
Article:
Meijer, A.J.H.M. orcid.org/0000-0003-4803-3488, Slate, E.C.S., Barker, R. et al. (2 more authors) (2019) On the formation of urea in the ISM. Proceedings of the International Astronomical Union, 15 (S350). pp. 363-364. ISSN 1743-9213

https://doi.org/10.1017/s1743921319007828

Laboratory Astrophysics: From Observation to Interpretation
Proceedings IAU Symposium No. S350, 2019
Farid Salama, Helen J. Fraser & H. Linnartz, eds.

DOI: 00.0000/X000000000000000X

On the formation of Urea in the ISM

Anthony J. H. M. Meijer, Eren C. S. Slate, Rory Barker, Ryan T. Euesden, and Max R. Revels

Department of Chemistry, University of Sheffield, Sheffield, United Kingdom, S3 7HF

Abstract. Potential routes to the formation of urea were investigated using electronic structure methods. The most likely pathways involve either the reaction of the formamide and amine radicals or involve protonated isocyanic acid as a starting point.

Keywords. ISM: molecules, molecular processes

1. Introduction

Urea, $CO(NH_2)_2$, is the simplest known dipeptide. It is viewed as a potentially important molecule in the abiotic origin of life, and was one of the identified products of the Urey-Miller experiment in the 1950s (Miller and Urey(1959)). Subsequently, it was proven to be crucial in the formation of cytosine and uracil (Robertson and Miller(1995)), key to the RNA world hypothesis for the formation of life.(Alberts *et al.*(2002))

Two mechanisms for urea formation have been suggested by Förstel *et al.*(2015) starting from formamide, detected along with urea in model ice experiments, as an intermediate. The first one is a concerted reaction between formamide and ammonia, leading to urea and dihydrogen. The second one involves reaction of either a formamide radical with ammonia or an amide radical with formamide. This work aims to test the feasibility of these proposed mechanisms using electronic structure calculations. We also investigate the reaction of formamide radical with the amide radical leading to urea and a hydrogen atom. Finally, we consider the reaction of protonated isocyanic acid with ammonia forming protonated urea, which loses a proton to give urea.

2. Methodology

All calculations involving charged species were performed using the GAUSSIAN 09 suite of electronic structure programmes (Gaussian 2009) using DFT (CAMB3LYP// 6-311G**). Calculations involving radicals used RASSCF with the same basis using the MOLPRO suite of *ab initio* programmes (Molpro 2015).

3. Results and Discussion

All the routes explored in this work are outlined in figure 1. It is clear from this figure that the proposed routes in Förstel *et al.*(2015) are not viable at the temperatures prevalent in the ISM. The concerted route is endothermic by 22 kJ mol^{-1}, whereas the single radical route has large barriers, which will be unsurmountable in the ISM.

Fig. 1 also shows the two other possible routes we investigated. In the reaction of a formamide radical with an amide radical there is a small barrier of 4 kJ/mol, which is associated with structural changes in the formamide radical. The reaction overall is highly exothermic. The charged route, on the other hand, starts with the protonation of isocyanic acid and leads barrierless to a stable molecule, protonated urea. Abstraction of

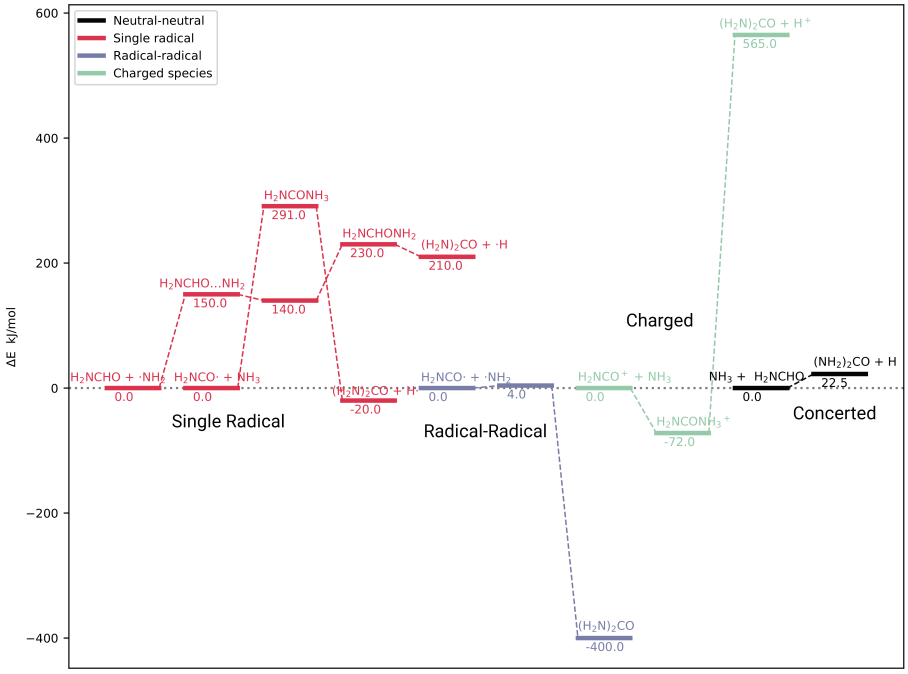

Figure 1. The reaction profiles for the urea formation routes investigated in this work. The energies in each route are plotted relative to the energy of the initial reactants.

the proton to get to urea is highly endothermic. However, in reality these reactions will happen in icy mantles and therefore it makes sense to include a three water molecules as an ice mimic in our calculations. In this case, there is only a small barrier to deprotonation of 11.9 kJ mol^{-1} with an endothermicity of 4.1 kJ mol^{-1}.

4. Conclusions

The calculations that were carried out to probe the feasibility of forming urea in the ISM show that the mechanisms proposed by Förstel *et al.* are not viable at the temperatures prevalent in the ISM. Instead, we propose two alternative mechanisms. The first one of those involves the reaction of the formamide radical with the amino radical. The second one starts with the formation of protonated isocyanic acid, which has been detected, which will react with NH_3 to form protonated urea. Deprotonation of urea is then facilitated by the ice mantle to lead to urea itself.

References

Miller, S. L. and Urey, H. C., 1959, *Science*, 130, 245.
Robertson, M. P. and Miller, S. L., 1995, *Nature*, 375, 772.
Alberts, B., Johnson, A., Lewis, J., Raff, M., Roberts, K. and Walter, P., *The RNA World and the Origins of Life* in *Molecular Biology and the cell*, 4th edition, Garland Science, 2002.
Förstel, M., Maksyutenko, P., Jones, B. M., Sun, B.-J., Chang A. H. H. and Kaiser, R. I., 2015, *Chem. Comm.*, 52, 741.
Gaussian 09, Revision D.01, Frisch, M. J. *et al.* Gaussian, Inc., Wallingford CT, 2009.
MOLPRO, version 2015.1, a package of ab initio programs, Werner, H.-J., Knowles P. J., Knizia G., Manby F. R., Schütz M., and others , see http://www.molpro.net.