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REACTIVITY OF CH_3^+ WITH BUT-2-YNE USING REACTION MONITORING WITH SYNCHROTRON RADIATION

A. Cernuto,¹ A. Lopes,³ C. Romanzin,^{3,4} B. Cunha De Miranda,⁴ D. Ascenzi,¹ A. Maranzana,² P. Tosi,¹ G. Tonachini,² M. Polášek,⁵ J. Žabka⁵ and C. Alcaraz^{3,4}

¹ Department of Physics, University of Trento, Italy

E-mail: andrea.cernuto@unitn.it; daniela.ascenzi@unitn.it

² Department of Chemistry, University of Torino, Italy

³ Laboratoire de Chimie Physique, CNRS-Univ. Paris-Sud, Orsay, France

⁴ Synchrotron SOLEIL, Saint-Aubin, France

⁵ J. Heyrovsky Institute of Physical Chemistry of the CAS, Prague, Czech Republic

The methyl carbocation is ubiquitous in astrophysical environments ranging from the interstellar medium (ISM) to terrestrial and planetary atmospheres, cometary comae, etc. In the ISM, CH_3^+ reactivity with simple molecules needs to be included to model cloud chemistry at elevated temperatures (e.g. hot cores), or inner regions of protoplanetary disks [1]. CH_3^+ is one of the key ions in the atmosphere of Titan [2], where it is responsible for formation of complex hydrocarbons [3].

Although methyl cation reactivity with saturated and unsaturated hydrocarbons up to C_3 have been investigated in the past (with CH_4 , C_2H_6 , C_3H_8 , C_2H_4 and C_2H_2) reactions with larger hydrocarbons are almost non-existent. In particular, the reactions with methyl substituted acetylenes (i.e. propyne C_3H_4 , and but-2-yne C_4H_6) are expected to be relevant for the growth of complex hydrocarbons in Titan's atmosphere, where they are proposed as responsible for the couples of ions ($\text{C}_4\text{H}_7^+/\text{C}_4\text{H}_5^+$ and $\text{C}_5\text{H}_9^+/\text{C}_5\text{H}_7^+$) observed by the Ion Neutral Mass Spectrometer on board of the Cassini probe [4].

Here we report on the reaction of CH_3^+ with but-2-yne C_4H_6 by measuring absolute reactive cross sections and branching ratios as a function of collision energy using both the home-built Guided-Ion Beam Mass Spectrometer (GIB-MS) at Trento and the CERISES-apparatus, installed on the DESIRS beamline of the synchrotron radiation source SOLEIL. While in the first set-up the methyl cation is generated with an uncontrolled amount of internal excitation, in the other one direct VUV photoionization with synchrotron radiation of methyl radicals is used to produce CH_3^+ . The latter method opens the way to investigation of the effect of internal degrees of freedom (vibrational) on CH_3^+ reactivity. Experimental results are interpreted under the light of a theoretical study of product formation mechanisms using DFT methods (with optimizations followed by CCSD(T) single-point energy calculations). The most abundant ionic products are C_4H_6^+ and C_4H_5^+ resulting from charge transfer and H^- transfer processes, while the third most abundant product is C_3H_5^+ plus C_2H_4 , formed via a complex mediated mechanism. Most relevant for the growth of complex organic species on Titan is the detection of a minor channel attributed to C_5H_7^+ and formed by H_2 elimination from a stable intermediate.

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