

Quantum Chemical Study of the Formation of Urea in Interstellar Medium

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ABSTRACT

Background: Many observational studies have found the presence of organic molecules in interstellar medium (ISM) via spectroscopy. NH_2CONH_2 (urea) was first detected in ISM in 2014. Containing two NH_2 groups, urea is an important biological molecule in metabolism as a carrier for waste nitrogen. The discovery of urea in ISM suggests the possibility of the formation of other biomolecules which contain peptide bonds, such as proteins. This supports the origin of life theory proposing that these biomolecules were initially formed in space and later arrived to Earth.

Methods: This study investigates two possible reaction pathways for the formation of protonated urea (urea H^+) in dense molecular clouds via molecules previously observed in the ISM, formamide (HCONH_2) and protonated hydroxylamine (NH_2OH_2^+). The thermodynamics and optimized geometries were calculated for the final steps of the formation of urea H^+ using Gaussian16 at the APFD/6-31G(d,p) level of theory and a transition state was confirmed.

Results: The overall mechanism, as well as the studied proton rearrangement of an intermediate to urea H^+ , were found to be exothermic and exergonic processes.

Conclusion: From the calculations, the conditions of ISM provide an adequate environment for the formation of urea H^+ and urea.

Keywords: Astrochemistry, interstellar medium, computational chemistry, origins of life

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INTRODUCTION

Over the past decade, various essential biomolecules have been detected in interstellar medium (ISM)^{3,5}. In 2014, the first tentative detection of urea (NH_2CONH_2) was observed, which affirmed the possibility of the formation of peptide bonds that constitute essential proteins in ISM¹. These discoveries suggest the origins of life began in space and were brought to Earth. Furthermore, it has been shown that the composition of amino acids and nitrile precursors found on meteorites matches that of prebiotic Earth in the Miller-Urey experiment².

The ISM is a unique environment that is split into multiple regions: diffuse clouds, translucent clouds, dense clouds, and hot molecular cores. Dense clouds, or cold clouds, are of interest because they contain a major portion of both atomic and molecular interstellar gas mass³. These regions have temperatures of only 10-15 K and number densities of $10^2 - 10^4$ atoms per cubic centimeter⁴. The main energy sources in these regions are ultraviolet (UV) light and cosmic rays that penetrate through the cloud and allow for the photodissociation of molecules⁵. While many reactions require too much energy to occur in ISM, there are viable pathways. Radio telescopes and infrared (IR) radiation have identified many biomolecules in ISM by detecting the rotational transitions in each molecule's emission^{6,7}. The detection of such biomolecules, however, is difficult due to complex IR stretching patterns that make characteristic bands hard to isolate. Furthermore, definitive detection of many complex organic molecules is difficult due to their low concentrations in ISM, which results in very weak signals⁸.

The recent detection of urea suggests the presence of other biomolecules in ISM, as its unique structure can enable the direct formation of peptides through N-C single bonds⁹. Urea also plays many critical roles in the maintenance of life; in many living organisms, urea facilitates the metabolism of nitrogen-containing compounds and the excretion of waste products through the urea cycle¹⁰. This metabolic cycle converts toxic ammonia to urea for excretion in the liver and kidneys. Urea is also used in the countercurrent exchange system that allows for the re-absorption of water and critical ions from urine in nephrons¹¹. Urea has been proposed as a possible precursor to the formation of cytosine and uracil, two essential DNA/RNA bases¹².

In this study, two possible reaction mechanisms for the formation of protonated urea (ureaH^+) through a formamide (HCONH_2) and protonated hydroxylamine (NH_2OH_2^+) reaction are proposed. This reaction is considered because earlier work eliminated many possibilities due to their respective energy barriers¹². In an example of protonated formamide and neutral hydroxylamine, the energy barrier was 78.7 kJ/mol¹².

Since there is no definitive precursor to urea, both proposed pathways occur as a continuation from an intermediate that can be easily formed from isocyanic acid (HNCO), protonated ammonia, and water. These three molecules are formed in the reaction between formamide and protonated hydroxylamine and have previously been detected in ISM^{6,13}. The intermediate, as proposed by Brigiano, Jeanvoine and Spezia, arises from a hydrogen abstraction of ammonia by isocyanic acid followed by a hydrogen migration, assisted by water¹². This molecule, isouronium (NHCOHNH_3^+), serves as the reactant for the two proposed reaction pathways for ureaH^+ .

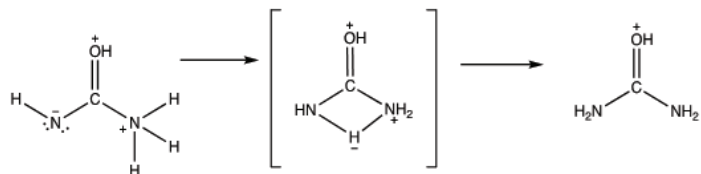


Figure 1 Proposed reaction 1 for the formation of ureaH^+ in dense molecular clouds in the gas phase through a hydride shift.

In reaction 1, the transition state arises from intramolecular attack on a hydrogen on the isouronium NH_3 . UreaH^+ is then achieved via a proton rearrangement.

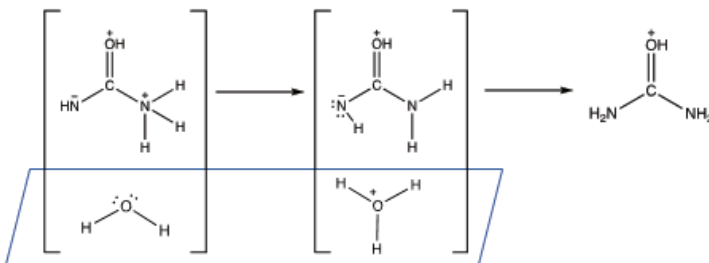


Figure 2 Proposed reaction 2 for the formation of ureaH^+ through a proton transfer on interstellar ice where water is present as a catalyst.

Reaction 2 often occurs on interstellar ice, which is highly abundant on dust grains in dense molecular clouds¹⁴. These ice are composed mainly of water and provide a rich chemistry conducive to the formation of biomolecules⁷. Furthermore, water lowers the activation energy of the reaction and serves as a catalyst by acting as a vehicle for hydrogen transport¹⁵. The reaction pathway proposed begins with a proton donation from isouronium to water to form a hydronium (H_3O^+). This is followed by a nucleophilic attack on the hydronium ion by one of the lone pairs on nitrogen. This produces ureaH^+ and water. As computational simulation of ice is difficult, a water molecule was used to mimic conditions in calculations.

METHODS

The optimization and thermodynamic calculations of each reaction mechanism was obtained with Gaussian16¹⁶ at the APFD¹⁷/6-31G(d,p)¹⁸ level of theory and visualized with GaussView¹⁹. Geometry optimizations and thermodynamic properties were calculated with a temperature of 15 K and a pressure of 0 atm. The total energy, Gibbs free energy, and enthalpy were analyzed relative to the reactant(s). A transition state was also confirmed.

RESULTS

The computed thermodynamic data of reaction 2 shown in figure 2 under conditions of ISM is shown in Table S8. The Gibbs free energy was used to analyze the stability of the individual molecules involved in the reaction and the viability of the overall reaction. The change in Gibbs free energy ($\Delta G_{\text{reaction}}$) was calculated to be -162.96 kJ/mol for the formation of ureaH⁺ at a temperature and pressure similar to that of dense molecular clouds, as shown in figure 3. Thermodynamic values for the transition states of reaction 1 were unable to be isolated. This suggests that the reaction is energetically unfavourable. The change in enthalpy ($\Delta H_{\text{reaction}}$) was calculated to be -162.96 kJ/mol for the formation of ureaH⁺ in dense molecular clouds in reaction 2. These properties suggest a release of energy that is very favourable in the ISM.

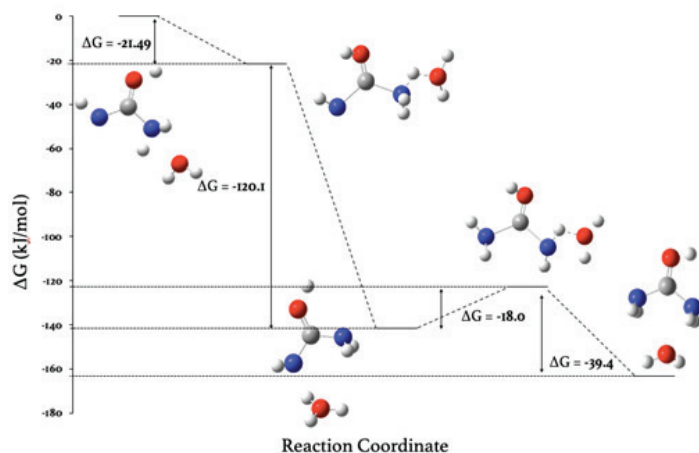


Figure 3 Changes in Gibbs free energy for reaction 2, with water as a catalyst, at a temperature of 15 K and pressure of 0 atm.

DISCUSSION

The stability of the product, ureaH⁺, and water relative to the reactant contribute greatly to the overall spontaneity of reaction 2. However, spontaneous formation suggests that there should be a large concentration or number of detections of urea in ISM, but that is not the case. Though the kinetics of the reactions cannot be directly calculated, it is reasonable

to assume that it is the source of this discrepancy. In experiments simulating conditions in dense molecular clouds, the rate constants were calculated to be approximately $10^{-9} \text{ cm}^3\text{s}^{-1}$ in order²⁰. Further, ion-neutral reaction rates can be limited simply by long-range attraction between reactants²⁰. Considering the relatively low concentrations of the isouronium species in ISM, it is likely that the overall rate of reaction is quite slow. This slow formation offsets the spontaneity of the reaction, accounting for the rare observation of urea in ISM.

The second transition state of reaction 2 has a small energy barrier of 18 kJ/mol that can be overcome by UV light or cosmic rays in ISM¹². In dense molecular clouds, the flux of the UV radiation field is $10^3 \text{ photons cm}^{-2} \text{ s}^{-1}$ and is largely dictated by cosmic ray particles⁷. In the gas phase, hydrogen in ISM absorb shorter wavelengths, leaving UV light of 13.59 eV ($2.23 \times 10^{-21} \text{ kJ}$) and below to photoionize molecules⁷. This energy is likely sufficient for the proposed reaction. On ice, UV light is absorbed within $0.05 \mu\text{m}$ while cosmic ray particles penetrate the dust grain and deposit up to 1 MeV, or $1.61 \times 10^{-16} \text{ kJ}$ ⁷. This energy is more than sufficient to break bonds in urea, which have a bond dissociation energy of approximately $2.22 \times 10^{-22} \text{ kJ}$ ⁸. Overall, reaction 2 is more viable in ISM than reaction 1 due to transition state energies.

The formation of ureaH⁺ may be impeded by competition between other products of formamide (HCONH_2) and protonated hydroxylamine (NH_2OH_2^+)¹². The formation of ureaH⁺ is only viable through the isouronium species used in both proposed reaction pathways, but isouronium is only one of many possible products of a formamide and hydroxylamine reaction. The energy barriers to most other products are too high for a reaction to occur in ISM, but two relevant reactions are proton transfers forming $\text{HCOHNH}_2^+ + \text{NH}_2\text{OH}$ or $\text{HCONH}_2 + \text{NH}_3\text{OH}^+$ ¹². Considering the first reaction, a study of the protonation of HCOHNH_2^+ with a hydrogen from NH_2OH_2^+ found all mechanisms to be improbable, with the lowest activation energy being 11.59 kJ/mol ²¹. For the latter reaction, NH_3OH^+ is the more stable isomer of NH_2OH_2^+ , thus making the formation of the product favourable, and thus a proton transfer quite plausible²¹. This competing reaction could account for the low rates of detection of urea in ISM, but does not discount the viability of the formation pathways investigated in this study. With water as a potential catalyst, reactions on ice surfaces may favor the formation of ureaH⁺. Ion-water clusters are more stable than free ions and therefore have lower transition state energies^{12,22}. This factor, and an increase in proton mobility on interstellar ice are critical to the spontaneity of the reaction^{12,22}.

CONCLUSION

Through the quantum chemical analysis, the theoretical viability of two reaction pathways for the

formation of ureaH⁺ in ISM was demonstrated. These results are significant in their implications on the theories surrounding the origin of life. The presence of urea, an essential biomolecule, in ISM indicates the formation of life in space. Further studies can be applied to better understand the competing mechanisms for isouronium and the kinetics of the reaction. The probability of the formation of the isouronium from formamide and protonated hydroxylamine should also be investigated to understand the effect of competing pathways, such as H⁺ transfer between the two reactant species. Looking forward, calculations using simple rate constants considering the interactions between the charged and neutral species can be done to understand the kinetics of the proposed reactions^{12,20}. Further studies of this pathway using higher levels of theory should be done, as well as investigating the kinetics of surface catalyzed or three body reactions. In 2016, urea was successfully synthesized on model ices using a mechanism in which NH₂ radical is added to hydrogenated CO²³. Studies of alternative pathways to urea would help verify our findings and further explain the presence of urea in the ISM. Along with the findings in this paper, further research may confirm the origins of life to be extraterrestrial.

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COMPETING INTERESTS

No competing interests declared.

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