Lyα irradiation of solid-state formamide

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ABSTRACT

Context. Formamide (NH₂CHO), a potential prebiotic precursor, has been proposed to play an important role in the context of origin of life on our planet. It has been observed in different environments in space including the protostellar regions and comets. The abundance and stability of NH₂CHO in the early stages of star formation can be better understood by incorporating the formation and destruction data in the astrochemical models.

Aims. We carried out an experimental investigation to study the destruction of pure NH₂CHO ice at 12 K by the interaction of Lyα (121.6 nm) photons.

Methods. The UV photo destruction of NH₂CHO was studied using Fourier-transform infrared spectroscopy.

Results. After UV processing, the intensity of NH₂CHO IR bands decreases and new bands corresponding to HCN, CO, NH₃, OCN⁻, HNCO, and CO₂ appeared in the spectrum. Destruction and cumulative product formation cross-sections were derived.

Conclusions. The comparison of destruction rate derived from the cross-section in cold and dense molecular cloud for diatomic centres, star-forming regions and comets [e.g. (Blake et al. 2012; Ferus et al. 2015; Botta et al. 2018)]. Moreover, it has been observed in many astrophysical environments such as galactic centres, star-forming regions and comets [e.g. (Blake et al. 1986; Turner 1991; Bisschop et al. 2007; Mendoza et al. 2014; López-Sepulcre et al. 2015; Bockelée-Morvan et al. 2000; Biver et al. 2014; Goesmann et al. 2015)]. In fact, mass spectrometric analysis by Cometary Sampling And Composition (COSAC) aboard Rosetta’s Philae lander on comet 67P/Churyumov–Gerasimenko, revealed that NH₂CHO [1.8% with respect to water (H₂O)] is the second most abundant molecule after H₂O (Goesmann et al. 2015; Altwege et al. 2017). Solid state NH₂CHO has also been identified tentatively in the interstellar medium by Infrared Space Observatory towards NGC 7538 IRS9 and W33A (Raunier et al. 2004; Gibb et al. 2004).

Based on experimental and theoretical studies, NH₂CHO has been proposed to be formed in space by a series of ion-molecule and neutral-neutral reaction channels in the gas phase whereas solid NH₂CHO could be formed via processing of interstellar ices on dust grain surface by electrons, ions, ultraviolet (UV) photons, heat and H atoms (López-Sepulcre et al. 2019 references therein). Once formed, NH₂CHO can undergo further processing both in the gas or solid phase to form simple and complex organic molecules. As a result, the abundance of NH₂CHO in a certain space environment will depend both on the formation and destruction channels. Therefore, understanding the destruction channels of NH₂CHO under energetic and non-energetic processing has been the subject of numerous studies.

Quantum mechanical calculations on the thermal decomposition of NH₂CHO revealed three main reaction channels (Nguyen et al. 2011). In decreasing order of kinetically favoured pathway, they are dehydration [H₂O loss to hydrogen cyanide (HCN)], decarbonylation [carbon monoxide (CO) loss to ammonia (NH₃)] and dehydrogenation [hydrogen (H₂) loss to isocyanic acid (HNO)]. High energy laser spark induces the decomposition of NH₂CHO gas to HCN, CO, NH₃, carbon dioxide (CO₂), nitrous oxide (N₂O), hydroxylamine (HN₃OH), and methanol (CH₃OH) which was identified by infrared (IR) spectroscopy (Ferus et al. 2013). NH₂CHO decomposition in matrices also leads to similar products as observed in the gas phase reactions (Lundell et al. 1998; Maier & Endres 2000; Duvernay et al. 2005). Only limited studies have been dedicated to investigate the destruction of NH₂CHO in the condensed phase. Ion irradiation experiments with 200 keV H⁺ were performed on NH₂CHO films deposited on inert silicon and olivine substrate (Brucato et al. 2006). IR analysis showed the formation of CO, CO₂, NH₃, N₂O, HCN, cyanide ion (CN⁻), ammonium ion (NH₄⁺), isocyanate ion (OCN⁻) and isocyanic acid (HNCO) on silicon whereas all the other products except CN⁻ and NH₃ were formed on the olivine surface. In a different set of experiments, pure NH₂CHO films show no significant degradation upon processing by UV-enhanced xenon lamp, whereas oxide minerals titanium dioxide (TiO₂) and spinel (MgAl₂O₄)

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used as substrate induce a gradual but minimal degradation (Corazzi et al. 2020). On the other hand, Lyman (Ly) photons and 1 keV electrons bombardment of amorphous or crystalline NH$_2$CHO film deposited on silica (SiO$_2$) nanopowder at 70 K revealed only OCN$^-$ and CO (Dawley et al. 2014a).

Very recently, two independent investigations were made to study the reaction of H atoms on NH$_2$CHO ice (Haupa et al. 2019, Suhasaria & Mennella 2020). HNCO was formed through H-abstraction reactions via a H$_2$NCO radical intermediate when NH$_2$CHO was subjected to H atoms in the para-hydrogen quantum-solid matrix host (Haupa et al. 2019). NH$_2$CHO at 12 K exposed to H atoms was studied to estimate the effective destruction cross-section. This quantity was used to evaluate the destruction rate of NH$_2$CHO by H atoms in space and compared with the destructive effects of cosmic rays and UV photons. However, the absence of destruction cross-section for NH$_2$CHO under Ly$\alpha$ (10.2 eV) photons only allowed the estimation of an upper limit for the destruction rate under interstellar medium conditions. The present study reports the results of the interaction of Ly$\alpha$ with pure NH$_2$CHO ice film at 12 K. The NH$_2$CHO destruction and new products formed after UV irradiation have been studied by Fourier-transform infrared (FTIR) spectroscopy. The destruction cross-section for NH$_2$CHO and the cumulative formation cross-section for the formed new species have been obtained. The determination of the destruction cross-section has then allowed us to compare the destructive effects of H atoms, cosmic rays and UV photons on pure solid NH$_2$CHO in dense interstellar cloud conditions.

2. Experimental methods

Experiments were performed in a high vacuum chamber, which is described in detail in previous works (Mennella et al. 2006, Suhasaria & Mennella 2020). The salient features of the set-up relevant to this work are briefly described here. The main chamber, with a base pressure better than 10$^{-8}$ mbar, is equipped with a closed-cycle helium cryostat and a dosing unit. A cesium iodide (CsI) substrate was mounted on the cold finger of the cryostat such that the substrate can be cooled down to 12 K. The cryostat is described in detail in previous works (Mennella et al. 2006). The UV beam forms an angle of 22.5$^\circ$ with the normal to the surface plane and the NH$_2$CHO ice density 0.937 g cm$^{-3}$ derived by Brucato et al. (2006a, 2006b). The NH$_2$CHO ice film was depleted. At the same time, several new bands corresponding to a hot OCN$^-$ with a pressure better than 10$^{-15}$ mbar, is also the present study reports the results of the interaction of Ly$\alpha$ with pure NH$_2$CHO ice film at 12 K. The NH$_2$CHO destruction and new products formed after UV irradiation have been studied by Fourier-transform infrared (FTIR) spectroscopy. The destruction cross-section for NH$_2$CHO and the cumulative formation cross-section for the formed new species have been obtained. The determination of the destruction cross-section has then allowed us to compare the destructive effects of H atoms, cosmic rays and UV photons on pure solid NH$_2$CHO in dense interstellar cloud conditions.

3. Results and Discussion

3.1. Ice growth

The IR spectrum of pure solid NH$_2$CHO at 12 K is displayed in Fig. 1 and the corresponding fundamental vibration modes reported in Table 1 are in good agreement with previous results (Brucato et al. 2006a, Suhasaria & Mennella 2020). The NH$_2$CHO ice film thickness was derived separately from the column density of combined symmetric and antisymmetric N-H, C-H and C=O stretching IR modes using the band strengths values listed in Table 1. The average value, expressed in units of monolayer (1 ML = 10$^{-12}$ molecules cm$^{-2}$), is 29.5 ML which is equivalent to 0.03 $\mu$m. For the thickness determination, we took into account the cosine of the angle between the IR beam and the normal to the surface plane and the NH$_2$CHO films (Gingell et al. 1997) are set in ordinate by d$_{UV}$ = 1/1 = 1/1σ where σ is the UV photon-absorption cross-section of NH$_2$CHO and $n$ is the number of NH$_2$CHO molecules per unit volume. In the absence of direct measurements of the UV absorption cross-section for NH$_2$CHO ice, the gas phase value of ca. 2 × 10$^{-17}$ cm$^2$ (Gingell et al. 1997) acquired at 10.2 eV photons is taken into the calculation.

3.2. UV irradiation of NH$_2$CHO

Figure 1 also presents the IR spectrum of NH$_2$CHO ice after exposure to UV photon fluence of 6.5 × 10$^{18}$ photons cm$^{-2}$. The intensity decrease of the NH$_2$CHO IR bands indicates that the NH$_2$CHO ice was depleted. At the same time, several new bands appear in the spectrum. The most intense band at 2341 cm$^{-1}$
band is due to the asymmetric stretch mode of CO$_2$. The second most intense band at 2163 cm$^{-1}$ shows a good agreement with the expected frequency of the N=O asymmetric stretching mode of OCN$^-$ (Gerakines et al. 2004). The counter ion N$_2$H$^+$ was clearly identified from the very broad N-H IR bending mode feature around 1483 cm$^{-1}$ (Raunier et al. 2004a). Further evidence for the presence of N$_2$H$^+$ ion comes from the broad features at 3210 and 3065 cm$^{-1}$ overlapping with formamide N-H stretching modes. These peaks are in close agreement with the NH$_2$ peaks at 3206 and 3074 cm$^{-1}$ assigned previously by Brucato et al. (2006a).

At 2138 cm$^{-1}$ there is the symmetric stretch feature of CO which appears as a shoulder to the OCN$^-$ peak. The band observed at 2259 cm$^{-1}$ and a shoulder peak at the lower wavenumber side, centred around 2240 cm$^{-1}$, were assigned to the N=C=O asymmetric stretching mode of HNCO (Raunier et al. 2004a). Furthermore, a shoulder peak at the higher wavenumber side of the 2259 cm$^{-1}$ band, centred around 2277 cm$^{-1}$, is attributed to $^{13}$CO (Modica & Palumbo 2010). Within the errors, the natural abundance ratio of $^{13}$C/$^{12}$C = 0.011 is in agreement with the band area ratio of $^{13}$CO/$^{12}$CO = 0.015. A peak around 2100 cm$^{-1}$ has been assigned previously to the C=O stretching mode of HCN (Brucato et al. 2006a). The 2100 cm$^{-1}$ band is the second strongest IR band of pure solid HCN ice after 3115 cm$^{-1}$ (Couturier-Tamburelli et al. 2013), which has not been identified in the present experiment but could be obscured by the broad stretching band of N-H in NH$_2$CHO. NH$_3$ has also been tentatively identified after UV irradiation from the band present at 3375 cm$^{-1}$ due to N-H stretching based on the assignment by Brucato et al. (2006a).

The evolution of column density of newly formed photo products normalised to the initial column density of NH$_2$CHO...
The band strength values used in the calculation of the individual column densities of the photo products are also listed in Table 1. Some photo products displayed similar behaviour while others behave very differently with the increasing $F_{\text{UV}}$. CO, OCN$^-$ and HNCO are formed immediately and rapidly at the beginning of the UV photolysis followed by slowing down and plateau within the error at UV fluence of about $4 \times 10^{18}$ photons cm$^{-2}$. As the $F_{\text{UV}}$ increases further, there is a decrease in the formation of all the three species. The formation of CO, OCN$^-$ and HNCO after UV irradiation of deposited NH$_2$CHO followed by a decrease in their intensity at the highest fluence is also clearly visible in the difference IR spectra in Fig. 4. On the other hand, HCN shows a delayed formation with respect to CO, OCN$^-$ and HNCO. HCN appears only after UV photon fluence of $1.4 \times 10^{18}$ photons cm$^{-2}$, but then the abundance increases rapidly and the normalised column densities are close to that of CO and OCN$^-$. Within the error, there is no apparent sign of the decrease in HCN formation at high fluences, as evident in Fig. 4 and Fig. 3. In the case of CO$_2$, there is an initial phase of slow formation with increasing $F_{\text{UV}}$ and only after UV fluence of $1.9 \times 10^{18}$ photons cm$^{-2}$, CO$_2$ starts to increase rapidly. One can clearly see in the Fig. 4 that CO$_2$ intensity at the highest UV fluence increases with respect to that at $1.9 \times 10^{18}$ photons cm$^{-2}$.

It is difficult to fit the abundance evolution of individual products over the entire UV fluence range by a single kinetic equation, due to the simultaneous formation and depletion behaviour. Therefore, following Chuang et al. (2021) a single first order kinetic relation was fitted to the cumulative abundance of all the photo products ($\chi(t)$):

$$\chi(t) = a_2(1 - e^{-\sigma_{\chi}F_{\text{UV}}})$$  \hspace{1cm} (2)

where, $\sigma_\chi$ is the formation cross-section and $a_2$ is the asymptotic formation. Fits to the experimental data allowed us to estimate the effective formation cross-section, $\sigma_1 = 7.8 \pm 0.6 \times 10^{-19}$ cm$^2$ and the asymptotic value, $a_2 = 0.76 \pm 0.02$ for the products formation. The asymptotic value of total products formation with respect to the initial formamide column density exactly matches the average formamide destruction of 0.77. Of course, there could be other minor species produced in the irradiation experiment that have not clearly been identified by IR spectroscopy.

In the Ly$\alpha$ processing reactions of pure NH$_2$CHO ice deposited on SiO$_2$ nanopowder, cross-sections $\sigma_{f,CO} = 3.9 \times 10^{-20}$...
and $\sigma_{f,\text{OCN}^-} = 3.6 \times 10^{-20}$ cm$^2$ were estimated for the formation of CO and OCN$^-$, respectively (Dawley et al. 2014a). Furthermore, in our previous study (Suhasaria & Mennella 2020) we estimated the effective formation cross-section of HNCO due to H atoms exposure of formamide to be $\sigma_{f,\text{HNCO}} = 4.4 \times 10^{-17}$ cm$^2$. Therefore, for the sake of comparison, we tried to fit only the individual growth curves of CO, OCN$^-$ and HNCO up to the UV fluence of $3.7 \times 10^{18}$ photons cm$^{-2}$ using the same exponential equation as used for the cumulative growth. We derived the formation cross-sections of $\sigma_{f,\text{CO}} = 1.5 \pm 0.1 \times 10^{-18}$, $\sigma_{f,\text{OCN}^-} = 1 \pm 0.1 \times 10^{-18}$ and $\sigma_{f,\text{HNCO}} = 4.2 \pm 0.5 \times 10^{-18}$ cm$^2$ for CO, OCN$^-$ and HNCO, respectively. The CO and OCN$^-$ formation cross-sections are two orders of magnitude higher than those estimated by Dawley et al. (2014a). The above two experiments differ in surface temperature and the surface type that impacts the formation cross-section. Out of the two, the primary impact would be of the surface temperature since there is an increase in the radical recombination efficiency with temperature as radicals diffuse faster within the ice. This would result in lower formation of CO and OCN$^-$ from NH$_2$CHO at higher surface temperature. On the other hand, the impact of SiO$_2$ nanoparticle surface could be less relevant since 600 ML thick ice was deposited on top of the surface for UV irradiation experiment. The HNCO formation cross-section that we derived in this experiment is an order of magnitude lower than that obtained previously by the exposure of H atoms on formamide (Suhasaria & Mennella 2020). The lower value of the HNCO formation cross-section can be taken as an indirect measure of the lesser stability of formamide under H atoms exposure compared to UV photons.

In Fig. 3 we see that growth curves of all the photo products except CO$_2$ resembles a first order kinetic behaviour, except for the very high fluences, which means they must be formed directly from NH$_2$CHO. CO$_2$ could have been formed by the effect of UV photons on CO and H$_2$O molecules formed in the reaction network (Watanabe & Kouchi 2002). This may explain why CO$_2$ formation rate is low at the initial fluences and increases only when more CO is produced in the ice mixture. At the highest UV fluence, there is not only a small decrease in the intensity of NH$_2$CHO but also of all the newly formed photo products except CO$_2$ and HCN. This suggests that in addition to NH$_2$CHO, there is processing of those species produced in the ice mixture at the highest fluence, hinting at a complex reaction network in
Table 2. Destruction cross-sections of NH$_2$CHO under different energetic processing and the corresponding rates in the dense interstellar clouds.

| Processing          | Destruction cross-section $\sigma_d$, (cm$^2$) | Flux $\Phi$, (cm$^{-2}$ s$^{-1}$) | Destruction rate $R_d$, (s$^{-1}$) |
|---------------------|-----------------------------------------------|----------------------------------|----------------------------------|
| UV photons          | $1.9 \pm 0.2 \times 10^{-18}$                | $4.8 \times 10^{12}$            | $9.1 \times 10^{-13}$            |
| H atoms             | $3.0 \pm 0.6 \times 10^{-17}$                | $9.1 \times 10^{14}$            | $2.7 \times 10^{-12}$            |
| Cosmic rays         | $3.7 \pm 0.4 \times 10^{-16d}$              |                                            | $3.7 \times 10^{-16}$            |

Notes. $^{(*)}$ Suhasaria & Mennella (2021) $^{(b)}$ Mennella (2006) $^{(c)}$ corresponds to 10 eV photons Mennella et al. (2003) $^{(d)}$ corresponds to 1 MeV protons under monoenergetic approximation (G. A. Baratta & M. E. Palumbo, 2020, priv. comm.) $^{(e)}$ Mennella et al. (2003)

Fig. 4. Difference IR spectrum of NH$_2$CHO after UV irradiation of: (a) $1.9\times10^{18}$ photons cm$^{-2}$ with the ice as deposited; (b) $1.9\times10^{18}$ with 6.5$\times10^{16}$ photons cm$^{-2}$.

Three specific routes were suggested for the formation of OCN$^-$ in the condensed phase from the UV irradiation of NH$_2$CHO ice (Dawley et al. 2014a). First is a direct photodissociation followed by ionisation reaction, second is direct ionisation followed by ion-electron recombination and electron capture, and third is a direct dissociative electron attachment (preceded by a direct excitation in formamide, indicated by an asterix).

$$\text{NH}_2\text{CHO} \xrightarrow{\nu} \text{OCN}^- + \text{H}_2 + \text{H}^+$$

(6)

$$\text{NH}_2\text{CHO} \xrightarrow{\nu} \text{NH}_2\text{CHO}^+ \rightarrow \text{OCN}^- + \text{H}_2$$

(7)

$$\text{e}^- + \text{NH}_2\text{CHO} \rightarrow (\text{HNCHOH})^{+*} \rightarrow \text{OCN}^- + \text{H}_2 + \text{H}$$

(8)

Since we can not rule out any possibilities, any of the three or all three reactions could potentially yield OCN$^-$ in our study.

4. Astrophysical implications

Solid state abundances of NH$_2$CHO molecule can be predicted from gas-grain chemical models only when a complete picture of its formation and destruction under different conditions are taken into account. The knowledge of the corresponding rates, related to the cross-sections, is therefore necessary. Formamide ice could most likely be present in the dense interstellar cloud conditions not in pure form but mixed with water or other interstellar ice components. However, formamide is more refractory than water or other volatiles which means small quantities of pure formamide ice could exist in elevated grain temperatures. In addition, to determine the extent of destruction under various energetic processing agents and to compare their effects we have considered here a pure ice as previously done. Dawley et al. (2014a) showed that H$_2$O plays a catalytic role by increasing the product formation when H$_2$O mixed NH$_2$CHO ice is exposed to Ly$\alpha$ photons. However, the impact of other volatiles is still unknown and would require dedicated experiments to gain further insight.

In fact, in our previous study we derived the effective destruction cross-section, $\sigma_{d,H} = 3.0 \pm 0.6 \times 10^{-17}$ cm$^2$ for pure NH$_2$CHO due to thermal H atoms exposure. This was found to be an order of magnitude lower than that derived for the destruction of formamide by 200 keV H$^+$, simulating the effects of cosmic rays. Under the approximation of monoenergetic 1 MeV protons, a value of $\sigma_{d,1\text{MeV}} = 3.7 \pm 0.4 \times 10^{-16}$ cm$^2$, was derived (G. A. Baratta & M. E. Palumbo, 2020, priv. comm.). Furthermore, due to the lack of experimentally derived NH$_2$CHO destruction cross-section under Ly$\alpha$ (10.2 eV) photons, we made...
an assumption to derive only an upper limit value of the
destruction cross-section, \( \sigma_{\text{d,UV}} = 7.5 \times 10^{-16} \text{ cm}^2 \). We argued that
high energy protons would induce multiple bond breaking in the
molecules along the “hot track”\(^1\) compared to a single photoly-
sis step by Ly\(\alpha\) photons and therefore the UV destruction cross-
section should be lower than that for energetic protons. In agree-
ment with the above argument, we found that UV destruction
cross-section of formamide, \( \sigma_{\text{d,UV}} = 1.9 \pm 0.2 \times 10^{-18} \text{ cm}^2 \), esti-
\( mated \) in the present work is two orders of magnitude lower than
that obtained for energetic protons. Moreover, \( \sigma_{\text{d,UV}} \) is about ten
times lower than \( \sigma_{\text{d,H}} \), the destruction cross-section by H atoms
(see Table 2).

The derivation of the cross-section further allowed to evalu-
ate the NH\(_2\)CHO destruction rate under UV photons in dense
clouds and compare it with the destruction rates induced by H
atoms and cosmic rays. In the dense cloud cores, formamide ice
should be shielded from the external UV radiation but there are
locally produced UV rays resulting from cosmic-rays in-
duced ionisation of hydrogen. The energy of the UV photons
that impinges on the interior of dense clouds resembles the Ly\(\alpha\).
Taking into account the UV photons flux of \( 4.8 \times 10^3 \text{ cm}^{-2} \text{ s}^{-1} \)\(^2\)
Mennella et al. [2003] in those environments, the destruction rate,
\( R_3 = 9.1 \times 10^{-15} \text{ s}^{-1} \) was obtained. Although this rate was
found to be an order of magnitude higher than the cosmic rays,
the rate was three orders of magnitude lower than that induced by
H atoms. This means that H atoms induce the higher destruc-
tion efficiency in formamide compared to UV photons or cosmic
rays in those environments. The destruction rates for formamide
under different energetic processing are also tabulated in Table 2.

5. Conclusions

This experimental study of Ly\(\alpha\) irradiation of NH\(_2\)CHO ice at 12
K under high vacuum conditions was intended to understand its
photo stability under dense cloud conditions. The UV photolysis
results in the formation of new products CO, NH\(_2\), OCN\(^-\), HCN,
HNCO, and CO\(_2\) which were identified by FTIR spectroscopy.
The formation mechanism of other photo products were also dis-
cussed. The destruction of N-H, C-H and C=O functional groups
in NH\(_2\)CHO occurred in a single step unlike the case of H atoms
bombardment as examined in our previous study. For the first
time, the Ly\(\alpha\) destruction cross-section of NH\(_2\)CHO and the cum-
ulative formation cross-section of different photo products are
estimated. The comparison of the destruction rate of NH\(_2\)CHO in
dense clouds obtained in the present work with those induced by
other processing indicates that H atoms interaction remains
the driving mechanism for the destruction of this molecule in
those environments.

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