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FT-ICR studies of anionic reactions for the chemistry of Titan ionosphere

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1. Introduction

Titan, Saturn's largest moon, exhibits a dense atmosphere characterized by a thick orange haze and mainly composed of molecular nitrogen and methane as well as numerous other organic compounds such as nitriles. The chemistry taking place in its atmosphere is complex and still not completely understood. Yet, results from the Cassini-Huygens mission have shown that ionospheric chemistry must play a more important role than previously thought. The discovery of CN^-, C_3N^- and C_5N^- together with a large amount of heavy cations and anions in the upper atmosphere [1-3] came indeed as a surprise and suggests that they could contribute to the formation of aerosols particles through an interplay between neutral and charged particules [4,5].

In this context, we have undertaken experimental investigations of ion-molecule reactions involving small anions such as CN^-, C_3N^- and C_5N^- in a common effort between several French and Czech groups [5-8].

In the 2011 EPSC meeting, we have presented the study of the $CN^- + HC_3N$ reaction in a tandem mass spectrometer as a function of the HC_3N target pressure in order to explore different collisional conditions. The primary and secondary reactions with HC_3N are found to be extremely efficient, resulting in anionic products of rapidly growing size. A detailed mechanism for the growth of these species has been proposed and its relevance to the growth of heavy anions in Titan's ionosphere discussed [5].

Our objective is now to precisely characterize each step of this mechanism by studying the reactions in the single collision regime and by measuring rate constant and absolute reaction cross section as a function of temperature and collision energy.

2. Experiment

In this contribution, we will present a FT-ICR study at 300 K [8] done at Orsay with the MICRA setup [9] of the following reactions:

$$CN^- + HC_3N$$

$$C_3N^- + HC_3N$$

$$C_3N^- + HC_3{}^{15}N$$

$$C_3{}^{15}N^- + HC_3N$$

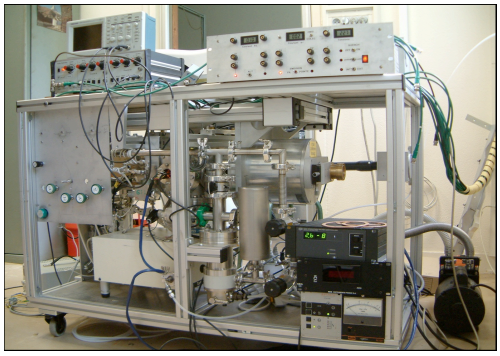

Figure 1: The FT-ICR MICRA setup [9]

CN^- and C_3N^- parent ions have been produced by dissociative electron attachment on BrCN and BrC_3N respectively. After ejection of the electrons, pulses of increasing length of cyanoacetylene (HC_3N) target gas are injected to probe the kinetics of the reactions and derive their rate constant at 300 K.

3. Results

Several mechanisms, including fast proton transfer and slower associative detachment have been identified, as illustrated in Figure 2, and will be discussed at the conference [8].

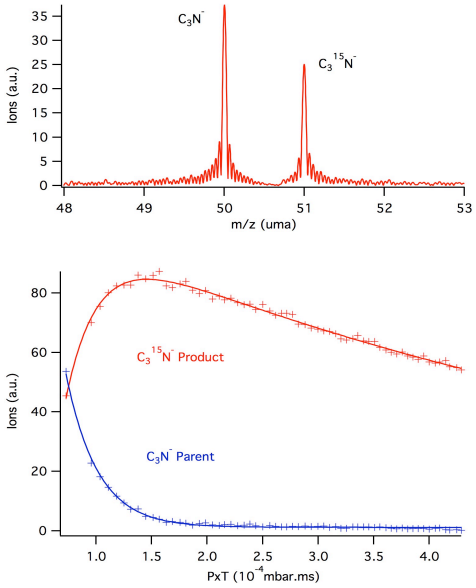

Figure 2: Kinetics of the C_3N^- + $HC_3{}^{15}N$ reaction. Top: Mass spectrum. Bottom: variation of C_3N^- parent and $C_3{}^{15}N^-$ product anions vs the $HC_3{}^{15}N$ target pressure for a fixed reaction time of T= 2s. The fast decrease of C_3N^- and rise of $C_3{}^{15}N^-$ is associated with the proton transfer and the decrease of $C_3{}^{15}N^-$ to the slower associative detachment.

These results are complementary to the ones obtained by the french group of S. Le Picard at the University of Rennes 1 who have measured the rate constant of the CN^- + HC_3N reaction as a function of temperature from 300 K down to 49 K [6,7] with the help of the CRESU technique [7].

Further studies are planned on the CERISES setup [10] at Orsay to characterize the reaction mechanism by measuring the absolute reaction cross section and product velocity distributions as a function of collision energy.

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