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

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Abstract

The CN^- + HC_3N reaction has been studied in a tandem mass spectrometer as a function of the HC_3N target molecule going from a single to a multiple collision regime. The primary and secondary reactions with HC_3N were found to be extremely efficient, resulting in anionic products of rapidly growing size through a simple mechanism [1]. Comparison of the experimental mass spectra with the spectrum observed on board of CASSINI with the CAPS-ELS instrument by Coates *et al* [2,3] suggests that the proposed mechanism may be of interest to describe the growth of negatively charged hydrocarbons in Titan's ionosphere [1].

1. Introduction

Among the numerous negative ions observed in Titan's upper atmosphere [2,3], CN^- is believed to play a key role in the formation of larger species [4]. In this context, the reaction of CN^- with cyanoacetylene (HC_3N) whose concentration is not negligible in Titan's upper atmosphere, is of particular interest. The kinetic of the CN^- + HC_3N reaction has recently been experimentally investigated by Carles *et al*. [5] under single collision conditions. The rate constant is $k = 4.8 \times 10^{-9}$ cm^3/s and C_3N^- could be identified as the main reaction product following the proton transfer $CN^- + HC_3N \rightarrow C_3N^- + HCN$.

2. Experimental section

In this work, the same reaction has been studied as a function of the HC_3N target pressure on a tandem mass spectrometer shown in Fig. 1. CN^- parent anions were produced from acetonitrile in a APCI (Atmospheric Pressure Chemical Ionisation) source. They are selected in mass in a 1st quadrupole mass filter and react with HC_3N in a RF travelling-wave collision cell. Synthesis of the HC_3N molecule was performed following [6]. Parent and product anions are analyzed in mass up to m/z = 400 in a 2nd quadrupole mass filter before their detection.

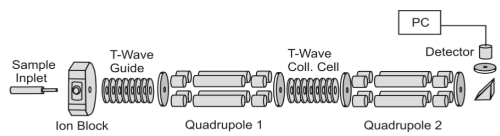

Figure 1: Experimental setup.

3. Results

Typical mass spectra shown in Fig. 2 reveal the fast decrease of the CN^- parent and apparition of larger anions of rapidly growing size. Most of the masses observed were found to belong only to two series of products: $(HC_3N)_x.C_{2p+1}N^-$ and $(HC_3N)_x.C_{2p}N^-$ resulting from the sequential additions of HC_3N molecules and loss of HCN or HCCN molecules. The intensity of each product has been followed as a function of the HC_3N pressure [1].

For a comparison with the spectrum recorded on Titan ionosphere [2-4], we have convoluted our measured spectra with the mass resolution ($\Delta m/m$ of 16.7 %) of the CAPS-ELS spectrometer and summed up in a similar histogram as shown in Fig. 3. Similarities can be found between the laboratory and observed spectra, in particular for the first peaks due to CN^- and C_3N^-, at m/z = 26 and 50, and the beginning of the broad structure at higher masses. Extended measurements at higher masses would be needed for a complete comparison.

Even if the conditions of pressure (0.02 – 0.7 Pa) in the experiment are different from those observed in Titan ionosphere, the same mechanism could account for the growth of anions in Titan through successive collisions on a larger time scale.

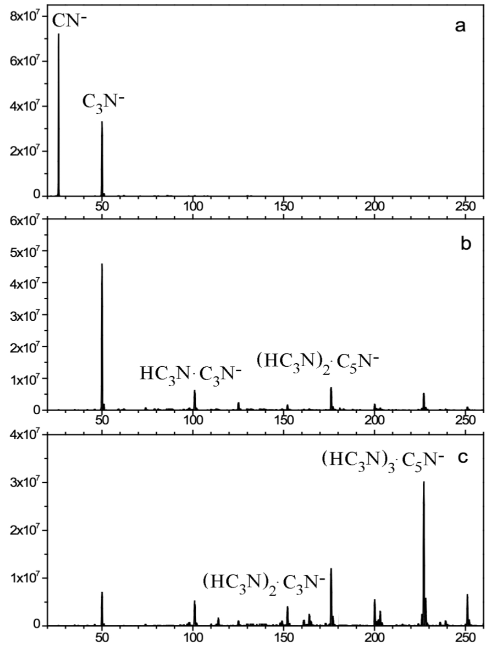

Figure 2. Mass spectra recorded at a HC_3N target gas pressure of 0.02 (a), 0.3 (b), and 0.5 Pa (c).

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References

[1] J. Žabka, M. Polášek, C. Romanzin, C. Alcaraz, "*Anion Chemistry: A possible route to large hydrocarbons in Titan ionosphere*" (submitted).

[2] A.J. Coates, F.J. Crary, G.R. Lewis, D.T. Young, J.H. Waite, E.C. Sittler, "*Discovery of heavy negative ions in Titan's ionosphere*", Geophys. Res. Lett. **34**(22) (2007).

[3] A.J. Coates, A. Wellbrock, G.R. Lewis, G.H. Jones, D.T. Young, F.J. Crary, J.H. Waite, R.E. Johnson, T.W. Hill, E.C. Sittler, "*Negative ions at Titan and Enceladus: recent results*", Farad. Discuss.**147**, 293-305 (2010).

[4] V. Vuitton, P. Lavvas, R.V. Yelle, M. Galand, A. Wellbrock, G.R. Lewis, A.J. Coates, J.E. Wahlund, "*Negative ion chemistry in Titan's upper atmosphere*", Planet. Space Sci. **57**(13), 1558-72 (2009).

[5] S. Carles, F.A., C. Monnerie, J.-C. Guillemin, J.-L. Le Garrec, *Kinetic studies at room temperature of the cyanide anion CN- with cyanoacetylene(HC3N) reaction.* Icarus, **211**(1), 901-905 (2011).

[6] Miller, F.A., Lemmon, D.H., *The infrared and Raman spectra of dicyanodiacetylene (NCCCCCCN).* Spectrochim. Acta Part A – Mol. Spectrosc. **A 23**, 1415 (1967)

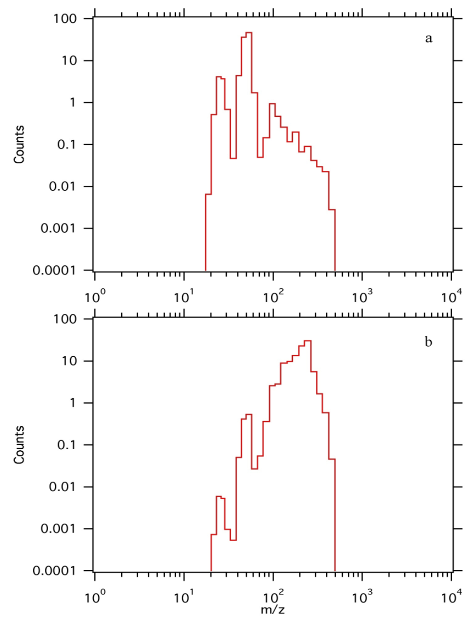

Figure 3. Convolution of mass spectra recorded at a HC_3N target gas pressure of 0.05 (a) and 0.5 Pa (b) with a gaussian apparatus function representing the resolution ($\Delta m/m$ of 16.7 %) of the CAPS-ELS spectrometer of CASSINI [2-4].