A combined DFT and kinetics approach to the radical reactions on and with interstellar water ices kinetics

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The formation of interstellar complex organic molecules (iCOM) is a hot topic in current astrochemistry discussions. Understanding how these species are formed, destroyed, and evolve in space is of high importance to predict the ultimate organic complexity reached in the interstellar medium (ISM) ([1],[2]). Two "classical" paradigms are usually invoked in the literature. The first one assumes that gas phase reactions are responsible for the formation of iCOMs after the release of simple precursors previously stored on interstellar dust grains. The second one assumes that radicals formed on in these icy mantles diffuse and react barrierless forming iCOMs. The latter model gained much popularity among astrochemical models in the last years, even if some of its basic assumptions are still under debate. This is the case of the radical-radical reactivity assumption, which is extremely difficult to quantify experimentally given that radicals are short lived species.

Here we propose a complementary, and sometimes, unique alternative method: theoretical quantum chemical calculations, which can provide a precious atomistic perspective from which to study such processes (e.g., [3, 4, 5]). Thanks to this approach we showed that (i) radical–radical reactions are not necessarily barrierless on water ices, that (ii) a competitive channel can exist involving a direct H-abstraction from one radical to the other (e.g., $CH_3 + HCO \rightarrow CO + CH_4$) and (iii) that a radical–radical case by case study is necessary.

In this contribution, we present our latest chemical kinetics results based on the microcanonical transition state theory on the radical–radical reactivity [5]. An example is the reaction between HCO and CH_3, leading to either acetaldehyde (CH_3CHO) or CO + CH_4, on amorphous solid water ices. In addition, the effects of deuterium substitution are also discussed. Finally, we present our latest work on non-diffusive iCOM formation, consequence of the reaction between a gaseous CCH and the water ice components leading to the efficient formation of vinyl alcohol and ethanol[6].

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