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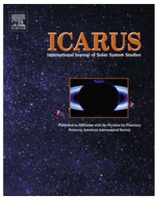

An experimental study of the reactivity of CN^- and C_3N^- anions with cyanoacetylene (HC_3N)

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ABSTRACT

The reactions of the CN^- and C_3N^- anions with cyanoacetylene HC_3N, of special interest for the chemistry of Titan's upper atmosphere, have been investigated by means of FTICR mass-spectrometry. Primary ions, CN^- and C_3N^-, have been produced by dissociative electron attachment (DEA) from BrCN and BrC_3N, and prepared in a clean way before reaction. Total rate constants have been measured for both reactions at 300 K and are found to be as follows: $(3.9 \pm 0.5) \times 10^{-9}$ and $(1.0 \pm 0.2) \times 10^{-10}$ $cm^3\ s^{-1}$ for the reaction of HC_3N with CN^- and C_3N^-, respectively. For the $CN^- + HC_3N$ reaction, proton transfer is found to be the only reactive channel within our detection limits. Proton transfer is also dominant for the $C_3N^- + HC_3N$ reaction but the resulting ionic product being identical to the primary ion C_3N^-, this process is transparent for the kinetics of the $C_3N^- + HC_3N$ reaction and the kinetic rate retrieved corresponds to a slow and competitive detachment pathway. Yet the nature and energetics of the neutral product(s) formed through this process remain unknown. Additional experiments using isotopic products have allowed to retrieve specific rate constants associated with the proton transfer channel in the $C_3{}^{15}N^- + HC_3N$ and $C_3N^- + HC_3{}^{15}N$ reactions and the measured rates are found to be significantly lower than for the $CN^- + HC_3N$ system. This decrease and the evolution of reactivity when going from CN^- to C_3N^- and the opening of a new detachment pathway are finally discussed.

1. Introduction

Ionic species are ubiquitous in space but it is only recently that the presence of negatively charged species has been evidenced. Although the question of their detection in the interstellar medium had been raised several decades ago (Herbst, 1981), the first detection of a negatively charged molecular species in an interstellar environment (C_6H^-) has been reported in 2006. Since then, several other anions (C_4H^-, C_8H^-, CN^-, C_3N^- and C_5N^-) have been observed either in dense clouds or in circumstellar envelopes (Agúndez et al., 2008, 2010; Brünken et al., 2007; Cernicharo et al., 2007, 2008; McCarthy et al., 2006; Thaddeus et al., 2008) and that changed the present view of inter- and circumstellar chemistry (Harada and Herbst, 2008; Millar et al., 2007; Walsh et al., 2009).

The presence of anions in the atmosphere of Titan had also been considered for a long time, but they were expected to lie in the cosmic-ray induced ionosphere, close to the surface, where pressure conditions enable three-body electron attachment processes (Borucki et al., 1987; Capone et al., 1976). The discovery of negative ions in the upper part of Titan's atmosphere in the frame of the Cassini–Huygens mission was thus completely unexpected (Coates et al., 2007; Waite et al., 2007) given the low pressure conditions prevailing there. Their presence was indeed inferred from data delivered by the electron spectrometer (ELS) of the CAPS (Cassini Plasma Spectrometer) instrument on board Cassini, *a priori* not dedicated to the measurement of ionic species. The mass-resolution obtained is thus quite poor but it is important to note that the spectra retrieved extend up to m/z 10 000. Additionally heavy positively charged species (up to m/z 350) were also observed in this region thanks to the ion beam sensor of CAPS (CAPS-IBS) and to the INMS (Ion Neutral Mass Spectrometer) instrument also on board the Cassini orbiter (Waite et al., 2007). The presence of such heavy species in significant abundances at high altitudes suggests that a more complex than previously thought ionospheric chemistry is at play, which is somehow related to the formation of the haze particles obscuring the surface

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of the satellite. Following measurements by CAPS, INMS and RPWS (Radio and Plasma Wave Science) instruments during appropriate flybys have allowed to confirm these results and to better characterize the distribution of the charged species in the 950–1400 km altitude range (Ågren et al., 2012; Coates et al., 2009; Crary et al., 2009; Shebanits et al., 2013; Wahlund et al., 2009). However some major questions remain opened, in particular concerning their chemical nature and reactivity. As stated above, given the poor resolution of the mass spectra retrieved, one can only speculate on the chemical nature of the anions observed in Titan's ionosphere. This ambiguity has been partially raised by the development of the first ionospheric model of Titan including negative ion chemistry (Vuitton et al., 2009) which provides some keys for the identification of the lower-mass anions. On the basis of this chemical model, the most likely candidates for the lighter anions are CN^-, C_3N^-/C_4H^- and C_5N^- with a significant contribution of polyyne-anions type (C_4H^- and C_6H^-) below 800 km. Yet, as underlined by the authors themselves, the chemical scheme suffers from a poor knowledge of negative ion-chemistry.

Actually the $C_{2p}H^-$ and $C_{2p+1}N^-$ species have triggered a lot of theoretical interest (e.g. Botschwina and Oswald, 2008a, 2008b; Harrison and Tennyson, 2011; Pascoli and Lavendy, 1999; Senent and Hochlaf, 2010; Wang et al., 1995; Zhan and Iwata, 1996). Their photoelectron spectroscopy has been investigated through a series of experiments by Neumark and co-workers (Bradforth et al., 1993; Garand et al., 2009, 2010; Sheehan et al., 2008a, 2008b; Taylor et al., 1998; Zhou et al., 2007) but, apart from some IR/UV spectra in rare-gas matrices (Coupeaud et al., 2008; Grutter et al., 1999; Kołos et al., 2008; Turowski et al., 2008) and rotational spectra (Amano, 2010; McCarthy et al., 2006; McCarthy and Thaddeus, 2008; Thaddeus et al., 2008), knowledge on their spectroscopy is still limited.

Owing to their presence in interstellar environments where atomic species and molecular hydrogen are their most probable collision partners, the reactions of $C_{2p}H^-$ and $C_{2p+1}N^-$ with O, N, H and H_2 have been studied both theoretically and experimentally (Barckholtz et al., 2001; Eichelberger et al., 2007; Snow et al., 2009; Yang et al., 2011, 2010) and studies of reactions with molecular species other than H_2 are scarce (Biennier et al., 2014; Botschwina and Oswald, 2010; Carles et al., 2011; Shi and Ervin, 2000; Žabka et al., 2012, 2014). In the context of the ionospheric chemistry of Titan, though, recent experimental efforts have been made to study the reaction of CN^- with cyanoacetylene (HC_3N), one of the neutral species abundantly present in Titan's upper atmosphere (e.g. Cui et al., 2009) and whose reaction with cyanide anion is identified as the main formation process of C_3N^- according to Vuitton et al. (2009).

In the present paper, we focus on the reaction of CN^- and C_3N^- with HC_3N. As suggested by previous results (Žabka et al., 2012), it could indeed be a potential pathway towards the production of larger species, especially C_5N^-, via the elimination of a HCN molecule. After a brief presentation of the experiments in Section 2, details on the experimental kinetic measurements performed are given in Section 3 and further discussed in Section 4. The last section, Section 5, presents some concluding remarks.

2. Experimental details

The experiments presented here have been performed on the MICRA (Mobile ICR Analyzer) set-up from the LCP in Orsay. A complete description of this apparatus can be found in Mauclaire et al. (2004). Briefly, MICRA is a compact mobile Fourier-Transform Ion Cyclotron Resonance Mass-Spectrometer (FTICR-MS) providing high-resolution mass-spectra and well-adapted for kinetic studies (Dehon et al., 2011).

Primary ions, CN^- and C_3N^-, are produced by dissociative electron attachment (DEA) from BrCN and BrC_3N. The formation of C_3N^- from BrC_3N and by DEA is unprecedented and opens the way for the production of cyanopolyyne anions. Cyanogen bromide (BrCN, 97%) is purchased from Sigma Aldrich. Bromocyanoacetylene (BrC_3N) is not a commercial product and is thus obtained by chemical synthesis following the procedure described in Cabezas et al. (2014) and Kloster-Jensen (1963). This is also the case for the cyanoacetylene (HC_3N and $HC_3{}^{15}N$) reactant molecule which is obtained according to the protocol reported by Miller and Lemmon (1967). To produce $C_3{}^{15}N^-$ parent anions, DEA cannot be used since $BrC_3{}^{15}N$ precursor is difficult to synthesize. $C_3{}^{15}N^-$ parent anions is thus obtained from the reaction of C_3N^- with $HC_3{}^{15}N$ (see Section 3.3) and isolated in the ICR trap thanks to the application of an appropriate RF sequence to eliminate all anions except $C_3{}^{15}N^-$. All the products were purified through several pump–thaw cycles prior to any use and their mass spectrometry analysis did not reveal the presence of major impurities.

The neutral precursor of the primary ions and the reactant gas are introduced via two separate gas-lines through independent three-way pulsed valves that direct the gas flow, either to the mass-spectrometer main chamber, or to a gas-inlet evacuation line. The admission of the different gases into the cell follows a well-defined sequence. A timing diagram for a typical measurement sequence is presented in Fig. 1 and detailed hereafter.

After a preliminary synchronization between the computer and the hardware [0], the parent ion neutral precursor BrCN (resp. BrC_3N) is introduced into the ICR cell ($P \approx 6.7 \times 10^{-7}$ mbar for 110 ms) [1]. A 300 ms low-energy electron pulse is then applied [2] to produce the CN^- (resp. C_3N^-) parent ions by DEA (Brüning et al., 1996; Royal and Orel, 2006) following:

$$BrCN + e^- \rightarrow CN^- + Br$$

$$BrC_3N + e^- \rightarrow C_3N^- + Br$$

Once the residual electrons have been ejected [3], the mass spectrum of the anions produced by DEA is checked. CN^- (resp. C_3N^-) is by far the major anion produced. A very small amount of Br^- ion is observed however, and an appropriate RF pulse is applied to eject it and keep the CN^- (resp. C_3N^-) parent anion only [4]. This method provides a clean way to completely prepare the reactant anion before the reaction to be studied starts. The reactant gas HC_3N (resp. $HC_3{}^{15}N$) is then admitted for a given period defined by the valve opening duration time t_{op} [5] which is increased step by step to vary the amount of reactant gas introduced. Following the beginning of the reactant gas introduction, the ions are allowed to react for a fixed 2000 ms-long period (t_{reac}). Parent and product ions are finally detected in a last step [6], before another sequence starts for a new value of t_{op}.

The pressure of the neutral reactant gas is adjusted with the valve maintained in open position (steady-state pressure – P_{cont} ranging from 1.3×10^{-7} to 2.1×10^{-6} mbar) before each series of measurements. The amount of gas contained in the gas pulse is expected to be proportional to P_{cont} and t_{op}. However, in order to insure a more precise control of this critical experimental parameter, a real-time pressure measurement $p(t)$ is performed over the whole reacting sequence. The integral $I_p = \int_0^{t_{reac}} p \cdot dt$ is thus equivalent to the real effective amount of cyanoacetylene introduced (see also Section 3.1) and is the variable used in the kinetics analysis. The $p(t)$ measurement is achieved by measuring the ion current on the collector of a Bayard-Alpert ionization gauge (Micro-ion gauge, Brooks automation) (Louarn et al., 2013). As the gauge sensitivity depends on the nature of the gas, an absolute calibration of the Bayard-Alpert gauge was carried out just before the measurements using a Baratron gauge (MKS Instruments,