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The N(2D) reaction with small aromatic compounds and implications in the aromatic chemistry of the upper atmosphere of Titan

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As in the case of the terrestrial atmosphere, the composition of the atmosphere of Titan is dominated by N_2, with a mole fraction of 0.97. The second most abundant species, with a mean amount of 2.7%, is methane, CH_4. Minor components include H_2, Ar, higher hydrocarbons (C_2H_6, C_2H_2, C_2H_4), and nitriles (HCN, HCCCN). The NASA/ESA/ASI Cassini-Huygens mission provided us with much information about this interesting object of our Solar System, which revealed itself as the body with the most chemically active atmosphere, notwithstanding the global low temperature (94 K at the surface and up to ca. 200 K at high altitudes). Surprisingly, the richest chemistry occurs in the upper part of the atmosphere, from the stratosphere up to the thermosphere where the first haze layer is found. The first measurements of the ionosphere of Titan revealed a totally unexpected complex composition with positive ions as large as m/z = 350 and negatively charged ions with m/z up to 4000. In recent years, the atmosphere of Titan has become the object of further ground-based observations with the ALMA interferometer. Among the species identified by Cassini Ion Neutral Mass Spectrometer (INMS), benzene is characterized by a considerable mole fraction (for instance, at 950 km the mole fraction of benzene is 1.3×10^{-6}). In the same range of altitude, molecular nitrogen is converted into N atoms or N^+ /N_2^+ ions by the interaction with extreme ultra-violet (EUV) photons or by other energetic processes. In particular, N atoms are produced by N_2 dissociation induced by electron impact/EUV photons or dissociative photoionization, galactic cosmic ray absorption, and N_2^+ dissociative recombination. All these processes lead to the formation of atomic nitrogen in its ground electronic state $^4S_{3/2}$ and, in a similar amount, in the first electronically excited $^2D_{3/2,5/2}$ states. The radiative lifetimes of the metastable $^2D_{3/2,5/2}$ states are long enough (6.1×10^4 s and 1.4×10^5 s for the $^2D_{3/2}$ and $^2D_{5/2}$ state, respectively) to enable their chemical reactions in binary collisions with other constituents of the upper atmosphere. This specific aspect is crucial because it is known that nitrogen is significantly incorporated into the large N-containing organic species that form the orange aerosol covering Titan. Some of the present authors have already characterized the reactions of $N(^2D)$ with several aliphatic hydrocarbons (CH_4, C_2H_2, C_2H_4, C_2H_6) which are abundant in the atmosphere of Titan [1-4]. Interestingly, in all the above-mentioned cases, the formation of products containing a novel C-N bond has been observed.

In this contribution, we extend our combined theoretical and experimental approach to the reaction involving $N(^2D)$ and small aromatics, namely benzene and toluene. In particular, we wish to establish whether the aromatic ring is preserved in this reaction (as in the case of other gas-phase reactions) and whether the N atom is incorporated in the ring of carbon atoms, forming pyridines, or their 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 C_5H_5N was inferred, indicating that either pyridine or one of its isomers is formed in the upper atmosphere of Titan starting from active forms of nitrogen.

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