Formation of amines : hydrogenation of nitrile and isonitrile as selective routes in the interstellar medium

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Abstract

Over 200 different species have been detected so far in the interstellar medium (ISM) and circumstellar shells. Among them, around 70 are referred to as "complex organic molecules" (COMs), and a large part contain nitrogen atoms. More specifically, COMs with a -C≡N functional group, i.e nitriles and cyanopolynes, are by far the most represented family (for example CH3CN, C3H7CN, CH2CHCN, HC**n**N, with n=4, 5, 7, 9, C6H5CN), whereas only three isonitriles have been identified, including CH3NC. By contrast amines, which are important for prebiotic chemistry are scarce. Indeed, beyond NH3, only one primary alkylamine, CH3NH2, has been identified in the ISM and the reason why is still not understood: it could occur in gas phase or at the surface of interstellar grains, which are often covered by ices. Considering that the most efficient chemical transformation of the molecular mantle during its formation on grains is hydrogenation, the formation of amine by reduction of nitriles seems intuitive: indeed H atoms are abundant and highly mobile on these surfaces at _˜ 10 – 20 K. However full hydrogenation of HCN/HNC, which has been studied both in the gas phase (1) and on HCN ice (2) leads to the same end product, methylamine.
In order to take into account any possible difference between the formation of primary and secondary amines, we investigated, at both the experimental and theoretical levels, the hydrogenation processes of CH3CN and CH3NC, which would lead to the simple primary

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CH3CH2NH2 and secondary CH3NHCH3 amines, (i.e. ethylamine and dimethylamine respectively). Observational results of molecules relevant to this study were also reported. (3)

The energetics of the hydrogenations paths, each composed of four successive elementary steps, were obtained using density functional theory, after benchmarking against high level post Hartree-Fock procedures. We found that, on the way to CH3CH2NH2 the first addition, however exothermic by 20 kcal/mol, is opposed by an activation barrier of _˜ 8 kcal/mol: this should be considered as a real obstacle to the reaction. By contrast, on the way to CH3NHCH3, reaching the first transition state requires less than 3 kcal/mol, whereas the barrier to the third hydrogenation is only 4.5 kcal/mol. Therefore hydrogenation of CH3NC is probable, at least by tunneling effect. These findings are in agreement with experimental results, carried out under ultra-high vacuum, in which CH3CN (or CH3NC) and H atoms are co-deposited onto gold surfaces: CH3CN does not react with H atoms, whereas the hydrogenation of the isonitrile works all the way through dimethylamine. In presence of H2O, the formation of dimethylamine is clearly enhanced, but our calculations failed to reproduce this trend: the reasons why will be discussed, and some clues to tackle this problem will be presented.

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