Synthesis of HCN and HNC in Ion-Irradiated N_2-Rich Ices

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Abstract

Near-IR observations reveal that N_2-rich ice containing small amounts of CH_4, and CO, is abundant on the surfaces of Triton, a moon of Neptune, and Pluto. N_2-rich ices may also exist in interstellar environments. To investigate the radiation chemistry of such ices we performed a systematic IR study of ion-irradiated N_2-rich mixtures containing CH_4 and CO. Irradiation of $N_2 + CH_4$ mixtures at 12 K, showed that HCN, HNC, diazomethane, and NH_3 were produced. We also found that UV photolysis of these ices produced detectable HCN and HNC. Intrinsic band strengths, $A(HCN)$ and $A(HNC)$, were measured and used to calculate yields of HCN and HNC. Similar results were obtained on irradiation of $N_2 + CH_4 + CO$ ices at 12 K, with the main difference being the formation of HNCO. In all cases we observed changes on warming. For example, when the temperature of irradiated $N_2 + CH_4 + CO$ was raised from 12 to 30 K, HCN, HNC, and HNCO reacted with NH_3, and OCN^-, CN^-, N_3^-, and NH_4^+ were produced. These ions, appearing at 30 K, are expected to form and survive on the surfaces of Triton, Pluto, and interstellar grains. Our results have astrobiological implications since some of these radiation products are involved in the syntheses of biomolecules such as amino acids and peptides.

1. Introduction

Near-IR observations reveal that N_2-rich ices containing small amounts of methane (CH_4) and carbon monoxide (CO) are abundant on the surfaces of Pluto and Triton, a moon of Neptune (3, 17). These ices undergo chemical changes due to various ionizing radiations such as solar UV photons, the solar wind plasma, and cosmic rays, with the latter being dominant. For Triton, (5) calculated that 167 - 293 eV $molec^{-1}$ is deposited in the upper ~ 10 m over 4.6 billion years. Pluto's dose is expected to be similar. To date, little has been published on the chemistry of N_2-rich ices (e.g., (9, 18, 2)). Here we report a systematic IR study of proton-irradiated N_2-rich mixtures relevant to Triton and Pluto. Ices were ion-irradiated at 12 K to study the production and stability of new species, and to investigate pathways for product formation. Of special significance in our results are (1) the formation of HCN, HNC, and NH_3 and (2) the reactions of these products on warming to ~ 35 K, producing CN^-, NH_4^+, and other stable ions.

2. Experimental

Details of our experimental set-up have been published (15). Briefly, ices a few micrometers thick are formed by condensation of gas-phase mixtures onto a pre-cooled aluminum mirror at ~ 12 K. Mid-IR spectra of ices were taken before and after energetic processing, usually as 60-scan accumulations (4 cm^{-1} resolution) or 120-scan accumulations (1 cm^{-1} resolution). Ion irradiations were done with a Van de Graaff accelerator (0.8 MeV protons), and UV photolyses with a microwave-discharged hydrogen flow lamp ($E_{avg} \sim 7.41 \pm 0.23$ eV, flux $\sim 3.1 \times 10^{14}$ photons cm^{-2} sec^{-1}). Reagents used were commercially available or prepared and purified with

standard procedures. Band strengths, termed "A" values, of HCN and HNC were needed to determine column densities and product yields in different experiments. A is defined as:

$$A = \frac{\int \tau(\tilde{\nu})\, d\tilde{\nu}}{N}$$

with the integral being a band's area (cm^{-1}), and N being column density ($molec\ cm^{-2}$) calculated from a sample's composition, density, and thickness. Details will be published later, so here we simply state that at 12 K in N_2, $A(\nu_3\ HCN) = 1.1 \times 10^{-17}\ cm\ molec^{-1}$ and $A(\nu_3\ HNC) = 7.2 \times 10^{-18}\ cm\ molec^{-1}$.

3. Results

Results at $\sim$ 12 K. IR spectra of pure N_2, CH_4, and CO, as well as binary mixtures of these three, were recorded, both for unirradiated and irradiated samples, and details will be reported in a separate publication.

N_2 + CH_4: Mid-IR spectra of N_2 + CH_4 (100:1) before and after ion irradiation are shown in Fig. 1a. Important radiation products in the bottom trace are HNC, HCN, diazomethane (CH_2N_2), and radicals N_3 and CH_3. NH_3 was found as a small band at 971 cm^{-1}. These results demonstrate a condensed-phase pathway for the formation of acids HNC, HCN, and a base (NH_3) in N_2-rich ices containing CH_4. Major products from UV photolysis experiments were CH_2N_2, C_2H_2, and CH_3, the same as reported by (2). The 3286 cm^{-1} feature of HCN was easily detected in irradiated N_2 + CH_4 ice spectra, but it was not easily seen after UV photolysis. Instead, in photolyzed N_2 + CH_4 a weak band of C_2H_2 was observed at 3270 cm^{-1}. To determine if HCN and HNC also were made by UV photolysis, experiments with isotopomers were needed. Figure 1b compares irradiated N_2 + CH_4 and N_2 + CD_4 (100:1). Good evidence that acetylene is not a major contributor in irradiated N_2 + CD_4 (100:1) is the presence of only a very weak C_2D_2 feature at 2435 cm^{-1} in Fig. 1b. This point is important because it implies that HCN is the major source of the 3286 cm^{-1} feature in ion-irradiated N_2 + CH_4. (These conclusions were supported with experiments on $^{15}N_2$ + CH_4 and N_2 + $^{13}CH_4$ ices.) The bottom spectrum of the figure shows that DCN and DNC were indeed made by UV photolysis. In short, these results demonstrate that HCN and HNC are made in both the irradiation and the photolysis experiments. In still other experiments we found that HCN and HNC were detected in irradiated N_2 + CH_4 for three different N_2/CH_4 ratios (100, 50, 4), as were IR features of CH_2N_2. Yields of C_2H_6 and C_3H_8 increased with the initial concentration of CH_4. The C_2H_2 absorption at 3273 cm^{-1} was best seen in the experiment with an N_2/CH_4 ratio of 4, although in more dilute mixtures it was present as a shoulder of the HCN absorption at 3286 cm^{-1}. HCN and HNC did not form when CH_4 was replaced by other simple aliphatic hydrocarbons (C_2H_6, C_2H_4, C_2H_2). To study trends in product formation, we examined N_2 + CD_4 (100:1) ices as a function of radiation dose. This experiment was done with CD_4, instead of CH_4, to circumvent the problem of overlapping bands from HCN and C_2H_2 in the 3290 - 3270 cm^{-1} region. We determined that at 12 K about half of the CD_4 was destroyed after a dose of $\sim$ 3.5 x 10^{19} eV cm^{-2} (2.3 eV $molec^{-1}$ for the calculated column density in this ice (1.5 $\times$ 10^{19} molec cm^{-2})). A similar radiation dose on Triton and Pluto would accumulate in $\sim$ 65 million years of exposure (11).
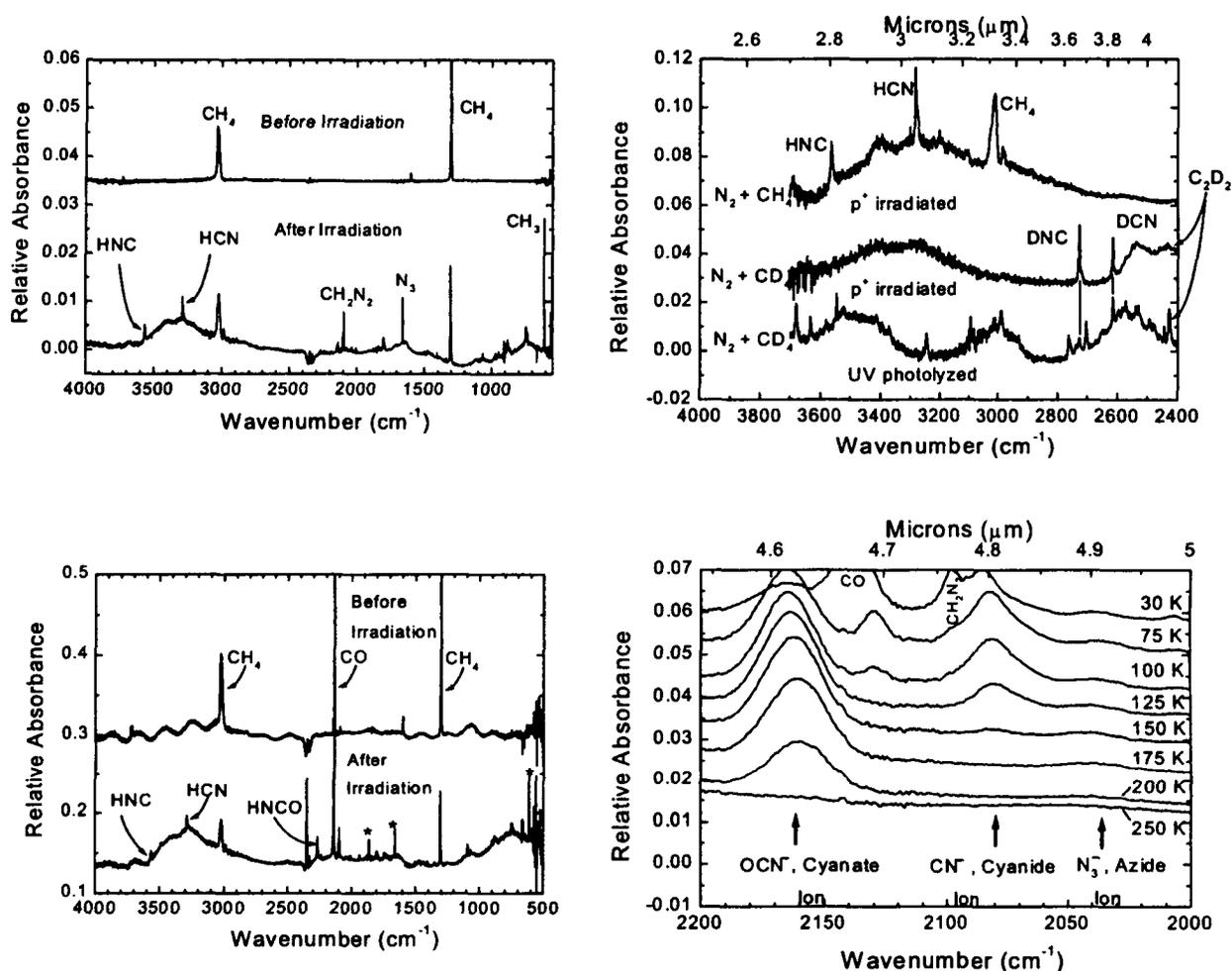
Fig. 1.— Figure 1a (top left), Figure 1b (top right), Figure 1c (bottom left), and Figure 1d (bottom right).

N_2 + CH_4 + CO: HNC and HCN also were detected in irradiated N_2 + CH_4 + CO (100:1:1), demonstrating formation of these products in the presence of CO. Figure 1c shows the relevant spectra. Note that isocyanic acid (HNCO), was seen in this three-component ice. Other products from our UV-photolysis of N_2 + CH_4 + CO (100:1:1) included CH_2N_2, C_2H_6, HCO, and CO_2 (reported in (2)). Ion-irradiated N_2 + CH_4 + CO ices for three $N_2/(CH_4$ + CO) ratios (50, 5, and 0.5) showed HNC and HCN only when the initial ratio was 50. When the ratio was 5 or 0.5, the dominant products included aliphatic hydrocarbons, CO_2, C_3O_2, and a molecule with a C=O bonded feature at 1720 cm^{-1}, probably acetaldehyde.

Results at T ≥ 30 K. The work just described was performed at ~ 12 K. To determine the likely reactions at the higher temperatures of Triton and Pluto, irradiated ices were slowly warmed to 35 - 40 K. As expected, all bands from free radicals (e.g., HCO, N_3, and CH_3) were lost on warming. Moreover, sharp IR features of the base NH_3 and acids HNC, HCN, HNCO, were diminished greatly. Concomitant with these changes was the rise of a broad ammonium, NH_4^+, band around 1460 cm^{-1} and several broad features in the 2200 - 2000 cm^{-1} region. Specifically, warmed irradiated N_2 + CH_4 + CO gave rise to OCN^- (2166 cm^{-1}), CN^- (2083 cm^{-1}), and N_3^- (2038 cm^{-1}), all identified by extensive experiments with isotopomers,

stability of these anions with temperature. The relative intensities of the ions' IR bands depend on initial concentrations of CH_4 and CO in the ice, the thickness of the ice, and the warming rate. These results demonstrate that reactions triggered by warming occur in our processed ices. Material is lost due to both sublimation and reactions, and residual ions are left behind.

4. Discussion

Reaction Mechanisms. HCN and HNC form in irradiated and in photolyzed N_2 + CH_4 and N_2 + CH_4 + CO ices. The most reasonable mechanism for acid formation comes from work by Maier(1996) and involves a rearrangment of diazomethane into nitrilimime (HCNNH), then a loose HN • • • HCN complex forms which can produce both HCN and its isomer, HNC.

Temperature Effects. The changes described above are from acid-base reactions of HCN, HNC, and HNCO with NH_3 to give CN^-, OCN^-, and NH_4^+. In addition, a broad band for N_3^- seen on warming implies that HN_3 + $NH_3 \rightarrow NH_4^+$ + N_3^- occurs and suggests that HN_3 was formed on ion irradiation.

Relevance to Icy Surfaces. A highlight of our work is the synthesis of nearly equal amounts of HCN and HNC in N_2 + CH_4 and N_2 + CH_4 + CO ices. An HNC/HNC ratio near one is appealing as comets typically have a ratio from 0.06 to 0.2 (e.g., (10, 1)), depending on the comet and its distance from the Sun. In addition, cold interstellar molecular clouds have HNC/HCN ratios of 0.2 to 1 (16). Since the molecules we studied, N_2, CH_4, and CO, are all either known or expected in interstellar and cometary environments, we expect our observed solid-phase chemistry to occur outside the laboratory. Ice chemistry may well provide a solution to the "problem" of the high HNC abundances in interstellar space and in comets. A second important finding is the solid-phase acid-base chemistry to produce ions. The icy origin of HCN and HNC, along with acids HNCO and HN_3 (likely) sets the stage for reactions with NH_3 to make NH_4^+, OCN^-, CN^-, and N_3^-. Since these ions are thermally more stable than the volatile reactants N_2, CH_4, and CO, they may accumulate on the surfaces of Triton, Pluto, and comets and be good candidates for future mid-IR observations. It is significant that observations of cold icy grains of embedded protostars already show condensed-phase NH_3 (7, 4), a prominent 2165 cm^{-1} feature due to OCN^- ion (8), and an unidentified 1460 cm^{-1} absorption band, almost certainly due to NH_4^+ (6). Although the actual N_2 and NH_3 budget in molecular clouds is not well determined, the existence of OCN^- supports the idea that low-temperature pathways occur on icy grains. Radiation processing of similar N_2-rich ices on Triton and Pluto could provide an endogenous source of HNC, HCN, HNCO, NH_3, NH_4^+, OCN^-, CN^-, and N_3^- for those worlds. The presence of these species would suggest interesting prebiotic chemistry, as it is well known that many of these are involved in reactions producing biomolecules. For example, the role of HCN and its derivatives in prebiotic evolution is discussed by many authors (e.g., (14)). More recently, the instability of NH_4CN, in the presence of H_2O and NH_3, was examined by (12) who found that adenine, guanine, and amino acids are formed after storage for 25 years at temperatures as low as 77 K. The Pluto-Kuiper Belt Mission will make the first reconnaissance of Pluto as early as 2015, and visit one or more smaller Kuiper Belt Objects. This will be an opportunity to look closely for HCN, HNC, HNCO, OCN^-, CN^-, N_3^-, and NH_4^+. Detecting, and mapping these species could help determine if Pluto and Triton will be

targets for future astrobiology missions. Understanding the radiation chemistry of these remote worlds with N_2-rich surfaces may provide support for the icy origin of HCN and HNC from similarly processed N_2-rich segregated cometary ices. This scenario would strengthen the idea that comets contain interesting biomolecules.

Acknowledgments

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