

Experimental Study of Water–Ice Catalyzed Thermal Isomerization of Cyanamide into Carbodiimide: Implication for Prebiotic Chemistry

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Water–ice surfaces can play the role of catalyst in heterogeneous reactions occurring between trapped impurities in stratospheric^{1–3} or interstellar medium.^{4–5} The most typical examples of ice-catalyzed reactions involve usually two components: HCl with either ClONO₂,⁶ ClOH,⁷ or C₃O₂⁸ molecules. The interstellar grain surface can induce the formation of molecular hydrogen H₂ by recombination of H atoms at low temperature.⁹ In prebiotic chemistry, cyanamide (NH₂CN) is a relevant molecule which can be converted into urea in liquid water.¹⁰ This molecule has been detected at low-column density (low abundance) in the gas phase in interstellar clouds ($T < 100$ K) using radio spectral techniques,¹¹ and it is the first known interstellar molecule to contain the NCN frame. By an isomerization process it can lead to the formation of carbodiimide (HNCNH)¹² which is considered as an important condensing agent able to assemble amino acids into peptides in liquid water.¹³ It has been reported that such an isomerization can occur in gaseous phase for temperature higher than 20 °C.¹² However, in these conditions the amount of carbodiimide yielded is lower than 1%. Considering the temperature range existing in the interstellar clouds, the carbodiimide formation is impossible in the gas phase. However, it has been reported recently from reliable theoretical predictions that an isomerization reaction cyanamide → carbodiimide can occur in the presence of water molecules.¹⁴

In this work using FT-IR spectroscopy, we give experimental evidence about the formation of carbodiimide when cyanamide is condensed on an amorphous water–ice surface. We show that it occurs in the very low-temperature range which agrees quite well with that expected in the interstellar clouds. This reaction can occur when NH₂CN is frozen onto dust grains in the clouds, in which H₂O is known as the most predominant constituent.¹⁵ Further, when interstellar dust aggregates, it can form a comet nucleus which is a relevant source of organic molecules delivered to the primitive earth.¹⁶

Cyanamide¹⁷ has a very low vapor pressure; however, at 40 °C it can be sublimated from a glass tube and deposited as a film on a gold-plated mirror held at low temperatures (10 K) and under a low pressure (10⁻⁷ mbar). The NH₂CN infrared spectrum (Table 1 in Supporting Information) recorded with a 1 cm⁻¹ resolution using a FT-IR spectrometer (Nicolet series II Magna system 750) is marked by broad and intense bands relative to the NH and CN stretching modes that span respectively the spectral ranges from about 3350 to 3100 cm⁻¹ (including the first harmonic of bending NH) and 2270 to 2210 cm⁻¹; this latter range is displayed in Figure 1a. Because of the existence of hydrogen bonding between NH₂CN molecules in the solid, the νNH mode frequencies are strongly downshifted with respect to the monomer values (ν_{asym}NH = 3490 cm⁻¹ and ν_{sym}NH = 3410 cm⁻¹). During the deposition of the sample on the mirror, carbodiimide which results from cyanamide isomerization in the gas phase ($T > 20$ °C) is also co-deposited. Supported by thermodynamic considerations, carbodiimide is about 4 kcal mol⁻¹ less stable than cyanamide;¹⁷ a very small amount

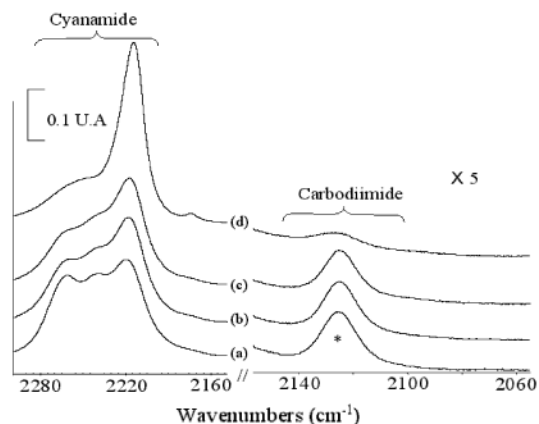


Figure 1. FTIR spectra of pure cyanamide deposited at 10 K, then recorded at (a) 10 K, (b) 80 K, (c) 120 K, (d) 140 K. *Carbodiimide trapped into cyanamide (2125 cm⁻¹) coming from gaseous phase.

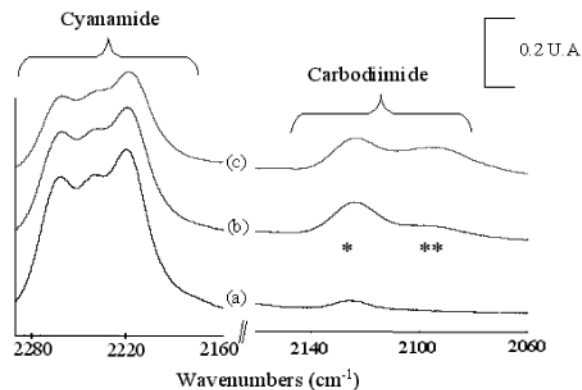


Figure 2. FTIR spectra of cyanamide deposited and recorded at 10 K (a) after deposition of the sample, (b) after 90 min of VUV irradiation using a SiO₂ window ($\lambda > 160$ nm), (c) after 420 min of VUV irradiation. *Carbodiimide isolated and trapped into cyanamide (2125 cm⁻¹). **Carbodiimide under an aggregate form into cyanamide (2095 cm⁻¹).

with respect to the cyanamide (less than 1% at 110 °C) is obtained in this way. Carbodiimide can be identified from its strongest band at 2125 cm⁻¹ (ν_aNCN) (Figure 1a) which is very characteristic for various carbodiimide derivatives.¹⁸ This feature is relative to carbodiimide in a solid NH₂CN environment.

Vacuum ultraviolet irradiation of NH₂CN realized at 10 K using a microwave discharge hydrogen flow lamp (Ophos Instruments) gives strong support to the identification of the carbodiimide in such an environment. Indeed, as it has been already reported for HCN and HC₃N which can be converted into CNH¹⁹ and CCCNH²⁰ by VUV irradiation, in the same way we observed that solid NH₂CN leads to monomer HNCNH trapped in solid NH₂CN (Figure 2). The outcome is that the band at 2125 cm⁻¹ grows at the beginning of the UV process and then decreases when the amount of carbodiimide becomes higher in the sample. Thus, we observe

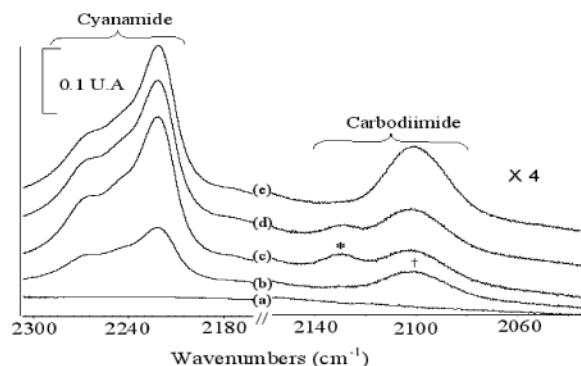


Figure 3. FTIR spectra of (a) water–ice film at 80 K, (b) cyanamide/Ar (10^{-2} mol) deposited at 80 K over the water–ice film, (c) cyanamide/Ar (5×10^{-2} mol) deposited at 80 K over the water–ice film, (d) 110 K, (e) 140 K. †Carbodiimide yielded at the water–ice surface (2100 cm^{-1}). *Carbodiimide trapped into cyanamide (2125 cm^{-1}) coming from gaseous phase.

another band at 2095 cm^{-1} which can be assigned to carbodiimide under an aggregate form which becomes prominent with respect to the 2125 cm^{-1} feature for extended irradiation.

By raising the temperature from 10 to 150 K (Figure 1b–d) a change in the infrared spectrum of cyanamide is observed above 50 K which can be interpreted as solid-phase change from an amorphous to a more crystalline form (this change is visible from the narrowness and the increase of the feature at 2260 cm^{-1}). During this crystallization process we observe that carbodiimide coming from the gaseous phase, which is embedded into the solid NH_2CN , can be evaporated and the infrared feature at 2125 cm^{-1} disappears. In summary, we observed that during the rise in temperatures, the solid cyanamide cannot be converted into carbodiimide.

Thereafter, we study the behavior of cyanamide deposited with a large excess of argon on a water–ice film at 80 K. Here, argon is added to minimize the cluster formation at the ice surface, and the temperature of the sample is fixed at 80 K to eliminate the dilution gas.

An amorphous water–ice film is previously prepared by condensing water vapor with argon (1/50) on the mirror held at 80 K under the constant and basic pressure of the cryostat ($P = 10^{-7}$ mbar).²¹ Its infrared spectrum²¹ is marked by bulk OH stretching and bending modes (respectively located as a broad bands at 3250 and 1600 cm^{-1}) and by a dangling OH mode at 3695 cm^{-1} in which the H atom is not involved in hydrogen bonding. This last mode can be a potential site for adsorption of proton acceptor molecules. No water vibrational band appears in the frequency range (2280 – 2060 cm^{-1}) where cyanamide and carbodiimide are expected to absorb (Figure 3 a).

When cyanamide is slowly deposited on the water–ice film at 80 K (Figure 3b), we observe the appearance of a new vibrational band at 2100 cm^{-1} which increases until the surface has been completely covered (Figure 3b). This band is not visible when NH_2CN is deposited on the bare surface. It can be assigned to carbodiimide formed from an ice-catalyzed cyanamide isomerization. Theoretically¹⁴ it was predicted that carbodiimide formation can proceed via an ionic intermediate ($\text{H}_3\text{O}^+\text{HNCN}^-$). This latter is $3 \text{ kcal}\cdot\text{mol}^{-1}$ higher in energy than carbodiimide in an environment of five water molecules. No trace of this species has been detected in our spectra. Carbodiimide is yielded at the surface in a weak amount which explains why the most intense band expected for this species is only observed. Further, when cyanamide goes on to be deposited, we observe again the band at 2125 cm^{-1} relative to carbodiimide trapped in cyanamide and coming from the isomerization reaction in the gaseous phase. During all this process

the dangling OH mode of water is not affected by the adsorbed species. This observation also confirms theoretical results which shows that cyanamide or carbodiimide acts as an electrophile by means of the acid hydrogen atoms.¹⁴ When the sample is warmed from 80 to 140 K, cyanamide goes on to react, and the vibrational band at 2100 cm^{-1} still increases, whereas carbodiimide trapped into cyanamide evolves as previously by sublimating above 80 K and completely disappears at 150 K. Above 150 K adsorbed carbodiimide begins to sublime, and it disappears at 170 K. The amount of carbodiimide yielded with respect to the cyanamide precursor is close to 4% at 80 K and 13% at 140 K from the estimation of their relative absorption band.

No trace of urea can be detected during this thermal process, showing that the hydrolysis of cyanamide or carbodiimide is unfavorable in a solid environment.

In conclusion, these experiments show that cyanamide can be converted into carbodiimide through a tautomerization reaction favored by the water molecules which are able to mediate the proton transfer which also explains why the dangling OH modes are not affected during this reaction. The observed reaction agrees very well with the DFT and MP2 calculations.¹⁴ According to them, this reaction is strongly favored by the presence of water molecules which contribute to lower efficiently the activation energy. In a system where cyanamide is in an environment from one to five water molecules, an energetic barrier of 36.3 – 8.6 kcal is respectively calculated. The strong lowering of the barrier is a sign of a reaction which can occur at low temperatures. Our results confirm that isomerization can become significant at low temperatures ($T \geq 80 \text{ K}$). The results of these experiments have important implications for both cometary and interstellar chemistry, and a vibrational band at 2100 cm^{-1} which could be relative to the carbodiimide presence should be investigated in the cometary or protostellar objects in which water is dominant.

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Supporting Information Available: Experimental frequencies of pure cyanamide deposited at 10 K and recorded at 10 K. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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