A computational study of the reaction N(2D) + C6H6: Implications for the upper atmosphere of Titan

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Abstract

The atmosphere of Titan, the largest moon of Saturn, is believed to be in some way reminiscent of the primordial atmosphere of Earth, being composed mainly by dinitrogen, methane, simple nitriles like HCN and HCCCN, simple hydrocarbons like C2H6, C2H4 and C2H2, H2 and Ar. Dinitrogen is the prevalent species, being the 97% of the atmosphere and the second relevant constituent is CH4 which represents an average amount of 2.7%. All the other species are present only in trace amounts, but their reactivity is very important as suggested by the plethora of information provided by the NASA/ESA/ASI Cassini-Huygens mission. Recent investigations suggested also the presence of positive ions and negatively charged ions in Titan’s ionosphere. More recent information were provided by the observations performed with the ALMA interferometer. Among the species identified by Cassini Ion Neutral Spectrometer (INMS), benzene shows a relatively important mole fraction, being 1.3‘10-6 at 950 km. However, the low number density and low temperature conditions (94 K at the surface and up to 200 K in the upper atmosphere of Titan) do not allow reactivity among neutral closed shell molecules because of the presence of relatively high activation energy barriers. In the range of altitude where benzene is present, however, molecular dinitrogen is converted into atomic nitrogen or ions by energetic processes or by the interaction with Extreme Ultra-Violet (EUV) radiation. The dissociation of molecular dinitrogen induced by dissociative photoionization, galactic cosmic ray absorption, N2+ dissociative recombination, or dissociation induced by EUV photons produces atomic nitrogen in its electronic ground state 4S and in the first excited 2D state in similar amounts. Atomic nitrogen in its 4S ground state exhibits very low reactivity with closed shell molecules. On the contrary, atomic nitrogen in its first electronically excited 2D state shows a significant reactivity with several molecules identified in the atmosphere of Titan. Atomic nitrogen in its excited 2D state is metastable but it shows a radiative lifetime long enough to react in binary collisions with other constituents of the upper atmosphere of Titan. We have already investigated the reactions of atomic nitrogen in its excited 2D state with various hydrocarbons, like CH4, C2H2, C2H4, C2H6, in laboratory experiments by the crossed molecular beam technique with mass spectrometric detection and time-of-flight analysis at different

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collision energies complemented by ab initio and kinetics calculations. More recently, with the same approach, we have investigated the reaction between N(2D) and benzene which is supposed to be very relevant in the upper atmosphere of Titan, from the stratosphere up to the thermosphere where the first haze layer is located.

In this contribution, we report on a theoretical characterization of the reaction involving N(2D) and benzene. The aim is to determine the chemical behavior of N(2D) with aromatic species after the previous investigation with aliphatic molecules. In particular, we wish to establish whether the aromatic ring is preserved in this reaction (as already observed in other cases) and whether the N atom is incorporated in the ring of carbon atoms, forming pyridine or its less stable isomers. Remarkably, by the analysis of the spectra recorded by the Cassini-INMS in the Open Source Ion mode the presence of a species with general formula C5H5N was inferred, indicating that either pyridine or one of its isomers are actually formed in the upper atmosphere of Titan starting from active forms of nitrogen.

With this aim, we have performed electronic structure calculations of the stationary points along the minimum energy path. These calculations will complement crossed molecular beam (CMB) experiments which are currently under way and will also be completed by kinetics calculations.