A Combined DFT and RRKM-Based Study on the Reactivity of HCO + NH_2 on Amorphous Water Ice Surface

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Abstract. Formamide is observed in the interstellar medium and it is thought to play an important role as a precursor of prebiotic molecules. In this work we study the reactivity of NH_2 and HCO on the open surface of amorphous ice model, which can either lead to the formation of formamide (through radical-radical coupling) or CO + NH_3 (through direct H-abstraction) by means of DFT electronic structure calculations, and derive their unimolecular rate constants within the RRKM scheme. We found that radical-radical coupling is faster and hence there is no competition between the two processes in this particular case. Despite of this result, the radical-radical mechanism in dust grain ices is still to be validated.

Keywords: Interstellar medium · Astrochemistry · DFT simulations · Kinetic RRKM calculations · iCOMs · Grains

1 Introduction

From the more than 200 molecular species detected in space, a subset called *interstellar complex organic molecules* (iCOMs), loosely defined as C-bearing species constituted by at least 6 atoms [6], is of special interest given that (i) they lock ∼20% of the interstellar carbon budget, (ii) they could be inherited from star-forming regions into planetary systems and (iii) they could be related to the origin of life on Earth and the possible presence of life elsewhere in the Universe as they are thought to be precursors of more complex prebiotic species [5,11,16].

Among all iCOMs, formamide (NH_2CHO) is a species of particular interest as (i) it contains the four most essential elements for biological systems (i.e., C, H, O and N) and (ii) it has been observed towards a variety of prestellar, protostellar sources (e.g. [12,13]) and in comets (e.g. [3,4]). The formation pathways of this species, through either gas-phase processes or reactions occurring on the

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surfaces of grains, have received much attention, specially from the computational chemistry community. This is because quantum computations are robust tools capable to provide unique atomic-scale pictures of the mechanistic steps of the reactions, alongside reliable structural and energetic information. For example, the gas phase route of $NH_2 + H_2CO \rightarrow NH_2CHO + H$ has been studied by means of quantum chemical and kinetic calculations [2,17,19], which has received support from observational studies such as [7]. On the other hand, the formation of formamide on ice-covered interstellar dust grains was initially thought to happen mainly through the hydrogenation of HNCO, which was experimentally ruled out [14] and theoretically predicted to be very slow [18]. A generally accepted pathway to form iCOMs like formamide is via radical-radical couplings (Rc) on or/and in ice mantles [10]. Recent works [8,15] investigated the formation of formamide adopting this mechanism (i.e. the radical-radical combination of NH_2 and HCO) by means of quantum chemistry calculations and using as amorphous solid water (ASW) a water cluster model of 33 water molecules. However, this route was not found as unique but it has a competitive channel: the direct H-abstraction (dHa) reaction $NH_2 + HCO \rightarrow NH_3 + CO$. [8] found that the ice vicinity strongly affects the reactivity of radicals. Specifically, formamide has more chances to be formed in cavities than in open surfaces, but there is still competition between Rc and dHa. Interestingly, the work by [15] proposed as an alternative route towards formamide formation the reaction of CN with a water molecule of the ice, assuming that the nascent energy of the first reaction steps is not quickly dissipated. In this contribution, the reactivity between NH_2 and HCO (i.e, both Rc and dHa reactions) on the same 33 water cluster model used in [8] in the side surface site (where the reactions exhibited the largest energy barriers) is extended by studying also the kinetics of the processes adopting the Rice–Ramsperger–Kassel–Marcus (RRKM) theory, which were overlooked in the previous paper.

2 Computational Details

All the electronic-structure calculations were carried out using the GAUSSIAN16 suit of programs [9]. The hybrid DFT BHLYP method in combination with a Pople's double-ζ basis set 6-31+G(d,p) was used, adopting an unrestricted and broken (spin)-symmetry formalism. The description of the stationary points (Fig. 1) identified in Enrique-Romero et al. (2019) were improved by introducing the Grimme's D3(BJ) dispersion correction in *a posteriori* way. The distance between radicals in the reactant geometry is longer than 5 Å (Fig. 1), and accordingly there is not interaction between them, but rather with the surface only. This means that BSSE is almost negligible, without any influence neither in the geometries nor in the reaction energetics and, therefore, BSSE corrections have not been accounted for.

Unimolecular rate constants for both Rc and dHa reactions were computed using an in-house developed code (e.g. [1,15,17]) based on the Ramspberger-Rice-Kassel-Marcus (RRKM) scheme. Under this approximation,

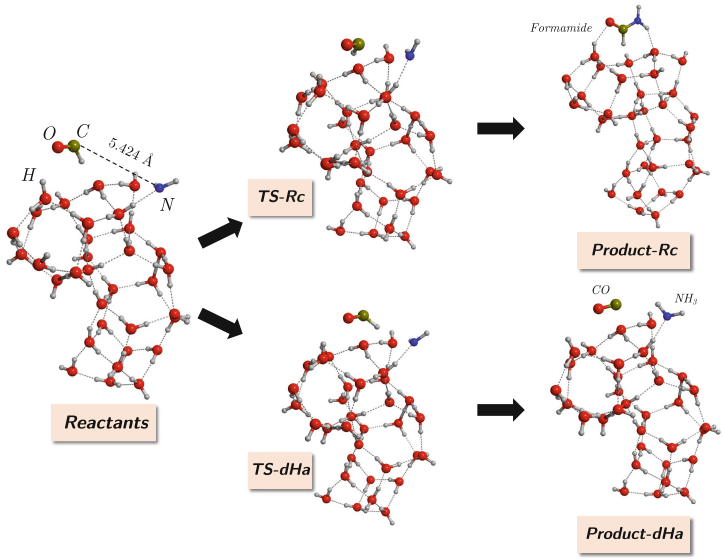

Fig. 1. Stationary points of the potential energy surfaces of the radical-radical coupling (Rc) and direct Hydrogen abstraction (dHa) reactions. Energetics can be found in the text (Sect. 3)

the ice + radicals system is considered to be a single supermolecule isolated from its surroundings, for which the fast intramolecular vibrational energy redistribution holds. The considered degrees of freedom include all the vibrational harmonic modes and the overall rotations of the cluster+radicals system. Under this circumstances, one computes the rates at a given total energy E by Eq. 1, where $N(E)$ is the sum of states of the transition state under the energy E, $\rho(E)$ is the reactant density of states and h is Planck's constant. This is followed by a Boltzmann averaging step in order to derive the temperature-dependent rate constant.

$$k(E) = \frac{N(E)}{h\rho(E)} \tag{1}$$

For the dHa case, tunnelling has been accounted for in an approximated way by means of the symmetric Eckart's barrier.

3 Results and Discussion: Arrhenius Plot

By adopting the BHLYP-D3(BJ)/6-31+G(d,p) theory level, the reaction and activation enthalpies at 0 K (i.e., the potential energy values including zero-point energy corrections) are: −390.1 and 2.3 kJ/mol for Rc, and −334.4 and 6.6 kJ/mol for dHa. Figure 2 shows the Arrhenius plots for both reactions.

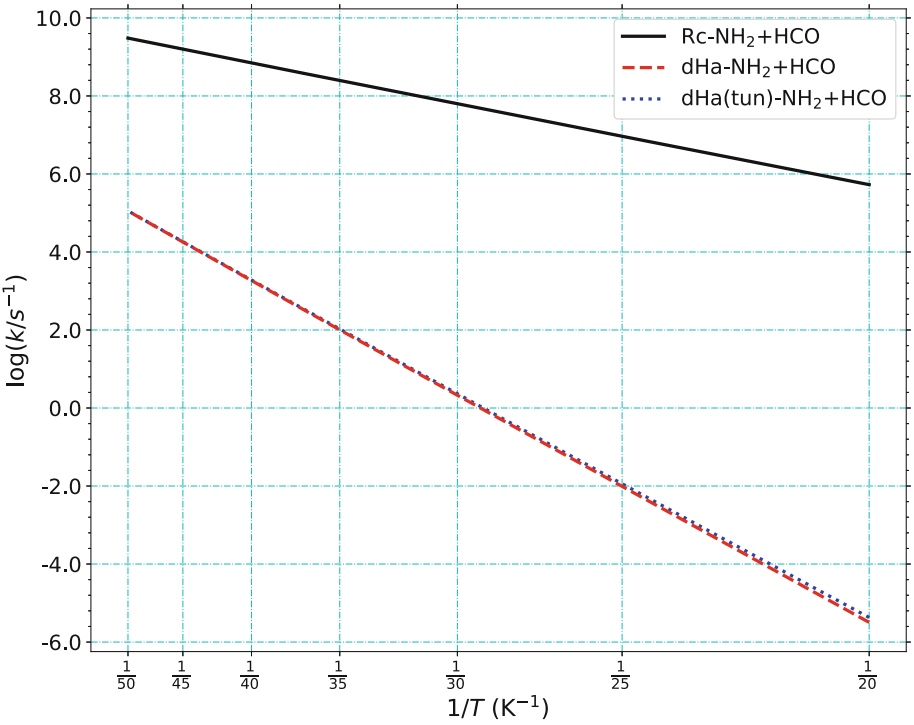

Fig. 2. Arrhenius plot for the radical-radical coupling (Rc) and direct H-abstraction (dHa) reactions between NH_2 and HCO on the side 33-water molecules cluster.

As a consequence of the lower energy barrier of Rc compared with dHa, calculated rate constants for the Rc reaction are larger than the dHa. That is, Rc rate constants stay over those for the dHa along the considered range of temperatures in the Arrhenius plot. It is worth mentioning that tunnelling does not exert any significant effect on the dHa rate constants. This is because the imaginary transition state frequency is very small ($\sim 43i$ cm^{-1}), and hence that the associated reduced mass is large, hindering tunneling to be dominant. In view of these kinetic results, therefore, the radical-radical coupling between NH_2 + HCO to form formamide actually dominates the chemistry on bare, open water ice surfaces (i.e. not taking into account pores nor cavities). We emphasis, though that, we are unable at this stage to say whether the radical-radical coupling reaction can actually occur on the grain surfaces. In order to verify it, the present rate coefficients should be incorporated into astrochemical models together with the other possible surface processes (such as diffusion and morphology effects, and their rates), which implies a change in the treatment of the grain surface chemistry of the current models.

4 Conclusions

DFT quantum chemistry computations alongside RRKM-based kinetic calculations indicate that formation of formamide on flat, compact water ice surfaces is actually a plausible channel by the coupling of the NH_2 + HCO radicals. It dominates over the direct H-abstraction reaction, which would lead to the formation of NH_3 and CO and that was previously postulated as a competitive channel to the radical-radical coupling. The dominance of the Rc over dHa is due to two factors: i) the Rc energy barrier is lower than the dHa one, hence giving rise to faster rate constants, and ii) tunnelling does not contribute to the rate constants of the dHa reaction, as a consequence of the associated low transition state frequency.

In order to validate whether radical-radical coupling mechanisms do actually take place in interstellar dust grains, the treatment of ice chemistry in astrochemical models should be modified incorporating kinetic data such as the one presented in this work, instead of assuming direct reaction upon encounter. Nevertheless, care must be taken given that the local surface properties may affect the potential energy surface and therefore the kinetics of any given radical-radical reaction, see for example [8].

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