



Anion chemistry on Titan: A possible route to large N-bearing hydrocarbons

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ABSTRACT

The reaction of CN^- with cyanoacetylene (HC_3N), has been studied as a function of the HC_3N pressure in a quadrupole tandem mass spectrometer. The mass spectra revealed the fast depletion of the CN^- parent ion and formation of larger anions of rapidly growing size. Most of the ions observed were found to belong to two series of products: $(\text{HC}_3\text{N})_x\text{C}_{2p+1}\text{N}^-$ and $(\text{HC}_3\text{N})_x\text{C}_{2p}\text{N}^-$ resulting from the sequential additions of HC_3N molecules and loss of HCN or HCCN molecules. The mechanism and energetics of the first two reaction steps are briefly discussed. The laboratory data are compared with those from the Cassini CAPS-ELS spectrometer. It is believed that the reactions observed could account for the growth of anions in Titan's ionosphere.

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1. Introduction

Observational evidence of the presence of molecular anions in space is very recent but these species are the object of a growing attention. So far, only two types of anions, C_{2n}H^- and $\text{C}_{2n+1}\text{N}^-$, have been detected but these are found to be present in various environments ranging from interstellar clouds (Agúndez et al., 2008; McCarthy et al., 2006) to circumstellar envelopes (Agúndez et al., 2010; Cernicharo et al., 2007; McCarthy et al., 2006; Thaddeus et al., 2008). The presence of some cyanopolyacetylide anionic species, e.g., CN^- , C_3N^- and C_5N^- , have been inferred from a model of Titan's ionosphere (Vuitton et al., 2009).

A wealth of heavy (up to $\sim m/z$ 10,000) unidentified negative ions and other cationic species (Coates et al., 2007; Wahlund et al., 2009; Waite et al., 2007) have been observed in Titan's upper atmosphere. The presence of such species at high altitudes (around 1000 km) was unexpected (Coates et al., 2007; Waite et al., 2007) and has triggered a complete reexamination of Titan's atmospheric chemistry. This is especially true concerning the formation of the aerosols responsible for the orange haze characteristic of Titan's atmosphere. The potential role of ion-neutral chemistry in this process is now considered and recent models also suggest that the formation of aerosol particles is initiated in the upper atmosphere (Lavvas et al., 2009; Liang et al., 2007; Wahlund et al., 2009). However, if some mechanisms for the production of neutral haze precursors based on electron recombination processes of heavy cationic species have been proposed (Wahlund et al., 2009), the

possible role of anion chemistry in the growth of larger species is still unclear though strongly supported by recent model results (Vuitton et al., 2009) and observations (Coates et al., 2009). Yet, other processes may also account for the observation of negatively charged particles. It is for instance possible that electrons are captured by already formed heavy neutral species (Vuitton et al., 2009). Waite et al. (2007) suggest that anions are formed after a first series of complex chemical processes involving cations. Positive and negative ion neutral chemistry would thus be closely linked as pointed out by Wahlund et al. (2009). Chemical structures derived from fullerenes and PAHs have also been proposed (Sittler et al., 2009).

Numerous theoretical and experimental studies have been devoted to the $\text{C}_{2p+1}\text{N}^-$ or C_{2p}N^- anionic species. Among these works, those concerning their stability, reactivity, or decay by interaction with photons, such as photodetachment, are of major importance for the modeling of Titan ionosphere. Both from the theoretical (Botschwina and Oswald, 2008; Wang et al., 1995; Zhan and Iwata, 1996a, 1996b) and experimental (Wang et al., 1995; Gupta and Ayyub, 2001; Huang et al., 1995) points of view, $\text{C}_{2p+1}\text{N}^-$ species are known to be more stable than C_{2p}N^- species, inducing alternations in the observed yields of C_nN^- species as a function of n . Apart from recent studies focusing on the reactions of C_nN^- ($n = 1-6$) with H atoms (Snow et al., 2009; Yang et al., 2011) and of CN^- with the cyanoacetylene molecule (HC_3N) (Carles et al., 2011), little is known about their reactivity. They might nevertheless be intermediates of importance for the chemistry related to the different astrophysical environments where they have been observed (Harada and Herbst, 2008; Vuitton et al., 2009; Walsh et al., 2009). Concerning their loss by interaction with photons, laser induced photodetachment studies by the Neumark group (Yen et al., 2010; Garand et al., 2009; Bradforth et al., 1993) provide very

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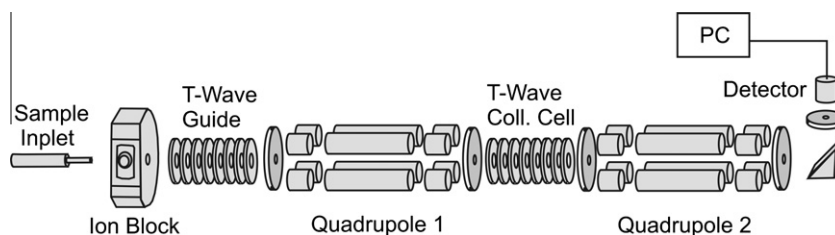


Fig. 1. Scheme of the tandem quadrupole mass-spectrometer.

precise electron affinities of the neutral species and spectroscopy information of both the anion and neutral species, but don't bring any data on absolute photodetachment efficiencies as a function of photon energy.

In the present work, we focus on the reaction: $\text{CN}^- + \text{HC}_3\text{N}$, which is of particular interest for Titan's chemistry. In fact, cyanoacetylene is expected to be present in significant abundance in Titan's upper atmosphere (Vuitton et al., 2006) where CN^- has also been identified as one of the major anionic species, together with C_3N^- and C_5N^- , on the basis of observations from the Electron Spectrometer instrument (CAPS-ELS) on board of the Cassini orbiter (Coates et al., 2007), and results from the first chemical model including negative ion chemistry (Vuitton et al., 2009). Moreover, according to this model, the reaction of cyanide anion with cyanoacetylene following: $\text{CN}^- + \text{HC}_3\text{N} \rightarrow \text{HCN} + \text{C}_3\text{N}^-$ would be the dominant formation process of C_3N^- above 800 km. The efficiency of that proton transfer mechanism as a pathway to C_3N^- is also confirmed by the kinetic study performed by Carles et al. (2011) under single-collision conditions. Here, we consider the possibility for this reaction to induce a chain of chemical processes leading to larger anionic species by exploring different reactive regimes going from single to multiple collisions conditions as determined by the pressure of the neutral HC_3N reactant in the collision cell.

After a brief description of the experimental set-up and conditions, a detailed analysis of the mechanisms associated with the growth of the observed reaction products is provided. The relevance of the mechanisms proposed for the interpretation of observations from the CAPS-ELS spectrometer and their eventual contribution to the growth of heavy anions in Titan's upper atmosphere is also discussed.

2. Experimental

The aim of the experimental study was to carry out the reaction of CN^- anion with cyanoacetylene, HC_3N , in a multiple collision regime to probe the appearance of secondary products. The experiments were performed on the Quattro Premier XE (Waters) tandem quadrupole mass spectrometer equipped with the T-wave[®] collision cell schematically displayed in Fig. 1. The sample is ionized at atmospheric pressure in the source to generate the parent ion. The ions enter the vacuum system through a sampling cone, then pass through the source traveling wave ion guide into the first quadrupole, where they are filtered according to their mass-to-charge ratio. The mass-separated parent ions pass into the T-wave collision cell where they either interact with neutral molecules or pass to the second quadrupole. Parent and product ions are then mass-analyzed by the second quadrupole.

The precursor ions were prepared from acetonitrile by atmospheric pressure chemical ionization (APCI) using a desolvation nitrogen gas flow maintained at 70 L h^{-1} . The source was at a temperature of $100 \text{ }^\circ\text{C}$ and the corona discharge current was $25 \text{ } \mu\text{A}$. The other instrument conditions were as follows: sample cone voltage 70 V , extractor voltage 2 V , and RF lens voltage 0.4 V .

The great advantage of this experimental setup is to control the dwell time of thermal product ions in the collision cell. To control

the residence time of ions in this device, a traveling voltage wave (T-Wave) moves along the device by application of transient DC voltage to successive ring electrodes. Through appropriate choice of wave amplitude and velocity, ions 'surf' on the front of this wave. In the experiment, an amplitude of 0.1 V with a speed of 500 m s^{-1} (thermal velocity) was used, thus achieving the independence of the dwell time of thermal ions in the direction of movement, corresponding to a collision energy of $\sim 0.07 \text{ eV}$ for the secondary collisions. For the primary reaction, $\text{CN}^- + \text{HC}_3\text{N}$, the parent ion has a translational energy of 1 eV , corresponding to a collision energy of 0.66 eV . Both quadrupoles were working at a unit mass resolution. Data acquisition and processing were performed using Mass Lynx v4.1.

Neutral reactant HC_3N was synthesized according to the literature procedure (Miller and Lemmon, 1967) and its purity was found to be 98% according to mass spectrometry analysis performed on a ZAB2-SEQ (Micromass) tandem mass spectrometer using the standard electron ionization source. Impurities were identified as air and water. Water content was estimated to be less than 0.3%.

Quantum chemistry calculations were performed using the Gaussian 09 suit of programs (Frisch et al., 2009). Structures were optimized using a hybrid B3LYP functional in connection with an augmented cc-pVDZ basis set. All the stationary points were characterized by harmonic frequency calculations to identify local energy minima (all real frequencies) and first-order saddle points (one imaginary frequency). Frequencies were used for calculation of zero point vibration energy (ZPVE) corrections.

3. Results and discussion

3.1. Mass spectra

Different reactive regimes were explored by varying the pressure of the neutral reactant HC_3N in the reaction cell. In the single-collision regime (vide supra), the only product observed was the C_3N^- anion (Fig. 2a), which is formed by the proton transfer mechanism:



With increasing pressure, i.e., in the multiple-collision regime, a rapid depletion of the primary ion CN^- was observed together with a series of complex product ions of variable size containing more carbon and nitrogen atoms than the original reactants (Fig. 2b and c).

Based on the observed pressure dependencies of the ionic products, a general reaction scheme (Scheme 1) is proposed here that accounts for most of the peaks observed in the mass spectra.

Evidence of the validity of this Scheme 1 can be found on the products that are highlighted on the mass spectrum in Fig. 3. A first series of peaks (in blue¹) is observed at m/z ratios that correspond to products of general formula $(\text{HC}_3\text{N})_x \cdot \text{C}_{2p+1}\text{N}^-$ ($x = 0-5$, $p = 1-5$), i.e.,

¹ For interpretation of color in Figs. 3–5, the reader is referred to the web version of this article.

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