



# Growth of hydrocarbon molecules in the Titan's atmosphere via ionic mechanisms

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## Abstract

Laboratory investigations based on guided ion beam mass spectrometric techniques, coupled to theoretical interpretations by quantum chemistry, are reported to unravel new chemical mechanisms leading to the synthesis of organic molecular species in planetary atmospheres. In particular we have focused our attention on ionic mechanisms for the growth of aromatic and polyaromatic hydrocarbons by association of pre-formed building blocks. Our studies can help planetologists to propose models for explaining the observational evidence of heavy molecular organic species in the ionosphere of Titan.

## 1. Introduction

Laboratory studies on the chemistry of planetary atmospheres and interstellar medium have been historically focussed on small molecules. Due to advances in infrared/microwave astronomy and to the settlement of space missions to outer planets, recently the attention has shifted towards larger molecules, mostly of organic nature.

Due to the tremendous complexity of its chemistry, the Titan's ionosphere is the most pertinent example showing the importance of good chemical models for the interpretation of Cassini data. Heavy ions with masses over 100 amu have been detected in significant amounts into the Titan's ionosphere below 1200 km [1]. Possible chemical structures include PAHs, nitrile aromatic polymers [2], fullerenes [3] and polyphenyls [4] and such heavy particles have been proposed to act as seeds for aerosols formations [5]. In spite of several laboratory investigations, new experimental and theoretical data are still required to provide a quantitative comparison between the *in situ* observations of the Cassini orbiter and the proposed models [5].

## 2. Experimental techniques

We study the chemical reactivity and microscopic mechanisms of charged particles by using tandem mass spectrometers, which allow selection and manipulation of both reactant and product ions. We can estimate absolute values of reactive cross sections as a function of the collision energy and branching ratios (from which rate constant values can be inferred). When carried out on large molecules, such studies pose several experimental and computational problems related to the increased number of degrees of freedom. A complementary experimental and theoretical approach is the key to obtain reliable information on reaction mechanisms [6-8].

## 3. Results and discussion

Several mechanisms have been suggested for the growth of large organic molecules under extraterrestrial conditions based on singly charged [9] and even multi-charged cations [10] and the idea is put forward that complex molecules build up by association of pre-formed building blocks. In the case of polyaromatic hydrocarbons great progress has been made in the knowledge of synthetic mechanisms based on radical and neutral reactions [11], while much less is known about ionic routes.

In the recent past we have explored ionic mechanisms for the growth of larger molecules starting from phenyl cations [7, 8]. Here we report on new measurements about the reactivity of the naphthyl cation  $C_{10}H_7^+$  with benzene. We have observed the growth of hydrocarbon ions via C-C bond forming reactions and a typical mass spectrum of products is shown in Figure 1. The condensation adduct  $C_{16}H_{13}^+$ , for which the most plausible structure is protonated phenylnaphthalene, is observed as the most abundant product in the absence of internal excitation of the reacting  $C_{10}H_7^+$  cation, at the smallest collision energies accessible with our experimental set-up for

this system and with a sufficient pressure of benzene in the scattering cell to allow for collisional stabilization. Other products are the ions  $C_{16}H_n^+$  ( $n=10-12$ ) coming from H and  $H_2$  elimination from the adduct and the  $C_{15}H_{10}^+$  ion formally corresponding to a  $CH_3$  elimination.

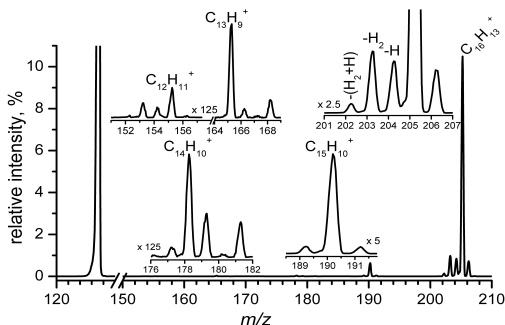
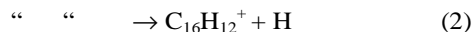
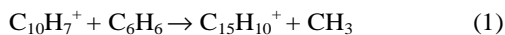


Figure 1: MS spectra of products from the reaction of  $C_{10}H_7^+$  with  $C_6H_6$ .

Product yields for all the above mentioned channels are highest at the lowest nominal collision energies and they have negative energy dependences. Values of  $2 \text{ \AA}^2$  and  $1 \text{ \AA}^2$  (with 30% error) for the absolute reactive cross section of reactions (1) and (2) are measured respectively at a collision energy of  $\sim 0.3$  eV in the center of mass:



Using such values and the branching ratios for channels (1) and (2) we can extrapolate a phenomenological total rate constant of  $\sim 5.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ . Theoretical calculations at the DFT (M06-2X/CBS//cc-pVTZ) level of theory show that naphthylum can act as an electrophile and add to the  $\pi$  system of benzene, leading to the barrierless formation of an ionic adduct with an exothermicity of about  $53 \text{ kcal mol}^{-1}$ . From this structure several rearrangements have been explored but special attention is placed on an overall exothermic pathway for reaction (1) that leads to elimination of the methyl radical via an intramolecular electrophilic addition followed by H shifts and ring opening steps. Finally, a significant mobility of the H atoms over both the phenyl and naphthyl rings has been demonstrated by the statistical H/D scrambling observed in the products by using mixed isotopic reagent pairs  $C_{10}H_7^+ / C_6D_6$ .

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