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Synthesis of urea in cometary model ices and implications for Comet 67P/Churyumov–Gerasimenko[†]

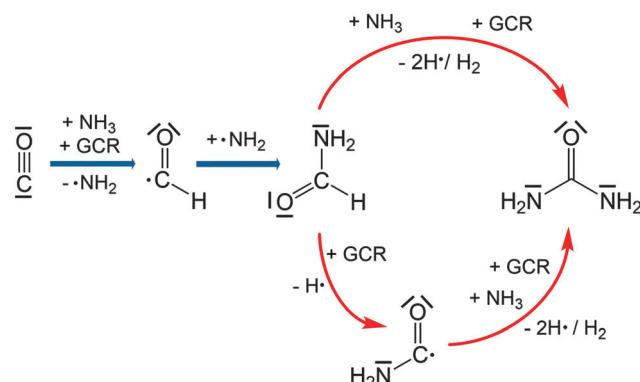
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Urea is considered a fundamental building block in prebiotic chemistry. Its formation on early Earth has not yet been explained satisfactorily and exogenous delivery has been considered. We report on the synthesis along with the first online and *in situ* identification of urea after exposing inorganic ices to ionizing radiation.

Urea is considered to be a key molecule to the ‘Origin of Life’ question,¹ and it is contemplated as a key reactant in prebiotic phosphorylation reactions² and in the prebiotic synthesis of the pyrimidine bases cytosine and uracil, which are present in deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) in all known living organisms.³ Various possibilities of an endogeneous formation of urea exist and have been discussed extensively.^{4–8} The key difficulty in a purely endogeneous formation of urea is connected to the seemingly low concentration of cyanates in the oceans of early Earth⁵ as well as to the limited stability of cyanates at pH values lower than 6 thus hydrolyzing cyanates to hydrogen cyanide over geological time scales.⁹ The detection of urea along with amino acids and nucleobases in the Murchison meteorite¹⁰ lets us expect that an interstellar origin of at least some of the urea on early Earth should also be considered. The abiotic processes contributing to the synthesis of urea in extraterrestrial environments have remained elusive to date. Accounting for data from the infrared space observatory, Spitzer, both carbon monoxide and ammonia were detected on ice-coated interstellar grains at levels of typically 20% and 5%, respectively, with thicknesses of a few hundreds of nanometers.^{11–13} Molecular clouds consist of carbon- and/or silicate-bearing grains of nanometer size at temperatures as low as 10 K accreting icy

layers including carbon monoxide and ammonia.^{14–16} These ice compositions can vary with the temperature of the environments as demonstrated, for instance, for carbon monoxide, whose abundance can vary from 3% to 50%.^{13,17,18} Through energetic GCRs and the internal ultraviolet field, these ices are chemically altered leading to the synthesis of complex organic molecules.^{19–22} In star forming regions, this matter enters circumstellar disks, where formation of planetary bodies and comets takes place, thus providing the material for meteoritic parent bodies.²³ Isotopic studies let us expect that the organic material found in carbonaceous chondrites, such as Murchison, comprises of a significant fraction of pristine interstellar organic matter.²⁴ Hence organics such as urea can be included into meteoritic parent bodies such as comets.^{25,26}

Here, we show in laboratory experiments on model ices of ammonia and carbon monoxide with a molecular ratio of 4:1 and a thickness of 500 ± 50 nm that urea can be formed abiotically along with formamide (HCONH_2) by exposing low-temperature interstellar and cometary ices such as those recently detected on Comet 67P/Churyumov–Gerasimenko²⁷ to



Scheme 1 Schematic representation of synthetic pathways to urea via formamide in carbon monoxide and ammonia seeded ices via galactic cosmic ray (GCR) exposure.

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ionizing radiation in the form of energetic electrons (5 keV) as produced in the track of galactic cosmic ray (GCR) particles (Scheme 1; and ESI†).

Our experiments were designed to extract reaction pathways to synthesize urea upon subjecting ices in deep space consisting of carbon monoxide and ammonia to ionizing radiation. During radiation exposure, several new infrared absorption features emerged (Fig. S1 and Table S2, ESI†).²⁸ The isocyanate ion (OCN^-) could be assigned *via* its ν_3 fundamental at 2150 cm^{-1} ^{28,29}. Formaldehyde (H_2CO) was identified through the ν_2 and ν_3 fundamentals at 1740 cm^{-1} and 1510 cm^{-1} , respectively.²⁸⁻³⁰ The carbonyl stretching (ν_4) at 1695 cm^{-1} was attributed to formamide.^{29,31} The ammonium cation (NH_4^+) was observed *via* the ν_4 mode at 1505 cm^{-1} .³² Additionally, a broad absorption from 1200 to 1050 cm^{-1} might originate from the $-\text{NH}_2$ moiety of urea (ν_5 rocking³³), but also from $-\text{NH}$ bending and rocking modes of amines and imides including the *cis*- and *trans*-formylhydrazine isomers (HCON_2H_3) (Fig. 1).³⁴ Finally, the carbonyl functional group can be linked to broad absorption from 1750 to 1660 cm^{-1} . After irradiation, the temperature was increased to 300 K with a rate of 0.5 K min^{-1} . As the temperature increases, the intensities of absorptions associated with OCN^- , HCONH_2 , H_2CO , and NH_4^+ decrease until vanishing at 260 K . However, after the sublimation of the ammonia reactant molecules is completed, the intensity of the 1150 to 1050 cm^{-1} absorbance levels off at an intensity of about 10% of its initial value suggesting that not all species leading to an infrared absorption in this wavelength regime sublime (Fig. S1, ESI†). These considerations make it clear that an identification of urea with infrared spectroscopy is problematic. Therefore, in order to obtain more detailed results we exploit fragment free single photon ionization coupled with reflectron time-of-flight (ReTOF-PI) mass spectrometry to identify urea upon sublimation in the gas phase during the temperature programmed desorption (TPD).³⁵ The ionization energies of urea (9.6 eV , calculated) and of the *cis*- and *trans*-formylhydrazine isomers (8.2 eV and 8.6 eV , calculated, Fig. 1;

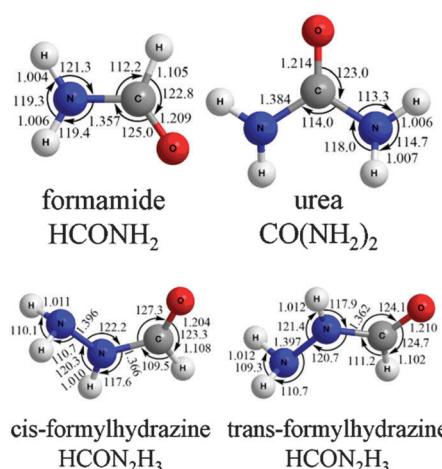


Fig. 1 Molecular structures of formamide and urea along with formylhydrazine isomers. Bond angles and bond lengths are given in degrees and angstrom, respectively. Calculation parameters are given in Table S3 (ESI†).

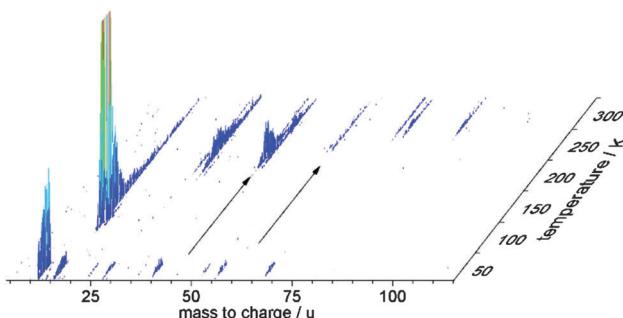


Fig. 2 Mass-to-charge dependent temperature programmed desorption (TPD) profiles obtained after photoionizing the desorbing molecules at 10.49 eV . The peak at 17 u (ammonia) was truncated to allow for better presentation. Masses 45 u and 60 u are indicated with arrows.

Table S3, ESI†) allow us to discriminate between them by conducting two separate experiments at different ionization energies. At 10.49 eV , urea and formylhydrazine are ionized while at 9.0 eV only formylhydrazine can yield a signal.

Fig. 2 displays the ReTOF mass spectra of the newly formed molecules recorded as a function of temperature after photoionization at 10.49 eV . The 9.0 eV spectra are shown in Fig. S2 (ESI†). The dominating signal stems from ammonia at $m/z = 17$. Carbon monoxide cannot be photoionized because it has an ionization energy of 14.01 eV . After ammonia desorbs, multiple species with higher mass-to-charge ratios are also observed. Most notably, at $m/z = 45$ and $m/z = 60$, we monitored ions which can be attributed to CONH_3^+ and CON_2H_4^+ , respectively. These stem from formamide as well as urea and/or *cis*- and *trans*-formylhydrazine, respectively. To discriminate between urea and/or formylhydrazine at $m/z = 60$, we lowered the photon energy below the ionization energy of urea (9.7 eV , experimental)³⁶ and stayed above the ionization energy of formylhydrazine. At photoionization of 9.0 eV no ions are observed at $m/z = 60$ (Fig. 3). This clearly shows that only urea is formed, but not its formylhydrazine isomer. Considering the similar polarities of formamide and urea and a molecular weight of urea higher by 15 u ($-\text{NH}-$) compared to formamide, the earlier onset of sublimation of formamide at 180 K compared to 200 K for urea is reasonable. Note that at room temperature (293 K) and standard pressure (760 Torr), urea exists as a solid. The vapor pressure of urea at 210 K is about $8 \times 10^{-12}\text{ Torr}$.³⁷ This partial pressure is within the detection limits of our systems.^{35,38} To conclude, the ReTOF-PI data provide compelling proof on the formation and sublimation of two molecules with an amide bond: urea and formamide.

Our results show that urea should be present in the interstellar medium as well. Once synthesized on icy grains, fractions of urea are expected to sublime upon evolution of the molecular cloud to star forming regions to be detected *via* rotational spectroscopy. Since the present experiments are used to synthesize not only urea, but also formamide, it is reasonable to suggest that both molecules should coexist in the gas phase if the temperature of the hot core is sufficient to sublime them. Considering that formamide has been firmly detected toward SgrB2(N) at fractional abundances relative to molecular hydrogen of a few 10^{-10} ,³⁹ urea should be

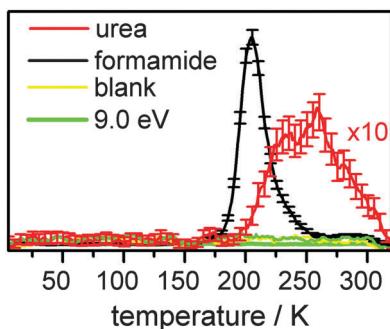


Fig. 3 The TPD traces of ions at mass-to-charge ratios of $m/z = 45$ and 60 obtained at photoionization energies of 10.49 eV (black, red, yellow) and 9.0 eV (green).

observable toward the same source. Very recently, Remijan *et al.*⁴⁰ conducted a multi-telescope search of interstellar urea toward the hot core SgrB2(N). Unfortunately, accounting for the spectral complexity of both urea and SgrB2(N), the authors only proposed a tentative identification of this molecule. Based on IR observations, urea and formamide have also been proposed to exist on icy grains toward the protostellar object NGC 7538 IRS9.⁴¹ As mentioned earlier, the temperatures and conditions of our ice and irradiation are simulating the conditions of icy grains in cold molecular clouds. Comet 67P/Churyumov-Gerasimenko originates from the Kuiper belt and was formed from (partly) this pre-solar system material. The recent discovery of formamide on 67P and its high abundance (the second most abundant molecule after water)²⁷ indicates that urea should be present on this comet as well.

We would like to address now potential formation pathways of urea in the irradiated ices (Scheme 1). The IR absorptions from urea and formamide overlap and the extraction of explicit formation mechanism information of urea is not possible. Nevertheless, we can still extract useful information from the infrared spectra. First, a potential formation pathway *via* the acid-base equilibrium $\text{NH}_4^+ + \text{OCN}^- \rightarrow \text{NH}_3 + \text{HNCO}$ followed by $\text{NH}_3 + \text{HNCO} \rightarrow \text{CO}(\text{NH}_2)_2$, the Wöhler synthesis,⁴² is unlikely, because we do not observe an increase of the intensity of any vibrational mode associated with urea while the intensities of the bands from ammonium and isocyanate decrease with temperature. Second, the only increase of intensity of the carbonyl stretching mode associated with urea is observed during the irradiation period. We therefore assume only radiation induced chemistry leading to urea. Based on the molecular structure of formamide and urea, the latter might be formed by inserting nitrene (NH) into the carbon–hydrogen bond of formamide. Third, an alternative pathway involves the formation of urea *via* the carbamyl radical (H_2NCO),⁷ beginning with the decomposition of ammonia to the amidogen radical ($\text{NH}_2(\text{X}^2\text{B}_1)$) plus atomic hydrogen. The amidogen radical was then proposed to add to the carbon–oxygen triple bond of the carbon monoxide reactant forming the carbamyl radical. However, laboratory studies by Jones *et al.* demonstrated that instead suprathermal hydrogen atoms add to carbon monoxide forming the formyl radical (HCO); a formation of the carbamyl

radical was not observed.²⁸ Therefore, we can conclude that due to the absence of the carbamyl radical, this third pathway is also unlikely. In conclusion, formamide might be the crucial precursor to eventually yield urea *via* insertion of nitrene (NH). A detailed study on the formation of formamide in similar ices is given in a previous publication.²⁸

Finally, we would like to discuss previous claims of identifications of urea in processed astrophysical model ices.^{29,43–45} Agarwal *et al.*⁴³ reported that they have detected urea by analyzing hydrolyzed residua of irradiated ices chromatographically. Grim *et al.*²⁹ used infrared spectroscopy and found ‘some evidence for traces of urea’. Nuevo *et al.* claimed a detection of urea in the residua of irradiated ices by gas chromatography after the residua were derivatized. Materese *et al.*⁴⁵ also believed to have sampled urea in the derivatized residua of irradiated ices along with over 5000 unidentified compounds. While we do not doubt that derivatized urea was monitored chromatographically, earlier off-line detections are doubtful. The main reason is that urea was probed after the residua were dissolved first (to remove them from the sample), then dried under vacuum and then dissolved again (for derivatization or HPLC analysis), all at room temperature or at elevated temperatures. During these steps, including solvents of different polarities, the solutes hydrolyze the organic residues and hence chemically modify the original residues.⁴⁶ Therefore, we have to conclude that the derivatized urea probed chromatographically could represent an artifact of the treatment (hydrolysis, thermolysis) of the residues sampled off line and *ex situ*. Furthermore, our experiments show that once formed, urea monomers sublime under vacuum conditions and should not be detectable; on the other hand, urea moieties chemically embedded in a complex polymeric residue can be hydrolyzed easily.

Summarizing, our online and *in situ* detection approach provides clear evidence that urea – a vital molecule with crucial relevance to astrobiology – can be easily synthesized upon interaction of anhydrous astrophysically relevant ices of carbon monoxide and ammonia upon exposure to energetic electrons formed in the track of galactic cosmic rays at ultralow temperatures as present on ice coated interstellar grains. Formed in the condensed phase *via* non-equilibrium chemistry, the subliming urea molecules were detected together with its formamide precursor in the gas phase. Our laboratory studies present a beginning to a systematic understanding of the formation of urea in astrophysically relevant ices and can be extended on several levels. These include the study of the effects of water incorporation into the model ices, the study of the effects of the radiation field and the study of possible mineral-catalyzed effects. These laboratory studies together with future astronomical searches for urea in the interstellar medium such as exploiting ALMA toward SgrB2(N) are extremely challenging but highly rewarding since they would reveal the formation pathways and also the distribution of urea in the interstellar medium thus providing vital clues on the availability of the building blocks of life on young planets including early Earth more than 4 billion years ago.

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