

A systematic computational study of radical–radical reactions on interstellar ice surfaces

J. Enrique-Romero,^{1,2} A. Rimola,² and C. Ceccarelli¹

¹*Univ. Grenoble Alpes, CNRS, Institut de Planétologie et d'Astrophysique de Grenoble (IPAG), 38000 Grenoble, France*

²*Departament de Química, Universitat Autònoma de Barcelona, Bellaterra, 08193, Catalonia, Spain*

Understanding how interstellar complex organic molecules (iCOMs) are formed and destroyed is of high importance to predict the ultimate organic complexity reached in the interstellar medium (ISM) ([1], [2]). Two paradigms are invoked in the literature. Both argue that simple molecules and atoms are hydrogenated on the interstellar grain surfaces during the cold prestellar phase. Following this first step, one paradigm assumes that iCOMs appear as a result of gas-phase chemical processes, whereas the other predicts that radical-radical reactivity on the grain surfaces is the major responsible for the observed chemical complexity. The latter has profited of much popularity among astrochemical models in the last years, even though some basic assumptions of the paradigm are still a topic of debate. Among them, the radical-radical reactivity assumption, which is extremely difficult to quantify experimentally. We propose a complementary and, sometimes, alternative method: theoretical quantum chemical calculations, which can provide a precious atomistic perspective from which to study such processes (e.g. [3], [4], [5]).

In this contribution, we present our recent systematic quantum chemical study on the surface reactivity of several radical pairs. Some of the studied systems are $\text{CH}_3 + \text{X}$ and $\text{HCO} + \text{X}$ ($\text{X} = \text{CH}_3, \text{HCO}, \text{NH}_2, \text{CH}_2\text{OH}$ and CH_3O). According to observational evidences, the icy mantles that cover interstellar dust grains are dominated by water ([6]). We, therefore, use two cluster-like ice models consisting on 18 and 33 water molecules to simulate the grain surface where the radical-radical reaction occurs. We then study the reactivity of the above biradical systems by means of static quantum chemical calculations to obtain the potential energy surfaces of several complex species and the approximate efficiency of the different reaction product channels. We found that many reactions leading to iCOMs have non negligible activation barriers and that the transfer of a hydrogen atom from a radical acting as a donor to its partner, acting as an acceptor are important competitive processes. The occurrence of one process or the other could entirely depend on the relative orientation of the radicals upon encounter, namely on the water ice structure and interaction with the two radicals. These results indicate that the fraction of iCOMs generated in the current astrochemical models is certainly overestimated since (i) it is assumed that reactions always occur and (ii) the competitive reactions are not included.

References

- [1] E. Herbst. & E. F. Van Dishoeck, 2009, *ARA&A* 47, p. 427-480
- [2] C. Ceccarelli, S. Viti, N. Balucani, et al., 2018, *MNRAS* 476(1), p. 1371-1383.
- [3] A. Rimola, D. Skouteris, N. Balucani, et al., 2018, *ACS Earth and Space Chemistry* 2(7), 720-734.
- [4] J. Enrique-Romero, A. Rimola, C. Ceccarelli, et al., 2019, *ACS Earth Space Chem.* 3(10), p. 2158-2170
- [5] J. Enrique-Romero, C. Ceccarelli, A. Rimola, et al., 2021, *A&A* (in press).
- [6] A. A. Boogert, P. A. Gerakines, & D. C. Whittet, 2015, *ARA&A* 53, p. 541-581.