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The reactions of atomic nitrogen in its first electronically excited state with the C3H4 isomers and implications for the atmospheric chemistry of Titan

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Molecular nitrogen (N_2) is the main component of the atmosphere of Titan, while minor constituents include organic molecules, such as methane and higher hydrocarbons [1,2]. Among them, propyne (methylacetilene) has been identified in the Voyager IR spectrum of Titan since 1981 [3], while its structural isomer propadiene (allene), already predicted to be present by photochemical models, has been only recently identified via the Texas Echelle Cross Echelle Spectrograph on the NASA Infrared Telescope Facility [4]. Given the presence of higher hydrocarbons, N-bearing organic molecules in trace amounts (nitriles and imines) and haze macromolecules, Titan has proved to be the object of the Solar System with the richest atmospheric chemistry. Understanding such complex chemistry requires a multidisciplinary approach based on the interaction between chemists and planetary scientists. In particular, the build-up of realistic photochemical models requires accurate estimates of reaction rate coefficients and product branching ratios. This has led several research groups working in the field of chemical kinetics to undertake systematic studies on gas phase reactions of relevance in the chemistry of Titan.

In our laboratory, we have used a combined experimental and theoretical approach to characterize the reactions involving atomic nitrogen in its first electronically excited state, ^2D, and simple hydrocarbons [5-9]. N(^2D) is produced in the thermosphere of Titan by several high-energy processes and, being a metastable state with a long radiative lifetime, is able to undergo reactive collisions before decaying by spontaneous emission of photons [10].

In this contribution, we report on a combined theoretical and experimental study of the reactions of N(^2D) with the two structural isomers methylacetilene (CH_3CCH) and allene (CH_2CCH_2). In many photochemical models, structural isomers are not distinguished and treated as only one species. However, we know that the reaction mechanism can be very different for each isomer leading to different final reaction products [11].

More specifically, the potential energy surfaces for the two reactions have been derived by performing electronic structure calculations at DFT and CCSD(T) level, while the reaction mechanism of the H-displacement channels have been investigated experimentally by the crossed molecular beam technique. Both the reactions start with a barrierless attack of the N atom to multiple bond of

the molecules, leading to the formation of cyclic intermediates. Different isomerization processes can then lead to various product channels.

The implications for the chemistry of the atmosphere of Titan will be also addressed.

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