra overlay showing the gas phase reaction between N_2H_4 and excess CH_3CHO resulting in $\text{CH}_3\text{CH}=\text{N}-\text{N}=\text{CHCH}_3$ formation

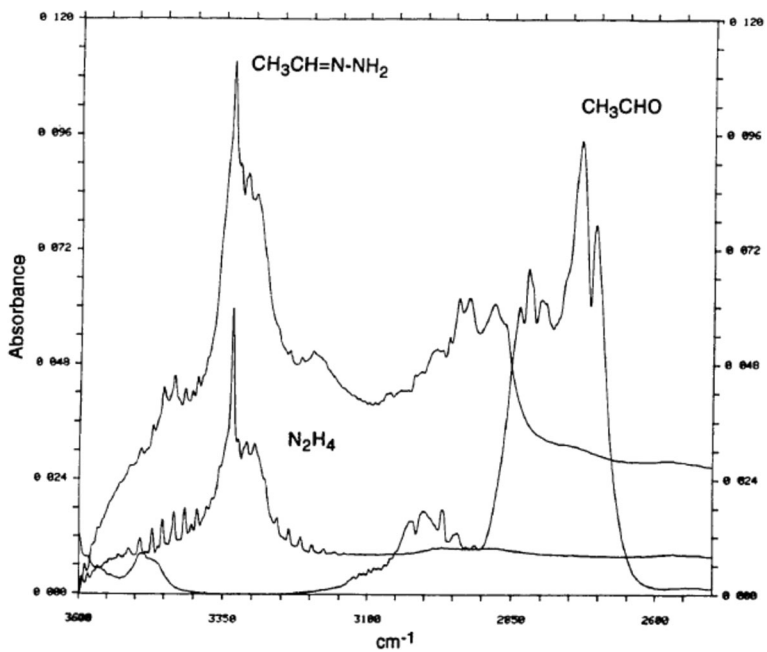
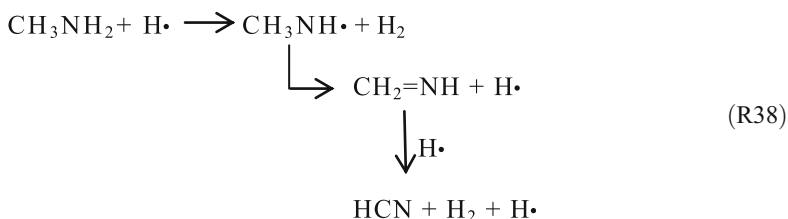
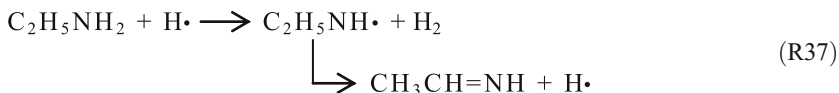
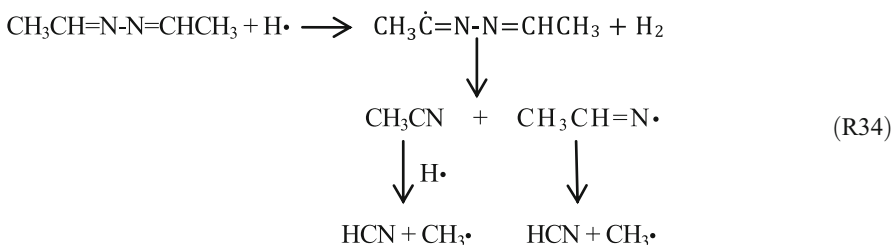
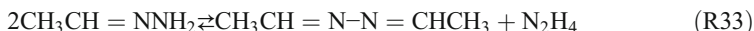
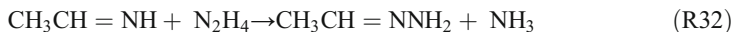


Fig. 8 FTIR spectra overlay showing the gas phase reaction between CH_3CHO and excess N_2H_4 resulting in $\text{CH}_3\text{CH}=\text{N}-\text{NH}_2$ formation



Implications for Astrophysical Environments

HCN on Jupiter and Extra-Solar Giant Planets

These laboratory studies were initially intended to test the theoretical proposal of Kaye and Strobel (1983) that a reported detection of HCN in Jupiter's atmosphere (Tokunaga et al. 1981) was the result of the coupled photochemistry of NH_3 and C_2H_2 . HCN is an important molecule in the synthesis of more complex organic molecules and therefore could have a major role in the chemical evolution of the atmospheres of the outer planets. This work enabled predictions to be made for the mass spectrometer measurements onboard the Galileo entry probe (Keane et al. 1996) and formed the experimental basis for a modeling study of the coupled photochemistry NH_3 and C_2H_2 on Jupiter (Moses et al. 2010).

However, aside from the detections of HCN subsequent to the impacts of Comet Shoemaker-Levy 9 (1–9) there is no solid observational evidence for the presence of non-cometary HCN on Jupiter. The reported detection of non-cometary HCN on Jupiter by ground-based observations presented by Tokunaga et al. (1981) have been challenged by subsequent non-detections in the infrared, sub-millimeter, and millimeter regions (Bézar et al. 1995; Moses et al. 2010). Calculated strict upper limits for a HCN mole fraction of 0.93 ppb to 0.16 ppb are indicated assuming HCN condenses in the upper troposphere, or uniform mixing throughout the troposphere and stratosphere respectively. (Davis et al. 1997; Moses et al. 2010) Nor was there any direct or convincing evidence for the presence of HCN in the GCMS results returned from the Galileo probe (Niemann et al. 1998).

The lack of detections of non-cometary HCN after the initial report of Tokunaga et al. (1981) and calculated severe upper limits may be explained by Moses et al. (2010). The results of their modeling study suggest that coupled carbon-nitrogen photochemistry on Jupiter is, at best, weak because of the removal of NH_3 from the upper atmosphere via condensation and a low eddy diffusion of C_2H_2 into the tropopause. This would prevent mixing of NH_3 and C_2H_2 and thus essentially uncoupling $\text{NH}_3/\text{C}_2\text{H}_2$ photochemistry.

However, the modeling remains somewhat speculative due to the limited experimental data available for individual reactions of interest. Thus, Moses et al. (2010) do not rule out that the coupled photochemistry of NH_3 and C_2H_2 could have implications for the atmospheres of Extra-Solar Giant Planets (EGP) and suggest alternative scenarios for such warmer giant planets. For example, a plausible scenario would be if an EGP were located closer to its parent star, such that NH_3 does not condense thus allowing for the mixing of $\text{NH}_3/\text{C}_2\text{H}_2$. In this scenario, and assuming it is not so close to the parent star that it is subjected to intense ultraviolet radiation, then the coupled photochemistry $\text{NH}_3/\text{C}_2\text{H}_2$ could proceed and be significant to the atmospheric chemistry of the planet (Moses et al. 2010).

Jupiter's Great Red Spot (GRS)

The reaction pathways for the coupled photochemistry of $\text{NH}_3/\text{C}_2\text{H}_2$ proposed in this work could elucidate, on a fundamental molecular level, non-equilibrium reactions leading to the production of complex hydrocarbons that might explain Jupiter's colorations. The possibility of chromophore formation and the observation of colored deposits formed on the quartz cell window directly below the UV light source were first reported and described by Ferris and Ishikawa (1987, 1988). Similar colored polymeric deposits were observed on the cell window directly underneath the lamp in this study but no further characterization of that polymeric material was pursued (Keane 1995).

Laboratory studies of the photochemistry of $\text{NH}_3/\text{C}_2\text{H}_2$ mixtures were recently extended by Carlson et al. (2016) and Sromovsky et al. (2017). They describe a detailed analysis and modeling of the spectral characteristics of what appears to be the same laboratory generated chemical compound or deposit initially reported by Ferris and Ishikawa (1987, 1988) and also observed by Keane (1995). Carlson et al. (2016) measured the spectral transmission of the deposits in the visible region and were able to model GRS reflection spectra from estimated imaginary indices of refraction. They then compared the results with observed and previously unreported visible spectra of the GRS obtained by the Cassini spacecraft and true color images. Carlson et al., conclude that the unknown GRS chromophore is spectrally consistent with the deposits formed during the photolysis of $\text{NH}_2/\text{C}_2\text{H}_2$ mixtures. Using high resolution mass spectrometry and infrared spectroscopy on the deposits formed, they infer the presence of di-

nitrogen functional groups (imine, azine, azo, diazo) that would be consistent with the various imine, hydrazones and azine compounds as possible precursors reported in earlier studies and this research (Ferris and Ishikawa 1987, 1988; Keane 1995; Keane et al. 1996).

Consistent with the somewhat speculative nature of the modeling studies by Moses et al. (2010), Carlson et al. (2016) note that only a single eddy diffusion coefficient profile was used in their work so there could be spatial variations with latitude, as well as underlying meteorological conditions. Carlson cites a study by Edgington et al. (1999) and Lara et al. (1998) suggesting that the eddy mixing rate at 250 mb is greater in the GRS region compared to regions to the north and south. Carlson suggests that GRS vortex activity could influence the dynamic properties of the atmosphere above, perhaps through the generation of upwardly propagating gravity waves. A plausible scenario would be an enhanced upward flux of gaseous NH_3 into high tropospheric altitudes where NH_2 and H radicals produced upon the photolysis of NH_3 would react with down welling acetylene and initiate chemical chain reactions such as those proposed in this study. The strength of such effects could vary with time and cause the observed temporal variations in the GRS color. Sromovsky et al. (2017) further extend the work by Carlson et al. (2016) and suggest that this same material could account for the color variations of many other cloud features on Jupiter.

These are significant results, for if the modeling and chemical analysis by Carlson et al. (2016) and Sromovsky et al. (2017) are correct, then the reaction pathways proposed in this study (Keane 1995; Keane et al. 1996) as well as earlier studies (Ferris and Ishikawa 1987, 1988) may elucidate the molecular pathways for organic chromophore formation in Jupiter's GRS and the variations in the visible color including other cloud features on Jupiter.

Another recent report indicates that the upper atmosphere above Jupiter's GRS is much warmer than elsewhere on the planet (O'Donoghue et al. 2016). In this study we uncovered a possible alternative mechanism for the formation of (azine) $\text{CH}_3\text{CH} = \text{N}-\text{N} = \text{CHCH}_3$ and (hydrazone) $\text{CH}_3\text{CH} = \text{N}-\text{NH}_2$ and N-ethylethylideneimine ($\text{CH}_3\text{CH} = \text{N}-\text{C}_2\text{H}_5$) via nucleophilic addition. These alternative reaction mechanisms are highly exothermic (Keane 1995). If these reactions occur within Jupiter's GRS, depending on the amount and rate of product formation, a speculative but plausible or partial solution to the observed heating and dynamics of Jupiter's GRS could be addressed with our proposed alternative condensation or nucleophilic addition reaction pathways and the exothermicity of those processes.

Comets and Interstellar Organic Synthesis

It is thought that the chemical composition of comets may provide information about the chemistry of the interstellar medium and the formation of the solar system (Cottin et al. 1999). Comets have been implicated in delivering important organic molecules to the pre-biotic earth and thus relevant to the field Astrobiology (Chyba et al. 1990; Thomas et al. 2006). NH_3 , C_2H_2 , CH_3CN and HCN , compounds present in the current study, have all been identified in cometary comae. (Mumma and Charnley 2011; Thomas et al. 2006). In addition, methylamine (CH_3NH_2) and ethylamine ($\text{CH}_3\text{CH}_2\text{NH}_2$) have been isolated from return samples as a result of recent spacecraft missions flown through cometary comae (Altwegg et al. 2016; Burchell and Kearsley 2009; Glavin et al. 2008; Sandford et al. 2006, Sandford 2009). Ethylamine is also a major product detected in this study (Keane 1995).

Since HCN , CH_3CN and ethylamine are products detected in laboratory studies of the coupled photochemistry of NH_3 and C_2H_2 (Ferris and Ishikawa 1987, 1988; Keane 1995; Keane et al. 1996) it is plausible that the coupled photochemistry of NH_3 and C_2H_2 might also

be important in the formation of important pre-biologic organo-nitrogen compounds present in cometary comae (Moses et al. 2010).

The role of photochemistry has long been considered important in studies involving interstellar organic synthesis (Agarwal et al. 1985; Briggs et al. 1992). Earlier calculations by Stief et al. (1972) suggested that polyatomic molecules can survive against photodecomposition to the order of 10^6 years within molecular clouds of moderate opacity. More recent work focused on the detection of organic molecules in the interstellar medium and their relative importance to prebiologic, planetary, and interstellar chemistry (Charnley et al. 2002; Ehrenfreund and Charnley 2000; Guillemin et al. 2004).

Some of the molecules identified in the laboratory simulations involving mixtures of NH_3 and C_2H_2 (Ferris and Ishikawa 1987, 1988; Keane 1995; Keane et al. 1996) have also been identified in the interstellar medium and circumstellar envelopes (Fuente et al. 2005; Johansson et al. 1984; Nguyen et al. 1984; Remijan et al. 2005; Ridgway et al. 1976; Snyder and Buhl 1971; Ziurys 2006). It is noteworthy that Ethylethylideneimine ($\text{CH}_3\text{CH}=\text{NH}$), an important reaction intermediate proposed in the pathways in these studies (Ferris and Ishikawa 1987, 1988; Keane 1995), has been detected in the interstellar medium (Loomis et al. 2013). Complex molecules have been reported to be in abundance towards Sagittarius B2 (Sgr B2), a dense interstellar cloud in between stars towards the galactic center (Miao et al. 1995). Surface-grain interactions are thought to be significant for interstellar chemistry (Agarwal et al. 1985; Briggs et al. 1992; Miao et al. 1995; Whittet 2013). So while highly conjectural, it would seem feasible that the photoproducts detected in this comprehensive study on the coupled photochemistry of $\text{NH}_3/\text{C}_2\text{H}_2$ (Keane 1995) and earlier by Ferris and Ishikawa (1987, 1988) could interact with the grain surface as a catalytic site for the alternative nucleophilic addition reactions proposed in this study (Keane 1995).

Summary and Conclusion

The photolysis of ammonia (NH_3) in the presence of acetylene (C_2H_2) produces a variety of organo-nitrogen compounds with significance to the fields of astrochemistry and astrobiology, specifically pre-biologic organic chemistry. The presence of NH_3 and C_2H_2 appears ubiquitous within many astrophysical environments ranging from Giant Planets to Comets to the Interstellar Medium. Thus the coupled photochemistry of NH_3 and C_2H_2 may be important wherever ammonia and acetylene are brought together in the presence of ultraviolet radiation.

The addition of H atoms and $\text{NH}_2\cdot$ radicals to C_2H_2 couples NH_3 photochemistry to C_2H_2 . Since NH_3 is the principal light absorbing species a proposed reaction mechanism for the formation of HCN and other molecular species resulting from the photolysis of $\text{NH}_3/\text{C}_2\text{H}_2$ mixtures should consider, in addition to the experimental data, the effect of pressure and temperature on the quantum yield for NH_3 decomposition and the pressure and temperature dependency of the addition of H atoms to C_2H_2 . While the mechanism which has been presented is in qualitative agreement with the experimental facts, it is quite possible that a more complex homogeneous and heterogeneous mechanism is involved which would give a more complete explanation of the results.

HCN is formed by the photolysis of $\text{NH}_3/\text{C}_2\text{H}_2$ mixtures at 296 K, 208 K, 195 K and 180 K. Acetonitrile and acetaldazine are efficiently converted to HCN under these reaction conditions. Quantum yield measurements indicate that $\text{C}_2\text{H}_5\text{NH}_2$ is an important reaction product therefore H atom addition processes effectively compete with H atom abstraction.

However under conditions that better approximate those found in the Jovian atmosphere the quantum yield for HCN formation is significantly reduced.

The experimental studies in this work used 206 nm light to photolyze NH_3 and thereby initiate the coupled photochemistry of NH_3 and C_2H_2 . The $\text{CH}_3\text{CH}=\text{N}-\text{N}=\text{CHCH}_3$ formed under these conditions is effectively shielded from the 206 nm photons so that H atom abstraction reactions were important. However, the solar flux at Jupiter includes longer wavelengths of light that increases with increasing wavelength (Huebner et al. 1992). Acetaldazine, an important source for CH_3CN , has a broad UV absorption which extends from below 200 nm out to 350 nm (Brinton 1955). The results of experiments using the 254 nm emission from the low pressure Hg lamp suggest that the azine can be rapidly photolyzed at the longer wavelength UV light that penetrates through the atmosphere and the NH_3 clouds of Jupiter. This would provide more CH_3CN for reaction with H atoms and thus HCN in the Jovian atmosphere. A critical factor being the residence time of any azine formed in the region of the atmosphere where photolysis will proceed. However, given the low temperatures found in Jupiter's atmosphere, it is unclear whether the rate of photochemical conversion of the $\text{CH}_3\text{CH}=\text{N}-\text{N}=\text{CHCH}_3$ in the gas phase will outpace its condensation to the solid state. Potentially more significant, the reaction pathways proposed may elucidate the molecular pathways responsible for organic chromophore formation in Jupiter's GRS and the variations in the visible color including other cloud features on Jupiter.

We encourage further investigation into the organic chemistry, thermodynamic and kinetic properties of the organo-nitrogen compounds observed in the photolysis experiments of Ferris and Ishikawa (1987, 1988); Keane (1995); Carlson et al. (2016) and Sromovsky et al. (2017). Specifically, ab-initio calculations and the temperature dependence of many of the thermochemical reactions need to be investigated in conjunction with the continued modeling of the possible relevance of these reactions to the GRS as well as other cloud features on Jupiter.

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