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Experimental investigation of aminoacetonitrile formation through the Strecker synthesis in astrophysical-like conditions: reactivity of methanimine (CH_2NH), ammonia (NH_3), and hydrogen cyanide (HCN)

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ABSTRACT

Context. Studing chemical reactivity in astrophysical environments is an important means for improving our understanding of the origin of the organic matter in molecular clouds, in protoplanetary disks, and possibly, as a final destination, in our solar system. Laboratory simulations of the reactivity of ice analogs provide important insight into the reactivity in these environments. Here, we use these experimental simulations to investigate the Strecker synthesis leading to the formation of aminoacetonitrile in astrophysical-like conditions. The aminoacetonitrile is an interesting compound because it was detected in SgrB2, hence could be a precursor of the smallest amino acid molecule, glycine, in astrophysical environments.
Aims. We present the first experimental investigation of the formation of aminoacetonitrile NH_2CH_2CN from the thermal processing of ices including methanimine (CH_2NH), ammonia (NH_3), and hydrogen cyanide (HCN) in interstellar-like conditions without VUV photons or particules.
Methods. We use Fourier Transform InfraRed (FTIR) spectroscopy to monitor the ice evolution during its warming. Infrared spectroscopy and mass spectroscopy are then used to identify the aminoacetonitrile formation.
Results. We demonstrate that methanimine can react with ^-CN during the warming of ice analogs containing at 20 K methanimine, ammonia, and [NH_4^+ ^-CN] salt. During the ice warming, this reaction leads to the formation of poly(methylene-imine) polymers. The polymer length depend on the initial ratio of mass contained in methanimine to that in the [NH_4^+ ^-CN] salt. In a methanimine excess, long polymers are formed. As the methanimine is progressively diluted in the [NH_4^+ ^-CN] salt, the polymer length decreases until the aminoacetonitrile formation at 135 K. Therefore, these results demonstrate that aminoacetonitrile can be formed through the second step of the Strecker synthesis in astrophysical-like conditions.

Key words. astrochemistry – ISM: molecules – methods: laboratory

1. Introduction

Understanding the chemical evolution and composition of interstellar and protoplanetary materials should provide important insight into the composition of the organic matter that could be available for the development of a type of prebiotic chemistry on planetary surfaces. A complex chemistry occurs in astrophysical environments, depending on the local conditions. In dense molecular clouds where temperatures are around 10 K, hydrogenation reactions are predominant. When parts of the molecular cloud collapse to form a protostar, thermal effects combined with VUV and cosmic-ray irradiation can occur and alter the chemical composition of the organic matter. The subsequent evolution on this object leads to a proto-planetary disk and then to a planetary system where the original matter is incorporated into comets and various small bodies.

On Earth, meteorites are regarded as interesting objects because they are the remains of various examples of these small bodies (Herd et al. 2011). Therefore, their analyses provide invaluable insight into the original composition of the organic matter in these objects. In particular, the hydrolysis of their soluble organic matter has been found to permit the detection of amino acids (Cronin et al. 1980; Cronin & Pizzarello 1999; Pizzarello 2004). Without hydrolysis, meteoritic amino acids are less abundant. These results can be correlated with the analysis of refractory residues obtained after the VUV irradiation and the warming of ice analogs (Bernstein et al. 2002; Muñoz-Caro et al. 2002). Without hydrolysis, amino acids are not identified, whereas amino acids are present after the residue hydrolysis (Nuevo et al. 2008). Further hypotheses have been proposed to explain these results, such as the possibility that amino acids are embeded in a matrix, from which they are released during hydrolysis. Another possibility is that the formation of amino acid precursors could produce the corresponding amino acids after hydrolysis. Finally, we note that the hydrolysis process breaks mainly peptide bonds, hence that of oligopeptides may

be present within these residues might be interesting to consider in the context of prebiotic material (Meierhenrich et al. 2004).

Different experiments have shown that nitriles could promote the formation of amino acids in astrophysical-like conditions (Liebman et al. 1995). When an acetonitrile and water ice mixture is bombarded with ions at 20 K, the resulting hydrolysis of the refractory residue does indeed lead to amino acid detections (Hudson et al. 2008). Therefore, nitriles have been proposed as potential precursors of amino acids (Elsila et al. 2007). Furthermore, some nitriles have already been detected in the interstellar gas phase, such as aminoacetonitrile (Belloche et al. 2008). The aminoacetonitrile is known to form glycine, the smallest amino acid molecule, after its hydrolysis in the liquid phase. This aminoacetonitrile could be formed by cyanogen hydrogenation (Belloche et al. 2008) or photochemically in astrophysical environments from nitrile and ammonia mixtures (Fig. 1A). The photochemical pathways have been experimentally studied, but only very low yields have been obtained (Danger et al. 2011). The Strecker synthesis (Strecker 1854) is another reaction that might lead to aminoacetonitrile formation in astrophysical-like conditions (Bernstein et al. 2002; Elsila et al. 2007, 2009). This reaction is well-known in prebiotic chemistry and considered the main pathway to the formation of amino acids in the Urey-Miller experiments (Miller 1955). In this reaction, aldehyde reacts in liquid water with ammonia to form the corresponding imine after dehydration. The imine then reacts with hydrogen cyanide leading to the corresponding aminonitrile. The following hydrolysis of these aminonitriles leads then to amino acid formation. However, can the Strecker synthesis occur in astrophysical environments in the absence of liquid water and at much lower temperatures?

Theoretical investigations have investigated this possibility (Basiuk & Bogillo 2002a,b; Koch et al. 2008; Rimola et al. 2010; Woon 2002; Xu & Wang 2007). These have proposed that the condensation of ammonia with formaldehyde can lead to the formation of the corresponding amino alcohol in such conditions (Rimola et al. 2010). The amino alcohol might then dehydrate in the presence of an acid to produce the corresponding imine (Walch et al. 2001). These data are strengthened by experimental results, which show that ammonia can condense onto either formaldehyde or acetaldehyde for the temperature range 50–100 K (Bossa et al. 2009; Duvernay et al. 2010) to form the corresponding amino alcohols. Furthermore, recent experiments on hexamethylenetetramine (HMT) formation suggest that the imine can be formed at 200 K in the presence of acid by dehydratation of the corresponding amino alcohols (Vinogradoff et al. 2011). Theoretical investigations also proposed that the subsequent condensation of hydrogen cyanide onto imine can occur in the solid phase in a water environment (Fig. 1B) (Rimola et al. 2010; Woon 2002). However, the hydrolysis of the resulting aminoacetonitrile is too high in energy for amino acid formation (Rimola et al. 2010).

In this contribution, we experimentally investigate the aminoacetonitrile formation in solid phase from the second step of the Strecker synthesis in astrophysical-like conditions. Hence, we test the possibility of forming aminoacetonitrile by the warming of an ice containing ammonia (NH_3), methanimine (CH_2NH), and hydrogen cyanide (HCN). We follow the ice evolution by means of infrared spectroscopy and characterize the aminoacetonitrile formation using infrared spectroscopy and mass spectrometry. As we show, aminoacetonitrile formation depends on the ratio of methanimine to [NH_4^+ $^-$CN] salt. The direct formation of aminoacetonitrile occurs when the methanimine is diluted in an excess of [NH_4^+ $^-$CN] salt (Sect. 3.2.2). The astrophysical implications of these results are discussed in Sect. 3.3.

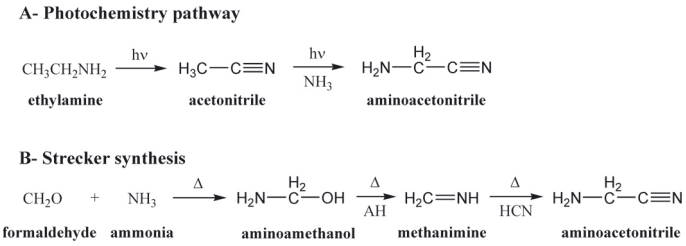


Fig. 1. Experimental pathways proposed for aminoacetonitrile formation in astrophysical like conditions either by VUV irradiation of ice analogs including at 20 K acetonitrile (also named methyl cyanide) and ammonia for the photochemistry pathway (A) or the heating of an ice analogs from 20 K to 300 K for the Strecker synthesis pathway (B).

2. Experimental

Potassium cyanide, aminoacetonitrile (97% purity), aminoacetonitrile hydrogensulfate, dichloromethane, and potassium hydroxide were purchased from the company Sigma Aldrich, stearic acid from Fluka Analytical, and ammonia (99.9% purity) from Air Liquide. Dichloromethane was distilled over phosphorus pentaoxide. Reagents were mixed in different ratios in a pyrex vacuum line using standard manometric techniques. Liquid reagents (acetonitrile, aminoacetonitrile) were vacuum transferred away from their liquid state by evaporation and if necessary, their resulting vapors were mixed in a glass bulb with other reagents. The gaseous mixture was deposited at a 6×10^{-1} mol min^{-1} rate on a gold-plated surface kept at 20 K with the help of a model 21 CTI cold head. The warming of the samples took place at a 5 K min^{-1} heating rate using a resistive heater along with a Lakeshore model 331 temperature controller. The infrared spectra of the sample were recorded in a reflection mode between 4000 and 600 cm^{-1} using a Nicolet Magna 750 FTIR spectrometer with a MCT detector. Each spectrum was averaged over one hundred scans and has a 1 cm^{-1} resolution. The mass spectra were monitored using a RGA quadrupole mass spectrometer (MKS Microvision-IP plus) as the products are desorbed during the controlled temperature ramp. The ionisation source is a 70 eV impact electronic source and the mass spectra are recorded between 1 and 70 amu for a full scan, or recorded for specific mass using the SIM mode. The hydrogen cyanide (HCN) gas used in these experiments was synthesized directly onto the pyrex line at 10^{-3} mbar using the following protocol (Gerakines et al. 2004). In a manifold, 378 mg of stearic acid ($CH_3(CH_2)_{16}COOH$, 1.32 mmol) are mixed with 86 mg of potassium cyanide (KCN, 1.32 mmol). The manifold is then directly connected to the pyrex line and left under vacuum 24 h. The HCN is then synthesized by slowly heating the manifold including $CH_3(CH_2)_{16}COOH$/KCN and cooled with a water bath (room temperature) after which the desired pressure is reached in the pyrex line. Five mbars of pure HCN are usually synthesized per experiment, which allows five to six experiments per $CH_3(CH_2)_{16}COOH$/KCN tube. The imine was synthesized from the dehydrocyanation of the aminoacetonitrile (Guillemin & Denis 1988). The reported synthesis partially modified for our present study but many details can be found in our previous article. Pure aminoacetonitrile was obtained from aminoacetonitrile hydrogensulfate. In a 250 mL three-necked flask equipped with a nitrogen inlet and a stirring bar, we introduced aminoacetonitrile hydrogensulfate in powder (15.4 g, 100 mmol) and

dry dichloromethane (150 mL). Dry ammonia was bubbled for 20 min in the solution at a rate sufficient to observe a degassing of ammonia. The solution was then filtered and concentrated under a vacuum, and the aminoacetonitrile was purified by distillation under vacuum (bp_1: 45 °C). The resulting yield was 5.1 g, 91%. The compound was kept for months at low temperature (–20 °C). From this pure aminoacetonitrile, the methanimine is obtained as follows: the vacuum line was equipped with a 20 cm quartz tube introduced in an oven heated to 600 °C, a 20 cm tube containing KOH in powder (20 g) in half section and heated to 80 °C, and a U-tube equipped with stopcocks. The apparatus was degassed and a pressure of 0.1 mbar was maintained during the synthesis. The U-tube was immersed in a liquid nitrogen bath. The aminoacetonitrile (1.0 g, 18 mmol) was slowly vaporized (20–30 min) in the vacuum line and thermolyzed at 600 °C to form methanimine and hydrogen cyanide. This latter selectively reacted on KOH and the pure imine was trapped in the U-tube. At the end of the vaporization of aminoacetonitrile, the stopcocks of the U-tube were closed and this cell was adapted to the spectrometer. Methanimine (378 mg, 13 mmol) was thus obtained in a 73% yield. It can be kept indefinitely at the liquid nitrogen temperature but only some hours at –78 °C (the temperature of dry ice).

3. Results and discussion

3.1. Reference spectra and temperature evolution of methanimine, HCN, and HCN/NH_3

We present infrared spectra of each reactant and investigate separately the thermal evolution of methanimine, HCN, or HCN/NH_3 mixture giving [NH_4^+ $^-$CN]. These results will serve as benchmarks for the reactivity of a methanimine, HCN, and ammonia mixture (Sects. 3.2). Figure 2 displays infrared spectra of an aminoacetonitrile, methanimine, HCN, or HCN/NH_3 mixture giving [NH_4^+ $^-$CN]. The corresponding attributions of infrared absorptions are presented in Table 1.

The aminoacetonitrile was deposited at 130 K (Fig. 2A), because below this temperature, carbon dioxyde can be co-deposited and reacts with aminoacetonitrile (data will be published later). The methanimine was deposited at 20 K (Fig. 2B). Since the methanimine decomposes rapidly in ammonia in the gas phase, it is difficult to obtain a deposit without ammonia, which is always present in small amounts as a byproduct. In the presence of ammonia, in excess or not, the methanimine does not react in solid phase. Therefore, for the rest of our investigation, we consider only deposits including methanimine, ammonia, and hydrogen cyanide, and not methanimine with hydrogen cyanide, since we cannot eliminate the presence of ammonia. Hydrogen cyanide is deposited as a pure ice at 20 K (Fig. 2C). The salt mixture [NH_4^+ $^-$CN] is obtained by mixing in the same line a stoechiometric ratio of ammonia to hydrogen cyanide. When this mixture is deposited at 20 K, HCN is not detected and a slight excess of ammonia is observed (Fig. 2D). Since our objective is to demonstrate that the aminoacetonitrile can be formed from an ice containing methanimine, ammonia, and hydrogen cyanide, the infrared study will be focused on the range 2000–2300 cm^{-1}. Indeed, aminoacetonitrile can clearly be identified in this range, since the CN stretching of aminoacetonitrile (2240 cm^{-1}) does not overlap with other bands. However, because infrared bands can evolve during the ice warming, for each species or mixtures, the temperature evolution of infrared bands for stretching of 2000–2300 cm^{-1} was monitored.

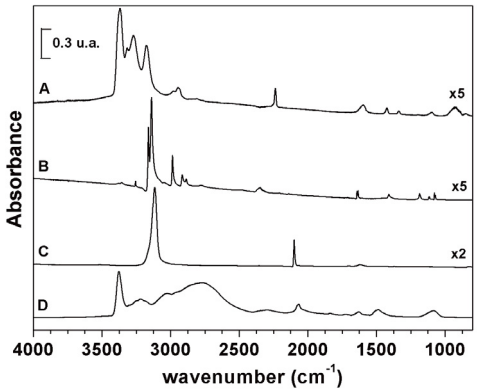


Fig. 2. Infrared spectra of aminoacetonitrile at 130 K (A) of methanimine at 20 K (B), of hydrogen cyanide at 20 K (C), and of [NH_4^+ $^-$CN] at 20 K (D).

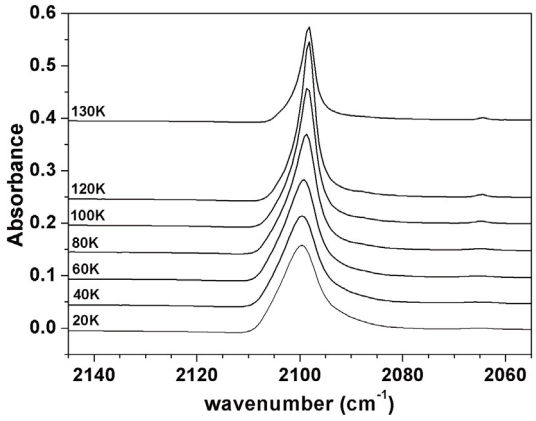


Fig. 3. Temperature evolution of HCN profile for the range 2060–2140 cm^{-1}.

The CN stretching band of aminoacetonitrile at 2240 cm^{-1} does not shift during the ice warming. From a pure solid, aminoacetonitrile has a temperature desorption with a maximum around 200 K (unpublished work by the authors). The temperature evolution of the CN stretching band (2100 cm^{-1}) of hydrogen cyanide is displayed in Fig. 3 from 20 K to its desorption at 140 K. When the temperature increases, the band at 2100 cm^{-1} becomes narrow because HCN ice cristallizes around 90 K, while the band position does not shift. Figure 4 displays the evolution of methanimine infrared bands in the range 2000–2300 cm^{-1}, from 20 K to its sublimation at 140 K. At 20 K, two unidentified weak bands at 2144 cm^{-1} and 2206 cm^{-1} probably related to either the combination or harmonic modes are observed for methanimine. When the temperature is increased, the band at 2144 cm^{-1} sharpens following the solid methanimine cristallization, while the band at 2206 cm^{-1} splits into three weak bands at 2182 cm^{-1}, 2207 cm^{-1}, and 2229 cm^{-1} caused by the methanimine cristallization. The temperature evolution of the pure [NH_4^+ $^-$CN] salt IR spectrum is more complicated than the previous reactants as previously observed for the [NH_4^+ $^-$OCN] salt (Raunier et al. 2003a,b). Figure 5 displays this evolution between 20 K and its sublimation at 160 K in the range 2000–2200 cm^{-1}. At 20 K, two bands are observed at 2075 cm^{-1} and 2065 cm^{-1}, which are consistent with the values expected for the combination mode of the NH_4^+ ion, as well as for the $^-$CN stretching mode. When the salt is warmed up, the band

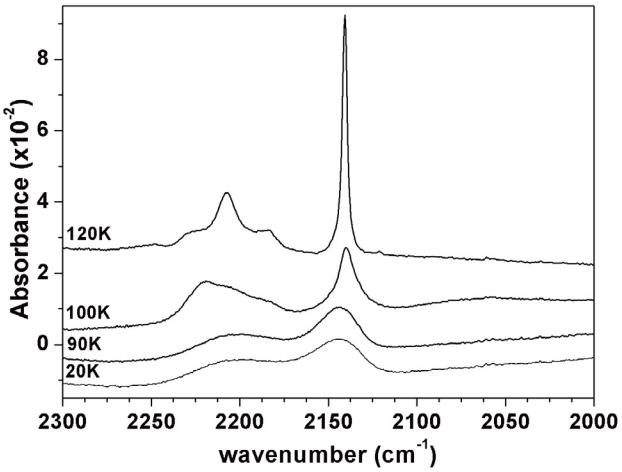


Fig. 4. Temperature evolution of methanimine infrared profile for the range 2000–2300 cm^{-1}.

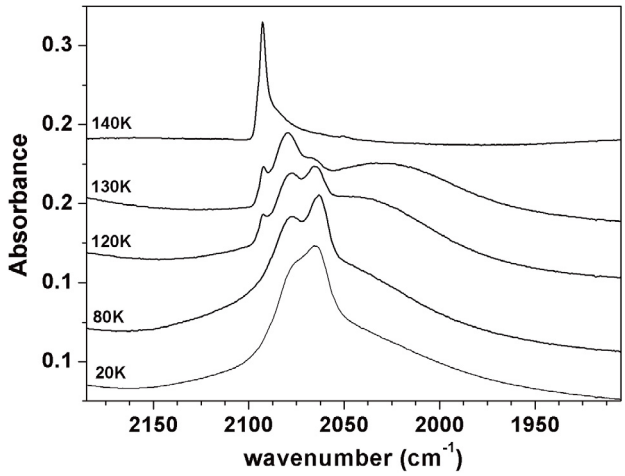


Fig. 5. Temperature evolution of the [NH_4^+ $^-$CN] salt infrared profile for the 1900–2200 cm^{-1} range.

at 2075 cm^{-1} increases, while the one at 2065 cm^{-1} decreases. From 100 K, a new band appears at 2092 cm^{-1} and increases in intensity with the temperature, while the ones at 2075 cm^{-1} and 2065 cm^{-1} progressively disappear. Above 140 K, only the band at 2092 cm^{-1} remains until the salt sublimates. These modifications reveal the complex evolution of the salt structure. The bands at 2065 cm^{-1} and 2075 cm^{-1} characterize the amorphous structure of the salt, obtained at low temperature during the deposit. When the salt is heated, it progressively restructures leading to the crystalline form of the salt characterized by the band at 2092 cm^{-1}. Furthermore, in subsequent sections, the maximum temperature of the desorption of the salt can fluctuate between 160 K (pure solid, Fig. 4) and 180 K (experiments with methanimine).

Our analysis of these observations demonstrate that the CN stretching band of the aminoacetonitrile at 2240 cm^{-1} can help us to identify the molecule at any temperature, since overlaps should not be observed. Furthermore, because the temperature desorption of aminoacetonitrile (around 200 K) is higher than the reactant ones (from 140 K for HCN and CH_2NH to a maximum 160 K–180 K for [NH_4^+ $^-$CN]), the monitoring of temperature desorption could also be used for the aminoacetonitrile identification. Therefore, we use the infrared signatures in the range of 2000–2300 cm^{-1} for the aminoacetonitrile

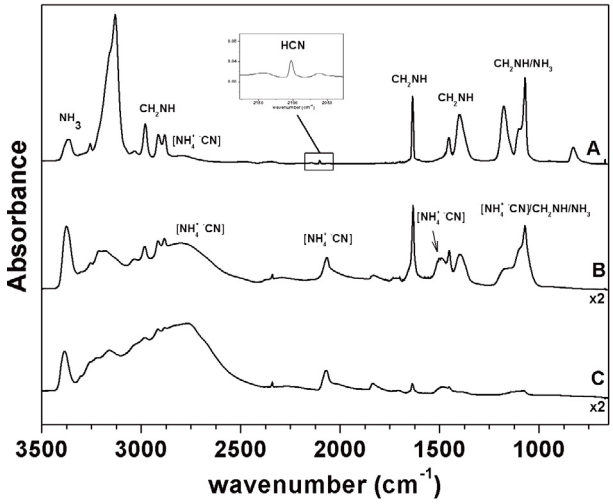


Fig. 6. Infrared spectra of methanimine/HCN/NH_3 deposit at 20 K in the presence of either a methanimine excess (A), methanimine with a more important quantity of [NH_4^+ $^-$CN] in comparison with spectrum A (B), or an excess of [NH_4^+ $^-$CN] (C).

identification, which are caused by the warming of ices including methanimine, ammonia, and hydrogen cyanide.

3.2. Temperature evolution of methanimine/[NH_4^+ $^-$CN] mixture

We study the heating evolution of ices including methanimine and NH_3/HCN mixture giving [NH_4^+ $^-$CN]. Our objectives consist of trying to understand the chemical reactivity that occurs during the warming of these ices, and determine the optimal conditions for the aminoacetonitrile formation. For this purpose, ices with different methanimine and NH_3/HCN proportions have been used. The corresponding infrared spectra of deposits are displayed in Fig. 6. Since many overlaps are present between infrared bands of ammonia, ammonium, and methanimine, and the methanimine quantity deposited is difficult to estimate with our experimental set-up, the quantification of each compound at 20 K cannot be obtained. Therefore, in the following discussion, only qualitative proportions are discussed.

Figure 6A displays the spectrum obtained in the presence of a methanimine excess. In this case, HCN is co-deposited with an methanimine/ammonia mixture. The methanimine is directly deposited from its synthesis tube by means of a rapid warm-up. The ammonia as an impurity comes from the methanimine tube and is identified by its bands at 3370 cm^{-1}. The methanimine is clearly identified with the bands at 2913 cm^{-1}, 2879 cm^{-1}, and 1635 cm^{-1}. The band at 2100 cm^{-1} characterizes HCN. The νCN band of the [NH_4^+ $^-$CN] salt is not detected because of its weak intensity. However, its presence can be identified through the broad band at 2781 cm^{-1} previously reported and corresponding to the stretching mode of NH_4^+. Therefore, we consider here that the methanimine is in excess with respect to [NH_4^+ $^-$CN]. To obtain an ice at 20 K presenting a more important quantity of salt in the initial ice, HCN, and ammonia are mixed in the same line. While the methanimine tube is rapidly warmed, the line is quickly opened. The infrared spectrum of this ice is presented on Fig. 6B. The amount of ammonia (3370 cm^{-1}) and salt (2781 cm^{-1} and 2065 cm^{-1}) relative to that of the methanimine (2913 cm^{-1}, 2883 cm^{-1} and 1635 cm^{-1}) clearly increases. The band of HCN is not present at 2100 cm^{-1}, because of the mixing of ammonia and HCN in the same line,

Table 1. Positions and attributions of infrared absorption bands of methanimine (CH_2NH) at 50 K, hydrogen cyanide (HCN) at 20 K, ammonium cyanide ($[NH_4^+\ ^-CN]$) at 20 K, pure aminoacetonitrile at 130 K, and refractory residues at 260 K.

Ices	Wavenumber (cm^{-1})	Attribution
Methanimine (CH_2NH)	3266	ν(N-H)
(ϵ NH_3, 50 K)	3162/3140	ν_{as}(C-H)
(Hamada et al. 1984; Jacox & Milligan 1975)	2987/2916/2886	ν_s(C-H)
	2206	Harmon or comb?
	2144	Harmon or comb?
	1642/1634	ν(C = N)
	1411	$\delta(CH_2)$
	1186	$\delta(NH_2)$
	1112	τ(NH)
	1077	$\omega(CH_2)$
	1069	$\rho(CH_2)$
Hydrogen cyanide (HCN)	3114	ν(C-H)
(pure, 20 K)	2100	ν(CN)
(Gerakines et al. 2004)	1618	Harmon
	849	δ(NCH
Ammonium cyanide $[NH_4^+\ ^-CN]$	3216	Comb
(NH_3 content, 20 K)	3024	ν(NH)
(Clutter & Thompson 1969; Gerakines et al. 2004)	2956	Comb
	2771	Harmon
	2080/2065	$^-$CN Comb/n
	1628	δ(NH)
	1488	δ(NH)
Aminoacetonitrile (NH_2CH_2CN)	3367	$\nu_{as}(NH_2)$
(pure, 130 K)	3271	$\nu_s(NH_2$
(Bernstein et al. 2004)	2981	$\nu_{as}(CH_2)$
	2945	$\nu_s(CH_2)$
	2240	ν(CN
	1595	$\delta(NH_2)$
	1424	$\delta(CH_2)$
	1335	$\delta(CH_2)$
	1095	ν(C-N)
	928	ω(NH
Refractory residues	3347	$\nu(NH_2)$
(260 K, based on PEI attributions)	3269	NH ?
(Kuptsov & Zhizhin 1998)	2913	$\nu(CH_2)$
	2840	$\nu(CH_2)$
	2230	ν(CN)
	1598	δ(NH)
	1450	δ(CH)
	1359	δ(CH)
	1100	ν(CN)

Notes. Vibration mode: stretching (ν), bending (δ), rocking (ρ), torsion (τ), wagging (ω). Type of vibration mode: asymmetric (as), symmetric (s). Comb: combination mode. Harmon: harmonic mode.

which directly leads to the salt formation during the deposition. The last deposit contains a methanimine diluted in $[NH_4^+\ ^-CN]$ salt (Fig. 6C). In this case, the methanimine tube is slowly warmed up, while the line including the ammonia and HCN is quickly opened. The resulting ice has at 20 K a large excess of $[NH_4^+\ ^-CN]$ in comparison with the two other ices. Each deposit was then warmed up at 5 K min^{-1}. The temperature evolution of each ice was monitored by infrared spectroscopy and/or mass spectrometry.

3.2.1. Temperature evolution of deposit leading to a methanimine excess and a variable amount of $[NH_4^+\ ^-CN]$ salt

Figure 7 displays the temperature evolution of an ice containing a methanimine excess with respect to $[NH_4^+\ ^-CN]$. Below 200 K, the evolution of infrared spectra is dominated by the crystallization of the $[NH_4^+\ ^-CN]$ salt, methanimine, and ammonia. Therefore, the monitoring is focused only on temperatures above 200 K. Around 190 K, a new band appears at 2230 cm^{-1}, while a band at 2060 cm^{-1}, which appears at 130 K, is still present. The band at 2060 cm^{-1} agrees closely with that of a $^-$CN stretching mode observed with the $[NH_4^+\ ^-CN]$ salt. However, even if $[NH_4^+\ ^-CN]$ salt crystallizes around 120 K, it sublimates between 160 K and 180 K, while here this species disappears around 260 K. The band at 2230 cm^{-1} does not correspond to any infrared bands present in the references seen in Sect. 3.1. As shown in Fig. 7, this band persists at temperature above 200 K, and only begins to decrease in intensity around 270 K, while the one of aminoacetonitrile (band at 2240 cm^{-1}) disappears due to its sublimation around 200 K, hence represents a new species. We can presume from its spatial position and the initial reactants

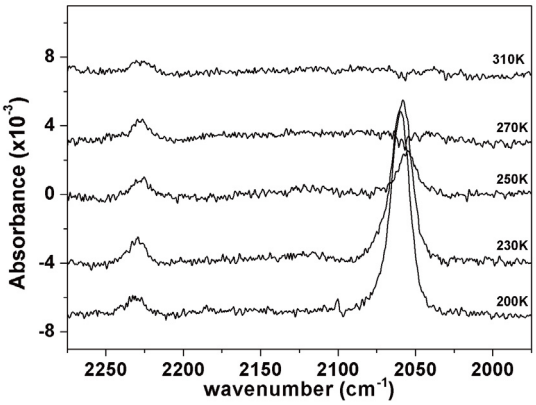


Fig. 7. Change in the range 1950–2300 cm^{-1} of the infrared spectrum after heating from 200 to 310 K and after the sublimation of methanimine, ammonia, and hydrogen cyanide (160 K). The deposit includes an excess of methanimine with respect to both NH_3 and HCN, producing traces of [NH_4^+ $^-$CN].

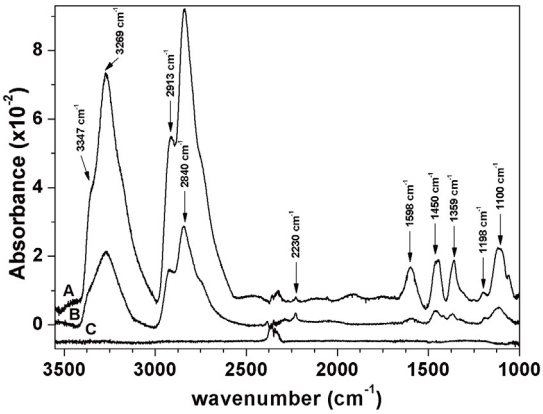


Fig. 8. Infrared profiles obtained at 260 K for a deposit presenting an excess of methanimine and trace of [NH_4^+ $^-$CN] (A) or methanimine and a larger amount of [NH_4^+ $^-$CN] than in the mixture A (B), or obtained at 230 K for a deposit containing an excess of [NH_4^+ $^-$CN] (C).

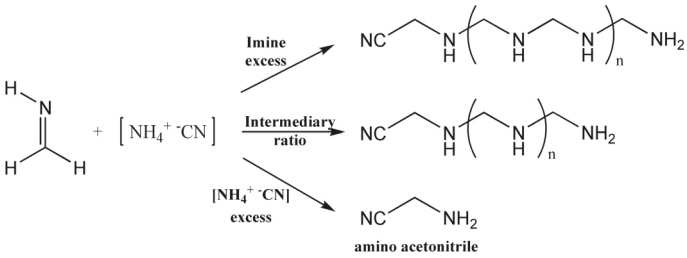


Fig. 9. Thermal reactivity observed during the warming from 20 K to 300 K at 10^{-8} mbar of an ice including methanimine and [NH_4^+ $^-$CN] salt.

that it can be related to a nitrile group. The monitoring of infrared signals in the same range for an ice containing a larger amount of [NH_4^+ $^-$CN] than in the previous mixture (data not shown) leads to the same conclusion. However, it is interesting to compare these results with the full spectra at 260 K (Fig. 8). While the band intensities differ, the band positions between the residue corresponding to an excess of methanimine with respect to [NH_4^+ $^-$CN] (Fig. 8A) and those produced by a larger amount of salt (Fig. 8B) are exactly the same. Therefore, the two residues seem to have the same molecular functions. They present intense bands at 3269 cm^{-1}, which could correspond to NH or/and NH_2 stretching, and at 2913 cm^{-1} and 2840 cm^{-1}, which could correspond to CH_2 stretching.

From these attributions and because the IR spectra of these residues display strong similarities to that of the poly(ethyleneimine) (Kuptsov & Zhizhin 1998), we propose that the molecular structure of these species could correspond to either linear or branched poly(methylene-imine) polymers (as shown in Fig. 9) with -CN and -NH_2 endings. In this context, $^-$CN could initiate the polymerization by reaction with methanimine; the resulting product, the aminoacetonitrile, could then react with another methanimine leading to the formation of poly(methyleneimine) polymers. Therefore, polymers with CN and NH_2 ending groups as well as -(CH_2NR)- monomers could be formed (R = H or CH_2NR'). This behavior can be related to the formaldehyde reactivity in the presence of ammonia. In this case, ammonia initiates the polyoxymethylene formation (Schutte et al. 1993) and can lead to the amino alcohol when formaldehyde is diluted sufficiently in ammonia (Bossa et al. 2009). This hypothesis is strengthened by the difference in the relative intensity of the band at 2230 cm^{-1} (attributed to a CN ending) and the other bands of the spectra. For example, in the presence of a methanimine excess, the intensity ratio $\frac{A_{(CH_2)}(2890-2920\ cm^{-1})}{A_{(CN)}(2230\ cm^{-1})}$ is 120, while it decreases to 24 when the salt proportion is increased in the initial ice. This suggests that the number of monomers is higher in the residue obtained with an initial methanimine excess, while this number decreases in polymers formed from an ice including a larger quantity of salt. Therefore, longer polymers are formed in ice concentrated in imine than in a more diluted ice (Fig. 9), which is a well-known result in polymer chemistry.

As it was previously described, the band observed at 2060 cm^{-1} in Fig. 7 fits well with the one of $^-$CN in [NH_4^+ $^-$CN]. However, the temperatures of desorption are different. This band could also correspond to ketenimine or isonitrile, but from our initial reactants and for only a thermally induced reactivity, it seems difficult to form such derivatives. The evolution of both the infrared band at 2060 cm^{-1} and those of the residue shows that the band at 2060 cm^{-1} is linked to the residue formation. It indeed appears around 130 K, while the residue appears around 150–160 K. Furthermore, the band at 2060 cm^{-1} disappears with a part of the residue. Therefore, we propose that this band could correspond to a ν(CN) of [NH_4^+ $^-$CN] clusters embeded in the polymer matrix during the polymer formation at 140–150 K. At high temperatures some polymers sublime leading to a salt release.

3.2.2. Aminoacetonitrile formation from the second step of the Strecker synthesis

On the basis of the hypothesis that the polymerization of the methanimine is initiated by $^-$CN, the methanimine was diluted in an excess of [NH_4^+ $^-$CN] to form the aminoacetonitrile. Figure 10 displays the thermal evolution from 135 K to 210 K of the infrared spectrum in the range 2215–2300 cm^{-1}. At 135 K, a new band appears at exactly 2240 cm^{-1}. It increases until 170–180 K, and slowly decreases to disappear at around 210 K. The infrared

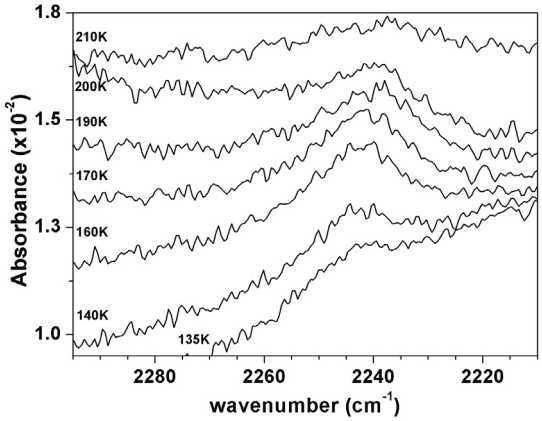


Fig. 10. Infrared spectra in the range 2215–2300 cm^{-1} relative to the thermal range 135–210 K for a deposit including an excess of [NH_4^+ $^-$CN].

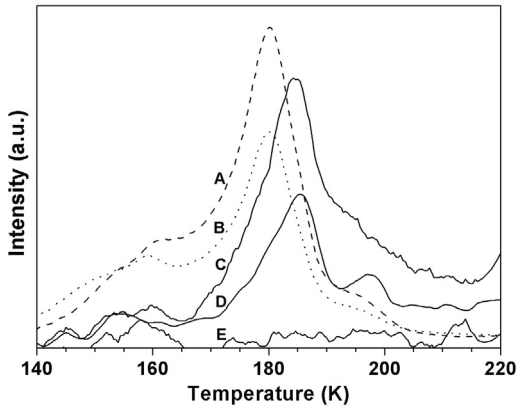


Fig. 12. Partial pressure in full-scan mode for ions *m/z* 27 (A), *m/z* 17 (B), *m/z* 55 (C), *m/z* 56, (D) and *m/z* 60 (E) as a function of temperature during the warm-up of an ice including an excess of [NH_4^+ $^-$CN]. *m/z* 27 is related to HCN, *m/z* 17 to NH_3, *m/z* 55 to [NH_2CHCN^+], *m/z* 56 to [$NH_2CH_2CN^+$], and *m/z* 60 serves as a mass reference.

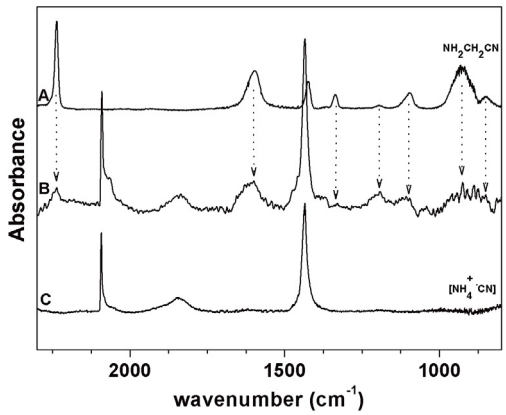


Fig. 11. Infrared spectra of aminoacetonitrile NH_2CH_2CN at 130 K (A), of refractory residue at 210 K coming from a deposit with an excess of [NH_4^+ $^-$CN] (B) and [NH_4^+ $^-$CN] salt at 160 K (C).

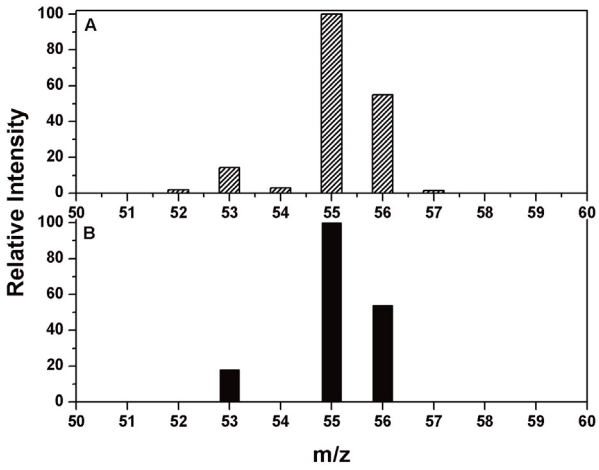


Fig. 13. Mass spectra presenting the relative intensity of aminoacetonitrile fragments obtained with electronic ionization (70 eV) from the NIST Mass Spectra Data Center (A), and the one detected in SIM mode at 185 K for ions *m/z* 55, *m/z* 56, and *m/z* 53 during the warm-up of an ice, including an excess of [NH_4^+ $^-$CN] (B). The *m/z* 53 is related to [$NHCCN^+$], *m/z* 55 is related to [NH_2CHCN^+], ans *m/z* 56 is related to [$NH_2CH_2CN^+$].

spectrum at 230 K does not display any of the bands observed in the two previous experiments (Fig. 8C), where a polymeric structure was observed. Therefore, a new product, not a polymer, is formed. The band position and the temperature sublimation of this species fit well with the aminoacetonitrile ones. This attribution is strengthened by the comparison between the spectra obtained from this ice at 210 K (Fig. 11B), and the spectra of both the aminoacetonitrile at 130 K (Fig. 11A) and the crystalline form of the pure salt at 160 K (Fig. 11C). The spectrum of Fig. 11B is exactly the sum of the two others. The aminoacetonitrile can be identified by seven of its bands in the range 900–2300 cm^{-1}, while the three other bands correspond to salt. Therefore, the aminoacetonitrile is formed by the reaction of the methanimine in presence of an excess of [NH_4^+ $^-$CN] salt.

To confirm these results, we performed mass spectroscopy analyses. Figure 12 displays the partial pressure of fragment ions as a function of temperature during the warming of an ice including at 20 K an excess of [NH_4^+ $^-$CN] salt with respect to methanimine. From the National Institute of Standards and Technology (NIST) base data, the most intense fragments obtained for the mass spectrometry of aminoacetonitrile (70 eV ionization) are ions at *m/z* 55 and *m/z* 56 (Fig. 13A). The mass at *m/z* 55 (Fig. 12C) and *m/z* 56 (Fig. 12D) were detected during the ice warming with a higher intensity for the ion at *m/z* 55, which is consistent with the NIST reference (Fig. 13A). The temperature desorption (185 K) is lower than the one obtained from a pure aminoacetonitrile ice (Fig. 12). This is explained by the [NH_4^+ $^-$CN] salt desorption at 180 K (Fig. 12A, HCN *m/z* 27, and Fig. 12B, NH_3 *m/z* 17), since this salt is the major product. The salt sublimation drives away a large amount of the aminoacetonitrile leading to this lower temperature desorption. In a final experiment, we attempted to increase the sensitivity of the mass analysis by using the selective ion monitoring mode (SIM) to monitor the fragment ions at *m/z* 53, *m/z* 55, and *m/z* 56. Figure 13B displays the relative intensity of each of the fragment ions. The fragments 53, 55, and 56 are detected at 185 K, with

exactly the same relative intensity as those observed from the NIST data base (Fig. 13A). From these two mass spectrometry analyses, we can therefore conclude that the fragment ions characterizing the aminoacetonitrile in mass spectroscopy (70 eV ionization) are detected during the warming of an ice containing at 20 K methanimine (CH_2NH) that is diluted in an excess of [NH_4^+ ^-CN] salt, which confirms that aminoacetonitrile can form in such conditions.

In these experiments, we note that the desorption temperature of the salt is 20 K higher than that of a pure salt (160 K). Furthermore, we observe at 210 K a small amount of the salt (Fig. 11), which is no longer present at 170–180 K in the reference experiment (Sect. 3.1, Fig. 5). Since the polymer and/or aminoacetonitrile formation occurs around 130 K, which is the temperature of the salt crystallization (120–140 K), the methanimine reactivity seems to produce a modification to the salt crystallization, which could explain any related modifications to the temperature desorption. This observation can be correlated to the presence of a salt cluster in the polymer matrix (Sect. 3.2.1), which show the interaction between the salt and the formed polymers.

In summary, infrared data combined with mass spectrometry studies demonstrate that the second reaction of the Strecker synthesis (Fig. 9) can occur in astrophysical-like conditions, where ^-CN reacts with methanimine to form the aminoacetonitrile.

3.3. Astrophysical implications

The Strecker synthesis is a well-known reaction in prebiotic chemistry, which leads to the formation of amino acid precursors consisting of nitrile derivatives. Since amino acids have been identified in meteorites or after the hydrolysis of ice-refractory residue analogs, it has been proposed that they are formed by means of the Strecker synthesis in astrophysical environments, where various mechanisms processing dirty ices are assumed to take place. Among them, the formation of aminoacetonitrile is the simplest one, which leads after its hydrolysis to glycine. Numerous theoretical studies (Basiuk & Bogillo 2002a,b; Koch et al. 2008; Rimola et al. 2010; Woon 2002; Xu & Wang 2007) have been performed to determine whether aminoacetonitrile can be formed by means of the Strecker synthesis and demonstrate this.

In this contribution, using species detected in extraterrestrial environments in either the gas or the solid phases, we demonstrate that aminoacetonitrile can be formed from the Strecker synthesis in astrophysically relevant conditions. Our starting material is composed at 20 K of a deposit including ammonia, hydrogen cyanide, and methanimine. The first two molecules react at this temperature to give [NH_4^+ ^-CN]. In the solid phase of the ISM, only ammonia, which represents up to 10% of the constituents of interstellar ice relative to water (Bottinelli et al. 2010) is observed. Hydrogen cyanide and methanimine have been detected not only in the gas phase of the interstellar medium in giant molecular clouds of our own Galaxy (Godfrey et al. 1973; Snyder & Buhl 1971), and in regions of massive star formation (hot cores) (Dickens 1997), but also extra-galactic environments (Salter et al. 2008). Comparison between the abundances found in astrophysical environments and models suggest that these molecules are formed on the dust grains followed by their release into the gas phase. From radio observations of comets, HCN, and NH_3 have been detected, but the search for CH_2NH has been inconclusive until now (Crovisier et al. 2004). The methanimine could be formed in the solid phase of the ice by the hydrogenation of hydrogen cyanide (Theule et al. 2011a) or by the dehydrogenation of methylamine (unpublished work by the authors). In the solid phase, methanimine can be also formed during the first step of the Strecker synthesis. In this step, the formaldehyde reacts with the ammonia to form the corresponding amino alcohol NH_2CH_2OH (Bossa et al. 2009). This step has been experimentally shown to occur in astrophysical-like conditions. The next step consists of dehydrating the amino methanol, which leads to the methanimine. This dehydratation can only occur in the presence of an acid such as the formic acid (Vinogradoff et al. 2011). Therefore, from species detected in interstellar environments, such as formaldehyde, ammonia, and formic acid, it is possible to form the methanimine simply by means of an ice warming at low temperature. The second step of the Strecker synthesis consists of the reaction of this methanimine with hydrogen cyanide on the grain surface. Since the hydrogen cyanide is not detected in the solid phase, we postulate that it can be present at the grain surface as a salt by its reaction with the ammonia, leading to [NH_4^+ ^-CN]. As we have shown in this contribution, according to the methanimine concentration in the initial deposit, different products can be formed. For instance, in diluted ice, aminoacetonitrile is formed. If astrophysical conditions are considered, the presence of water can increase the methanimine dilution, hence enhance the aminoacetonitrile formation. However, an excessive dilution could have the opposite effect leading to a decrease in the reactivity between methanimine and ^-CN. This reaction occurs at around 130 K on the laboratory timescale, which opens the possibility of this reaction occurring at lower temperature on a longer timescale in different astrophysical environments such as in protoplanetary disk regions or in cometary environments. These experimental results demonstrate that the aminoacetonitrile can be formed in astrophysical-like conditions by means of the Strecker synthesis. In futur studies, we propose to pursue our investigations of this reaction, and estimate the effect of water as well as the possibility of producing aminoacetonitrile from a combination of formaldehyde, ammonia, formic acid, and hydrogen cyanide. These results open a new pathway for the formation of amino acids precursors in astrophysical conditions. Nevertheless, the possibility of forming directly amino acid in these environments from their nitrile derivatives seems difficult. Experiments conducted to study aminoacetonitrile reactivity in water environments at temperatures from 20 K to 300 K do not find evidence of any glycine formation (data not published), as predicted by theoretical studies (Rimola et al. 2010). One possibility is that glycine is formed by the hydration of the nitrile derivatives inside asteroids, where it is presumed that a liquid water phase has occurred (Abramov et al. 2011; Herd et al. 2011). In these conditions, a wide range of amino acids could be formed in interplanetary (asteroidal) environments, as detected on Earth inside carbonaceous meteorites (Herd et al. 2011; Pizzarello 2004, 2007).

4. Conclusion

We have investigated whether aminoacetonitrile can be produced by the Strecker synthesis in astrophysical-like conditions involving interstellar ice analogs. We have focused on the second step of this reaction, which consists of forming the aminoacetonitrile from the reaction of methanimine (CH_2NH) with hydrogen cyanide (HCN). We have experimentally investigated the reaction of methanimine with the [NH_4^+ ^-CN] salt. An ice containing these two reactants was formed at 20 K and progressively warmed to 330 K. We used infrared and mass spectroscopy to monitor the ice evolution during the warming, and clearly

demonstrated that $^{-}$CN reacts with the methanimine leading to the formation of products in which the structures depend on the initial ratio of methanimine to salt. In the presence of a methanimine excess, we found that $^{-}$CN initiates the polymerization of the methanimine leading to either long or branched polymers. When we decreased the proportion of methanimine relative to salt in the ice mixture, the polymer lengths decreased until the formation of the aminoacetonitrile around 130 K, for our experimental conditions. These results demonstrate that a complex chemistry can occur in interstellar ice analogs, hence in interstellar environments. Furthermore, these thermal effects should be considered as part of an important physical process when considering other chemical reactions that can occur, as well as photochemical or hydrogenation processes.

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