

Cryogenic Synthesis of Molecules of Astrobiological Interest: Catalytic Role of Cosmic Dust Analogues

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Abstract We have studied the effects of the substrate, namely amorphous olivine (MgFeSiO_4) cosmic dust analogues (CDAs), in synthesis of molecules obtained after 200 keV proton irradiation of formamide (NH_2COH). Formamide has been deposited on the olivine substrate at 20 K. The abundances of new molecular species formed after an irradiation dose of 12 eV/16 amu in formamide pure (i.e. deposited on an inert silicon substrate) and deposited on CDAs have been compared. Specifically, MgFeSiO_4 amorphous olivine is a selective catalyst preventing formation of NH_3 and CN^- molecules and changing the relative abundances of $\text{NH}_4^+\text{OCN}^-$, CO_2 , HNCO , CO . We have shown that the role of CDAs has to be taken into account in experiments simulating processes occurring in astronomical environments.

Keywords astrochemistry · astrobiology · methods: laboratory · techniques: spectroscopy

Introduction

The dust grains could have played an important role in driving the formation of complex molecular compounds relevant for the prebiotic chemistry occurred in the early Earth. Dust and molecular compounds present in space experienced very different environments, with

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temperatures ranging from few to thousands of Kelvins, and with very harsh conditions due to particle and UV irradiations. Astronomical observations of the interstellar medium, coupled with direct in situ investigations of solar system bodies performed by space missions and laboratory analyses of extraterrestrial material have shown the presence of large amount of organic molecules. The detection of more than 100 molecules demonstrates that chemical reactions can proceed successfully in space (for a complete inventory of molecules observed see <http://www.cv.nrao.edu/~awootten/allmols.html>). However, due to low efficiency, formation of complex molecules in gas phase is not feasible, then an active chemistry has been suggested to take place at cryogenic temperatures (~ 10 K) on cosmic dust grains acting as catalysts (Gould and Salpeter 1963; Allen and Robinson 1977; Tielens and Hagen 1982). Furthermore, laboratory experiments have shown that different chemical–physical mechanisms might be responsible for the richness of molecules observed in space. Surface catalysis at low temperature is considered necessary to justify the presence of, e.g., H_2 , H_2O or CO_2 . As demonstrated experimentally (Vidali et al. 2005) according to the Langmuir–Hinshelwood mechanism (Langmuir 1981), an impinging atom coming from the gas phase becomes equilibrated with the surface, diffuses and, if it finds another atom adsorbed on the solid surface might react with it. However, to describe the presence of more complex molecules, as CH_3OH , or radicals and even organic refractory material, irradiation processes of ice by ions and UV photons are required (Moore and Hudson 1998, Greenberg et al. 1999, Strazzulla and Johnson 1991). Therefore, chemical compounds synthesized on dust grains may become even more complex in high-energy astronomical environments.

The dust grains occur in space in more or less fluffy aggregates with variable proportions of silicate, oxide, pure metal, pure carbon and organic components, which could be amorphous or crystalline, structurally-mixed, and complex. The catalytic effects of cosmic dust analogues in prebiotic reactions have been studied in laboratory at high temperatures (Hill and Nuth 2003) and in conditions simulating the environments found on the early Earth (Saladino et al. 2005). Synthesis of methyl amine, acetonitrile, *N*-methyl methylene imine and hydrocarbons have been showed to occur in the gas phase through Fisher–Tropsh- and Haber–Bosch-Type catalytic reactions on the surface of cosmic dust analogue silicates at 200–600°C and pressure ≤ 800 torr (Hill and Nuth 2003). A large suite of pyrimidines (including cytosine and uracil) and purines have been synthesized at 160°C from formamide (NH_2COH) in the presence of cosmic-dust analogues silicates, and the stabilizing effect of the catalysts on formamide degradation of polynucleotides has been showed (Saladino et al. 2005).

Formamide is a simple molecule detected in the gas phase in the interstellar medium (Millar 2004), in the long period comet Hale-Bopp (Bockelée-Morvan 2000) and, tentatively, in the solid phase on grains around the young stellar object W33A (Schutte et al. 1999). It is considered an interesting reactive prebiotic precursor for the chemistry of purine and pyrimidine derivatives (Bredereck et al. 1957, 1959; Yamada and Okamoto 1972, Yamada et al. 1975; Saladino et al. 2004, 2005). Therefore, it is interesting to characterize the reactions that are expected to occur in space considering, in particular, that impacts of comets are believed to be a way to deliver extraterrestrial material on the early Earth, mechanism that might have supported the origin of life.

In the following sections, we present the laboratory results on catalytic effects of cosmic dust analogue silicate in the synthesis of new molecular species by ion irradiation of formamide ice, deposited on olivine dust at cryogenic temperatures. The results are compared with those of formamide ice deposited on inert (silicon) substrates and irradiated with proton (Brucato et al. 2006).

Results

Cosmic dust analogue (CDA) was produced by laser ablation technique (see for more details Colangeli et al. 2003; Rotundi et al. 2002; Brucato et al. 1999). The target was an oxide mixture of SiO_2 , MgO , FeO prepared in order to have the exact stoichiometric composition of olivine MgFeSiO_4 . Pulsed Nd-YAG laser at the wavelength of 266 nm and with a power density of 10^9 W cm^{-2} was used for the target ablation. Fast condensation of vaporized target occurred inside a chamber with O_2 atmosphere at 10 mbar. Once condensed dust grains were collected on a silicon stub substrate. The cosmic dust analogue showed a fluffy chain-like morphology of spheroids with amorphous structure and with sizes following a log-normal distribution with an average size of 25 nm.

Two experiments were performed. In the first case, pure formamide ice was condensed at 20 K on the silicon stub substrate and, secondly, it was condensed at the same temperature, on the CDAs sample. The vacuum chamber ($\sim 10^{-6}$ mbar) containing the ice sample was connected to an ion accelerator device where protons at energy of 200 keV were produced for the irradiation. In order to avoid macroscopic heating of the target, the ion current density was maintained in the range of 100 nA cm^{-2} to a few $\mu\text{A cm}^{-2}$.

Chemical evolution during ion irradiation was monitored by infrared transmission spectroscopy in the $4,000\text{--}500 \text{ cm}^{-1}$ spectral range. Spectra of formamide ice pure and mixed with CDA olivine at temperature of 20 K and after ion irradiation are shown in Figure 1. Note that this paper is focused on the role of dust grains in driving the chemistry under ion irradiation then, the spectrum of amorphous CDA olivine was removed from the figure for sake of clarity. The strongest absorption features of solid formamide are reported in Table I. The assignment of vibrational modes was derived from those for gaseous and liquid samples (McNaughton et al. 1999; Rubalcava 1956).

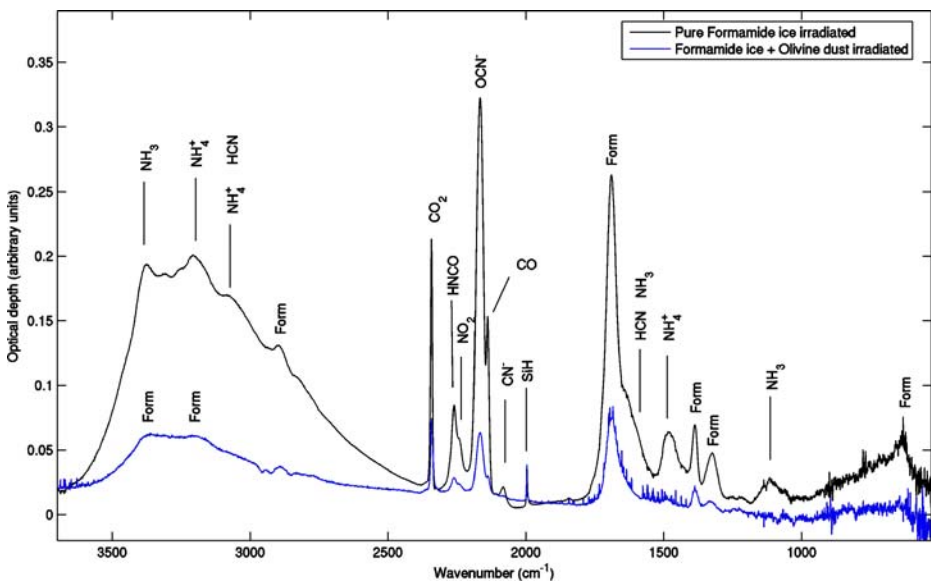


Figure 1 IR spectrum in optical depth scale, of pure formamide (upper spectrum) and mixed with amorphous olivine (MgFeSiO_4) CDAs (lower spectrum) at 20 K after irradiation at a dose of $12 \text{ eV}/16 \text{ amu}$ with 200 keV H^+ ions.

TABLE I Peak position and assignment of the IR bands of formamide (NH₂COH) ice at 20 K

Peak positions		Assignment
cm ⁻¹	μm	
3,368	2.97	ν_1 asym. NH ₂ stretch
3,181	3.14	ν_2 sym. NH ₂ stretch
2,881	3.47	ν_3 CH stretch
1,708	5.85	ν_4 CO stretch
1,631	6.13	ν_5 in plane NH ₂ scissoring
1,388	7.2	ν_6 in plane CH scissoring
1,328	7.53	ν_7 CN stretch

We performed 200 keV proton irradiation of both pure formamide and deposited on CDA at the same fluence of $6.25 \cdot 10^{14}$ (200 keV H⁺cm⁻²) that correspond to a deposition dose of 12 eV/16 amu. The effects of olivine dust on ion processing of formamide are active at the interface dust–ice. Hence, a frozen layer of formamide as thin as possible (0.113 μm) was prepared reducing the volume effects on new molecular species formation. This sample was about five times thinner of the pure formamide ice deposit (0.556 μm). Thickness was obtained taking in account the absorbances of the IR bands of formamide ice at 20 as measured by Brucato et al. (2006).

In Figure 1 the IR spectra of pure formamide and mixed with olivine CDA after ion processing are reported. Spectral features appear consistent with the formation of new molecular species. Their assignments are reported in Table II and labeled in Figure 1. A residue of formamide ice is still present in both the spectra as showed by the bands labeled with “Form”. Bands of carbon oxides are observed peaked at 2,342 (CO₂), 2,140 (CO). A

TABLE II Peak positions, feature assignments, and fraction of molecules synthesized to formamide molecules lost by 200 keV proton irradiation of pure formamide and mixed with olivine CDA at 20 K

Species	Feature	Position		Fraction	
		cm ⁻¹	μm	Pure	CDA
NH ₃	NH stretch	3,376	2.96	–	–
	NH deformation	1,624	6.16	–	–
	Umbrella	1,070	9.35	0.139	0
NH ₄ ⁺	NH stretch	3,206	3.12	–	–
	NH stretch	3,074	3.25	–	–
	NH sym. bending	1,478	6.77	0.099	0.039
HCN		3,074	3.25	–	–
		1,624	6.16	–	–
CN ⁻	CN stretch	2,083	4.80	0.078	0
CO ₂	OCO asym. stretch	2,342	2,342	0.048	0.034
	bending	656	15.24	–	–
HNCO	NH stretch	3,365–3,220	2.97–3.11	–	–
	NCO asym. stretch	2,260	4.42	0.024	0.008
N ₂ O	NN stretch	2,238	4.47	–	–
OCN ⁻	OCN asym. stretch	2,165	4.62	0.176	0.083
CO	CO stretch	2,140	4.67	0.124	0.013
SiH	SiH stretch	1,997	5.01	–	–

feature appearing as a shoulder at about $2,238\text{ cm}^{-1}$ is attributable to N_2O . Evidence of isocyanic acid (HNCO) formation is given by the presence of the band at $2,260\text{ cm}^{-1}$. Particularly of interest for astrobiology is the synthesis of ammonium cyanate complex $\text{NH}_4^+\text{OCN}^-$ evidenced by the presence of an intense band at $2,165\text{ cm}^{-1}$ assigned to asymmetric stretching vibration of cyanate anion OCN^- and of the bands at $1,478$, $3,074$, $3,206\text{ cm}^{-1}$ due to NH_4^+ .

Implantation in the silicon substrate of protons that have passed through the sample is showed by the band at $1,997\text{ cm}^{-1}$.

The fraction of synthesized molecules with respect to the number of formamide molecules destroyed by proton irradiation is reported in Table II. The surface density number of molecules observed were calculated by measuring the integrated areas of infrared bands and using the respective absorbances. In the case of irradiated formamide deposited on olivine CDA, it is evident the missing of bands at $1,116$ and $2,082\text{ cm}^{-1}$ of NH_3 and CN^- , respectively.

Discussion

Dust is ubiquitous in space and it plays a catalytic role in astrochemistry. Most of the molecules observed in the interstellar medium (e.g. H_2 , H_2O , CO_2 , CH_3OH , etc.) might be formed on the dust grains. Low temperatures (less than 20 K) of molecular clouds favor the adsorption of atoms or radicals from the gas phase. These species, after diffusion on grain surface, might react yielding new molecular species, with grain acting as third body absorbing part of the formation energy. The formation of formamide on grain surfaces was theoretically calculated starting by the reaction of CO with H . The resulting radical HCO can react with atomic O , N and C to ultimately lead to NH_2COH . Grain surface chemistry calculations predict abundances of the order of 1% for a wide range of environmental conditions (Tielens and Hagen 1982). Low energy cosmic rays irradiate grains in the interstellar medium with different fluxes that were estimated by Moore (1999). In cold dense clouds, ions deposit about 30 eV/molecule in 10^8 years, which is a factor of 10 less than in the diffuse medium. Usually, laboratory experiments of ion irradiation of ices have been used to evaluate the amount of synthesized species expected in space. In Table II the fraction of species produced in our experiments with respect to formamide molecules lost by proton irradiation are reported. The first result obtained by comparing the irradiation experiments of pure formamide and mixed with CDA is that the presence of dust grains reduces the overall amount of synthesized species. This could be an effect related to larger surface of CDAs exposed to proton irradiation, which might favor a larger ejection of formamide in the gas phase. Local enhancement of temperature due to low thermal conductivity of CDA could be responsible for sublimation of extremely volatile CO molecules. This could justify the decreasing of about 10 times of carbon monoxide formed when CDA is present. In addition to physical mechanisms, olivine CDA acts chemically on the synthesis process of molecular species, as it is possible to note from Figure 1 and Table II. In particular, NH_3 and CN^- molecules are absent when olivine CDA is present. In the latter case, this could be related to the charge exchange due to presence of iron and magnesium metals in CDA and acid–base reaction of ammonia with HNCO favored. In Table II an overall decreasing of molecules is observed if CDAs are present. This result indicates a specificity of olivine in driving the chemistry in solid phase under ion irradiation. Considering that no different molecules are synthesized in solid phase with

CDA but those observed irradiating pure formamide, a larger molecular yield in gas phase is expected when fluffy core silicates covered with icy mantles are ion irradiated.

More important is the case of ammonium cyanate for its considerable theoretical importance in prebiotic chemistry. Thermal annealing of ammonium cyanate in aqueous solution forms urea $(\text{NH}_2)_2\text{CO}$ through dissociation into ammonia and isocyanic acid (Warner and Stitt 1933). Urea was also synthesized at 10 K by UV irradiation of isocyanic acid and tentatively detected in protostellar object (Raunier et al. 2004). As observed by Brucato et al. (2006), ammonium cyanate synthesized by proton irradiation of pure formamide at 20 K is stable up to room temperature. Then ammonium cyanate and formamide could have an important linking role between astrophysical and terrestrial environmental conditions.

Normalizing the abundances reported in Table II to that of more intense OCN^- , the ion NH_4^+ is observed under abundant of about 7% in experiments with CDA. Only for the CO_2 case a larger production of about 14% is observed in presence of olivine dust.

In this work we have demonstrated, for the first time, that laboratory cosmic dust analogue of amorphous silicate condensates of olivine composition has important effects on molecular synthesis at cryogenic temperature under ion irradiation of formamide. Specifically, MgFeSiO_4 amorphous olivine is a selective catalyst preventing formation of NH_3 and CN^- molecules and changing the relative abundances of $\text{NH}_4^+\text{OCN}^-$, CO_2 , HNCO , CO . Here we have demonstrated that the role of CDAs has to be taken in account in simulation experiment. CDAs significantly influences the chemistry of formation and evolution of ices in space under irradiation processing at low temperatures. Primitive dust condensate as typically observed in the expanding envelopes of evolved stars, in interstellar medium or in the proto solar nebulae are extremely interesting catalysts for prebiotic chemistry occurring in the gas phase (Hill and Nuth 2003), in liquid phase (Saladino et al. 2005) and, promisingly, in the solid phase.

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