A laboratory study on the thermally induced transformation of hydrogen cyanide (HCN) to the cyanogen anion (CN⁻) in Solar System analog ices

Corey S. Jamieson [a], Agnes H.H. Chang [b], Ralf I. Kaiser [a,*]

[a] *Department of Chemistry, University of Hawaii at Manoa, Honolulu, HI 96822, USA*
[b] *Department of Chemistry, National Dong Hwa University, Hualien 97401, Taiwan*

Abstract

Mixtures of molecular nitrogen and methane have been identified in numerous outer Solar Systemices including the icy surfaces of Pluto and Triton. We have simulated the interaction of ionizing radiation in the Solar System by carrying out a radiolysis experiment on a methane – molecular nitrogen ice mixture with energetic electrons. We have identified the hydrogen cyanide molecule as the most prominent carbon–nitrogen-bearing reaction product formed. Upon warming the irradiated sample, we followed for the first time the kinetics and temporal evolution of the underlying acid–base chemistry which resulted in the formation of the cyanide ion from hydrogen cyanide. On the surfaces of Triton and Pluto and on comets in Oort's cloud this sort of complex chemistry is likely to occur. In particular, hydrogen cyanide can be produced in low temperature environments (Oort cloud comets) and may be converted into cyanide ions once the comets reach the warmer regions of the Solar System.
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1. Introduction

Methane (CH_4) and nitrogen (N_2) ice mixtures are common in the outer Solar System where the temperatures are low enough for them to be solid. On Pluto and Triton (Neptune's largest moon), spectral features can only be fit with methane diluted in nitrogen ice (Owen and et al., 1993; Cruikshank et al., 1984; Cruikshank and Silvaggio, 1979; Quirico et al., 1999). Comets, Kuiper Belt Objects (KBOs), and trans Neptunian objects (TNOs) also have intense methane features and may also contain nitrogen ice (Licandro et al., 2006). These bodies are exposed to energetic radiation from the sun (UV flux and solar wind) and from galactic cosmic rays (GCRs). Over the lifetimes of these bodies, they have undergone chemical processing due to these irradiation effects. For example, the detection of non-methane hydrocarbons (NMHCs) on the surface of Pluto may be evidence for chemical alterations of methane that produce the higher order hydrocarbons (Niemann and et al., 2005; Sasaki et al., 2005; Krasnopolsky and Cruikshank, 1999). In this paper, we focus on the chemical interactions that take place in irradiated methane (CH_4)–nitrogen (N_2) ices at 10 K and during the subsequent warm-up. This study allows us to isolate low-order, primary and secondary reaction products that result from the interactions of nitrogen and methane molecules when exposed to ionizing radiation. We attempt to identify new molecules and comment on the formation pathways that are likely to be responsible for the production of the observed molecules and also focus of possible acid–base reactions occurring during the warm-up of the irradiated sample. Our experiments have been specifically tailored to unravel the elementary chemical processes that take

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* Corresponding author.
E-mail address: ralfk@hawaii.edu (R.I. Kaiser).

place between irradiated nitrogen and methane molecules so that we may better understand their interactions in/on extraterrestrial icy objects.

2. Experimental

The experiments were carried out in an ultra high vacuum chamber at a pressure of 4×10^{-11} Torr (Bennett et al., 2006). Temperatures down to 10 K are reached using a two-stage closed-cycle helium refrigerator that is interfaced to a polished single crystal silver mirror onto which the ices are condensed. The ice condensation is assisted by a precision leak valve. The methane (CH_4)–nitrogen (N_2) ice was prepared at 10 K by depositing premixed gases at a pressure of 10^{-7} torr for 6 min. Methane (99.999%) and nitrogen gas (99.9999%) were obtained from Gaspro. This yielded a total thickness of about 960 nm with a mixture of methane (CH_4) and nitrogen (N_2) (1:1).Bennett et al., 2006 The ice sample was then irradiated isothermally with 5 keV electrons to simulate the secondary electrons releases in the track of galactic cosmic ray particles penetrating the ices of outer Solar System objects (Bennett et al., 2006). In our experiments, the electron beam was operated at 100 nA with an extraction efficiency of 78.8% and scanned over the sample area 1.8 cm^2 to avoid heating of the ice for 3 h. The reaction was monitored using a Nicolet 510 DX Fourier Transform Infrared Spectrometer (FTIR) online and in situ; a resolution of 2 cm^{-1} was chosen.

3. Results

The experiment with the mixture of methane (CH_4) and nitrogen (N_2) (1:1) was performed in three stages. While the ice mixture was irradiated with 5 keV electrons for 3 h, the chemical evolution of the ice was monitored via infrared spectroscopy. The irradiation was then terminated and the sample was left at 10 K for 1 h to test the stability of the newly formed products, evidenced by the constancy of their corresponding infrared bands. Finally the sample was warmed at heating rates of 0.5 K min^{-1} – typically to 300 K – so that thermally initiated reactions could be observed. (Fig. 1) depicts the infrared spectrum of the ice after 3 h of irradiation. Prominent methane features (CH_4) are observed along with – similar to the irradiation of pure methane ices – a number of ethane (C_2H_6) bands that formed as a result of the radiation (Bennett et al., 2006). In this paper, we concentrate on the analysis of prominent features of nitrogen–carbon bearing molecules that are created due to the irradiation effects on a methane (CH_4)–nitrogen (N_2) ice mixture, since we expect that these intense absorptions are also observable on Pluto and/or Triton. For completion, it should be mentioned that the following hydrocarbons and their radicals have been observed in the irradiated methane (CH_4) and nitrogen (N_2) mixture: C_2H_6 (ethane), C_2H_5 (ethyl radical), C_2H_4 (ethylene), C_2H_3 (vinyl radical), C_2H_6 (acetylene), CH_3
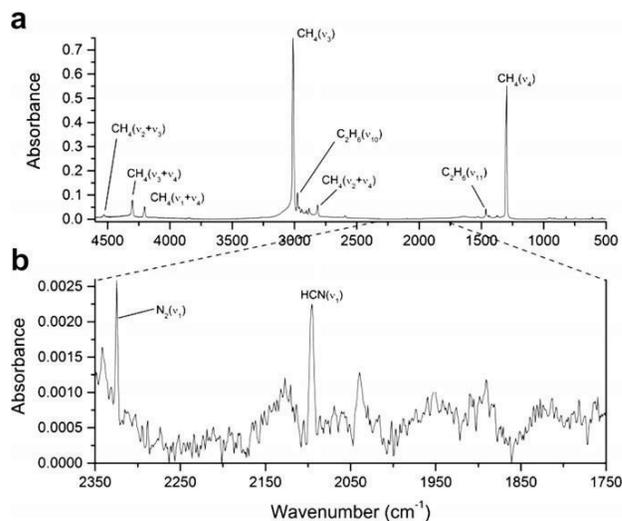

Fig. 1. The infrared spectrum is shown after 3 h of irradiation of the methane (CH_4) and nitrogen (N_2) ice at 10 K for (a) the spectral region 4550–500 cm^{-1} and (b) a magnified portion of the spectrum. In (a) only bands attributed to the hydrocarbons methane (CH_3) and ethane (C_2H_6) are labeled.

(methyl radical); these species were also formed in the irradiation of pure methane ices at 10 K with energetic electrons. Their formation mechanisms have been compiled in Bennett et al. (2006).

The most prominent molecule is hydrogen cyanide (HCN). It was identified by its ν_1 vibrational mode centered at 2096 cm^{-1} (Fig. 1). This absorption agrees with the previous matrix isolation studies by King and Nixon and Milligan and Jacox (1967). The more intense ν_3 (3286 cm^{-1}) and ν_2 (747 cm^{-1}) vibrational modes were obscured by acetylene (C_2H_2) absorptions centered at 3269 and 735 cm^{-1}, respectively (Bennett et al., 2006). The assignment for hydrogen cyanide as the carrier for the 2096 cm^{-1} band has been further confirmed by Moore and Hudson (2003). An absorption centered at 2128 cm^{-1} was detected, which may correspond to the asymmetric NNN stretch of either hydrazoic acid (HN_3) or methyl azide (CH_3N_3). Calculated and experimental data put a strong absorption for these molecules between 2140 and 2100 cm^{-1} (Basiuk et al., 2001; Eyster and Gillette, 1940; Zhizhong, 1998; Badawi, 2002; Shen and Durig, 2003). However, hydrazoic acid should also have an intense absorption near 1150 cm^{-1}, which was not observed. This may indicate that methyl azide is a more likely source of this absorption. It should be stressed that upon warming, the 2096 cm^{-1} band of HCN, which was mentioned earlier, was observed to decrease while, concurrently, a new band began to form at 2077 cm^{-1} ($\sim$23 K) (Fig. 2). This new band was assigned to the cyanide anion (CN$^-$) (Moore and Hudson, 2003; Forney et al., 1992) and – as will be discussed later – provides evidence of acid–base chemistry that occurs during warm-up. Note that the column densities (molecules cm^{-2}) of HCN and CN$^-$ were calculated via a modified Lambert–Beer law (Bennett et al. 2006) to
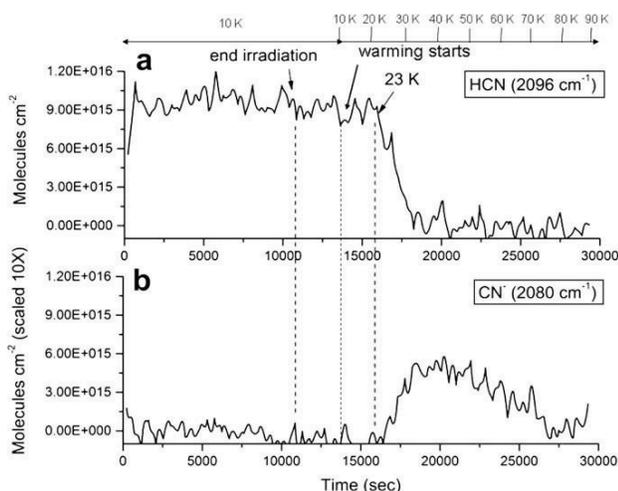
Fig. 2. The column densities (molecules cm^{-2}) of HCN and CN$^-$ are plotted over the course of the experiment in graphs (a) and (b), respectively. Column densities were calculated using absorption coefficients found in Georgieva and Velcheva (2006).

account for the angle between the surface normal of the silver wafer and the infrared beam (75°) and the incoming and outgoing infrared beam using absorption coefficients (A_{exp}(HCN) = 3.1 × 10^{-19} cm molecule^{-1}; A_{exp}(CN$^-$) = 6.9 × 10^{-18} cm molecule^{-1}) found in Georgieva and Velcheva (2006).

4. Discussion

We now investigate the formation of the previously identified species in our irradiated ice mixture. As the electrons penetrate the ice sample, they may interact with the molecules causing a unimolecular dissociation of the ice molecules (Bennett et al., 2006). For example, radiation-induced dissociation of methane can produce a methyl radical and a hydrogen atom (Eq. (1)). This dissociation is endoergic by 428 kJ mol^{-1} (Bennett et al., 2006). The net translational energy resulting from this dissociation is primarily carried by the hydrogen atom due to its low mass. This is important because it is this excess energy that allows non-equilibrium chemistry to occur within the ice and allows entrance barriers at low temperatures to be overcome. Another primary effect from the radiation is the dissociation of molecular nitrogen (Eq. (2)). Dissociation into two ground state nitrogen atoms (^{4}S) requires at least 941 kJ mol^{-1} of energy to be absorbed by molecular nitrogen. Electronically excited atoms may also be produced where the energy of N(^{2}D) lies 231 kJ mol^{-1} above the ground ^{4}S state. Consequently, to produce two excited nitrogen atoms in the ^{2}D state would require 1403 kJ mol^{-1} of total energy, just below the ionization limit of molecular nitrogen (1503 kJ mol^{-1}) (Cosby, 1993). With the host matrix species (N$_2$, CH$_4$) and the newly produced species from irradiation (N, CH$_3$, H), we now investigate how the molecules observed in our experiment can be synthesized.

$$CH_4(X^1A_1) \rightarrow CH_3(X^2A_2'' + H(^2S_{1/2}) \tag{1}$$

$$N_2(X^1\Sigma_g^+) \rightarrow N(^2D/^4S) + N(^2D/^4S) \tag{2}$$
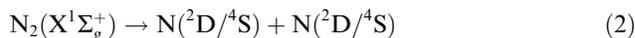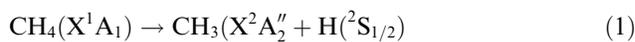
How can these initial steps lead to the formation of hydrogen cyanide (HCN) and of the cyanide anion (CN$^-$)? In order to gain an understanding about the synthesis of hydrogen cyanide, its abundance (column density in units of molecules cm^{-2}) was plotted over time for the duration of the experiment (Fig. 2). It is most useful to notice how quickly the abundance of hydrogen cyanide becomes saturated (within 15 min of irradiation) indicating that its formation may occur via fast reactions and without many intermediate steps. There are a few reaction pathways to consider for the formation of HCN. From Eqs. (1) and (2), it is clear that methyl radicals and nitrogen atoms are readily produced. Upon reaction, they may form methylnitrene (CH$_3$N) with an exoergicity of 304 kJ mol^{-1}. The decomposition of methylnitrene to hydrogen cyanide has been previously studied theoretically (Nguyen et al., 1996). From the ground triplet state of methylnitrene, it was found that the most facile way to form HCN was by the stepwise loss of two hydrogen atoms where the energy requirements are 137 and 161 kJ mol^{-1} for loss of the first and second hydrogen atoms, respectively. The hydrogen loss processes should occur quickly due to the high internal energy of methylnitrene that is likely to accompany its formation. Alternatively, there is enough energy from reaction to produce methylnitrene in its first excited singlet state (a^{1}E ← X^{3}A$_2$ = 130.4 kJ mol^{-1}). In fact, reaction of the methyl radical with an excited nitrogen atom in the ^{2}D state would produce methylnitrene in the singlet state. This opens a spin-allowed decomposition to HCN and H$_2$ (Eq. (3)).

$$CH_3N(a^1E) \rightarrow HCN(X^1\Sigma^+) + H_2(X^1\Sigma_g^+) \tag{3}$$
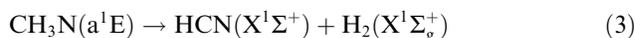
From singlet methylnitrene, a barrier of 29.2 kJ mol^{-1} exists to the molecular hydrogen elimination, while the overall reaction is exoergic by 343 kJ mol^{-1} (Nguyen et al., 1996). For example, a nitrogen atom could insert into a C–H bond of methane where the high energy methyl amidogen (CH$_3$NH) molecule can then undergo hydrogen loss processes to form HCN. This nitrogen insertion has been found to have a nominal barrier of somewhere between zero and 4 kJ mol^{-1} making this pathway also likely (Kurosaki et al., 1998).

The abundance of HCN remained constant for the 1 h after irradiation at 10 K and until about 23 K of the warm-up. Then the HCN peak at 2096 cm^{-1} began to decline until it had completely disappeared by 48 K. This decrease of the 2096 cm^{-1} peak was marked by a coincident increase of a peak at 2080 cm^{-1} (Fig. 2), which has been assigned to the cyanide anion (CN$^-$). The cyanide anion was not found to be produced during irradiation but rather as a result of the warm-up. Because of the correlation of the disappearance/appearance of these bands, it would be consistent with the observations to describe a

mechanism in which hydrogen cyanide undergoes deprotonation to form the cyanide anion. This reaction was also investigated by Gerakines et al. (2004) by irradiating low temperature (18 K) HCN and HCN + NH_3 ice mixtures. In the simplest case, hydrogen cyanide could lose a proton and form the cyanide anion. This deprotonation is endoergic by approximately 1460 kJ mol^{-1} (Berkowitz et al., 1969). However, in the ice of our experiment, this process would realistically occur in conjunction with a base pair that would accept the proton. For example, Moore and Hudson (2003) proposed an acid–base reaction between hydrogen cyanide and ammonia to yield the cyanide anion and the ammonium cation. This would make the energetics feasible, however, we could not confirm the existence of the ammonium cation since its band at 1460 cm^{-1} overlaps with the intense v_{11} ethane feature. However, we do have a tentative assignment for the formimidoyl cation ($HCNH^+$) at 3182 cm^{-1} as obtained from the NIST database (http://webbook.nist.gov). Its presence could then be explained by the reaction of two hydrogen cyanide molecules where one acts as an acid resulting in CN^- while the other is a base giving $HCNH^+$. Unfortunately, the temporal development of the 3182 cm^{-1} band corresponding to the formimidoyl cation could not be derived during the beginning of the warm-up due to intense methane features that obscured its observation.

Now, we compare our results with those of previous experiments. The most obvious spectral features that result from irradiation in our experiment were due to hydrocarbon production like ethane. These have been also observed in the electron irradiation of pure methane ices (Bennett et al., 2006). Several groups have found HCN to be one of the major products after irradiation of methane (CH_4) and nitrogen (N_2) mixtures, and our detection of hydrogen cyanide at 2096 cm^{-1} supports this (Bohn et al., 1994; Baratta et al., 2003; Strazzulla and Palumbo, 2001). Moore and Hudson were able to confirm two other absorptions of the HCN molecule at 3286 cm^{-1} and 747 cm^{-1}, however, intense acetylene absorptions inhibited our detection of these features. It should be noted that Moore and Hudson proposed a different reaction mechanism to form hydrogen cyanide (HCN). First, methane was suggested to decompose to carbene (CH_2) plus molecular hydrogen (H_2). Carbene was suggested to react with molecular nitrogen to for the CH_2N_2 molecule which decomposed via molecular hydrogen loss to HCNNH; the latter was postulated to form HN plus HCN. In our study we have no evidence for the formation of any reaction intermediate postulated by Moore and Hudson – not even for the carbene intermediate, which is readily observable in irradiated ices (Kaiser and Roessler, 1998). Therefore, the reaction mechanisms proposed by Moore and Hudson does not play a role in our system. It should be stressed that ionizing radiation used by Moore and Hudson transfers energy via electronic and nuclear interaction to the surrounding ice molecules. In our case, however, energetic electrons only transfer energy via electronic interaction to the methane

and nitrogen molecules. We have shown that in the pure methane and nitrogen systems, this leads initially to the formation of the methyl radical (Eq. (1)) and the synthesis of nitrogen atoms (Eq. (2)), but not to the formation of carbene. Therefore, based on these considerations, methane–nitrogen ices exposed to radiation which exclusively (electrons) or predominantly transfers energy via electronic interaction, should form hydrogen cyanide via reaction sequence (1)–(3) as proposed.

Lastly, the CN^- anion was observed only during the warm-up phase of the experiment and not until 23 K, which matches the observations by Moore and Hudson during warm-up from 12 to 35 K. However, Moore and Hudson have not investigated this process quantitatively and did not plot the decay of the HCN feature versus the simultaneous rise of the CN^- anion. By following the temporal evolution of the absorption features, our experiments show for the first time that the decay of the HCN molecule is *correlated* with the appearance of the CN^- anion.

5. Conclusions

We have identified the hydrogen cyanide molecule as the most prominent reaction product formed during the interaction of ionizing radiation in the form of energetic electrons with methane–nitrogen ices at 10 K. It was our goal to understand the elementary reaction pathways that occur between methane (CH_4) and nitrogen (N_2) upon interaction with ionizing radiation so that we may build more accurate reaction models to interpret fundamental chemistries as they occur on these bodies. Previous experiments utilized energetic particles which transfer their kinetic energy via nuclear (S_n) and electronic (S_e) interaction to the target molecules. This made it impossible to elucidate the reaction mechanisms and the main contributor (electronic versus nuclear energy loss) to the formation of hydrogen cyanide. However, in the present work, the selection of energetic electrons made it possible to investigate for the first time the irradiation effects of ionizing particles transferring energy to the ice *solely* via electronic interaction. Two reaction mechanisms were proposed. These are: a recombination of methyl radicals with nitrogen atoms followed by unimolecular decomposition of the CH_3N intermediate via molecular hydrogen loss or an initial insertion of atomic nitrogen into the carbon–hydrogen bond of methane yielding the CH_3NH intermediate which fragmented to hydrogen cyanide. Also, upon warming the irradiated sample, we followed for the first time the temporal evolution of the acid–base chemistry which resulted in the formation of the cyanide ion from hydrogen cyanide. On the surfaces of Triton and Pluto and on comets in Oort's cloud this sort of complex chemistry is likely to occur. In particular, hydrogen cyanide can be produced in low temperature environments (Oort cloud comets; our experiments correspond roughly to a radiation exposure of Oort cloud bodies of about 1.5×10^7 years) and be con-

verted into cyanide ions once the comets reach the warmer regions of the Solar System.

Acknowledgments

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