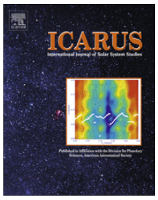
Icarus 227 (2014) 123–131

Contents lists available at ScienceDirect

Icarus

journal homepage: www.elsevier.com/locate/icarus



Low temperature reaction kinetics of $CN^- + HC_3N$ and implications for the growth of anions in Titan's atmosphere

Ludovic Biennier [a,*], Sophie Carles [a], Daniel Cordier [b], Jean-Claude Guillemin [c], Sébastien D. Le Picard [a], Alexandre Faure [d]

[a] *Institut de Physique de Rennes, Département de Physique Moléculaire, Astrophysique de Laboratoire, UMR CNRS 6251, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France*
[b] *Université de Franche-Comté, Institut UTINAM, CNRS/INSU, UMR 6213, 25030 Besançon Cedex, France*
[c] *Ecole Nationale Supérieure de Chimie de Rennes, UMR CNRS 6226, 11, Allée de Beaulieu, 35708 Rennes Cedex 7, France*
[d] *UJF-Grenoble 1/CNRS-INSU, Institut de Planétologie et d'Astrophysique de Grenoble (IPAG), UMR 5274, Grenoble F-38041, France*

ARTICLE INFO

Article history:
Received 21 June 2013
Revised 2 September 2013
Accepted 3 September 2013
Available online 21 September 2013

Keywords:
Titan, atmosphere
Atmospheres, chemistry
Ionospheres

ABSTRACT

The Cassini–Huygens probe has uncovered the existence of a profusion of negatively charged molecular species in the upper atmosphere of Titan (~950 km). The presence of large amounts of anions was unexpected and the chemical pathways leading to their formation mostly unknown. The investigation of the negative ion chemistry appears therefore to be a key factor for modeling Titan's upper atmosphere. We present here the first low temperature experimental kinetic study involving CN^-, proposed by Vuitton et al. (2009) to be one of the negative ions detected by the CAPS-ELS instrument onboard the Cassini spacecraft. The temperature dependence of the rate coefficient of the reaction $CN^- + HC_3N$, was explored over the 49–294 K temperature range in uniform supersonic flows using the CRESU technique. We find that the kinetics of this reaction is fast ($k \gtrsim 4 \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1}) and presents a weak negative temperature dependence which, considering the experimental error bars, agrees with long-range based capture theory. We also observe that $C_3N^- + HCN$ represents the main exit channel demonstrating that the studied reaction participates efficiently to the chemical growth of negative ions in the atmosphere of Titan.

1. Introduction

Negative ions have been discovered in various astrophysical environments during the last decade. So far, six anions have been detected in the gas phase in the interstellar medium through radio-astronomy on the basis of laboratory spectra: C_4H^-, C_6H^-, C_8H^-, CN^-, C_3N^- and C_5N^- (Cernicharo et al., 2007; McCarthy et al., 2006; Remijan et al., 2007; Brunken et al., 2007; Agundez et al., 2010; Thaddeus et al., 2008; Cernicharo et al., 2008). Latest research suggests that carbon chain anions are relatively abundant in a variety of interstellar objects and that their presence correlates with the abundance of their neutral counterparts (Cordiner et al., 2011). Closer to us, the presence of numerous negative ions has also been revealed in Titan's upper atmosphere by the Electron Spectrometer sensor of the Cassini Plasma Spectrometer (CAPS-ELS) on-board the Cassini spacecraft (Waite et al., 2007; Coates et al., 2007). Heavy ions up to 13,800 amu/q have been detected at the altitude of 950 km. Despite the low resolution of the spectrum ($\Delta m/m \sim 17\%$), three peaks at 22 ± 4, 44 ± 8 and 82 ± 14 amu/q can be distinguished on the low-mass side and were attributed to CN^-, C_3N^-/C_4H^- and C_5N^- by Vuitton et al. (2009) with the help of an ionospheric photochemical model. It is worth noting however, that most of the anion–molecule reactions present in the model have not been studied, especially below room temperature. It is therefore necessary to acquire laboratory data on the kinetics of elementary reactions involving anions including their branching ratios in relevant physical conditions in order to improve the accuracy of the predicted abundances of the molecular species. More experimental work has been performed on reactions involving neutral and positively charged ions. For instance, a critical review of the main processes involving nitrogen species, including N^+, N_2^+, N^{++} and N_2^{++}, relevant for Titan's atmosphere was recently published by Dutuit et al. (2013). Several studies (Waite et al., 2007; Vuitton et al., 2007, 2009; Krasnopolsky, 2009; Zabka et al., 2012) have also highlighted the importance of positive and negative ion-neutral chemistry in the molecular growth in the upper atmosphere of Titan. A recent experimental work by Zabka et al. (2012) showed that in the multiple collision regime, negative ion chemistry could lead to the formation of large anions. Using a model coupling aerosol microphysics and photochemistry, Lavvas et al. (2013) established that the formation of aerosols is directly related to ion processes

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[*] Corresponding author.
E-mail address: ludovic.biennier@univ-rennes1.fr (L. Biennier).

http://dx.doi.org/10.1016/j.icarus.2013.09.004

in Titan's upper atmosphere, revealing the fundamental role of ion chemistry and the consequent importance of determining accurately the kinetics of the chemical reactions involved.

The dense atmosphere of Titan has revealed a rich organic chemistry initiated by the dissociation and ionization of N_2 (composing 90–98% of the atmosphere) and CH_4 (1–6%) by energetic solar photons combined with Saturn magnetospheric electrons (Niemann et al., 2005; Waite et al., 2005, 2007). Decades of astronomical observations have led to the identification of a wealth of hydrocarbons and nitrogen-bearing species. Among those molecular compounds, acetylene C_2H_2 and polyynes such as di-acetylene C_4H_2 have been detected and their abundance established (Coustenis et al., 2007; Waite et al., 2005, 2007). Larger polyynes such as C_6H_2 and C_8H_2 are also likely to be present. All these compounds are suspected to play a major role in molecular growth. In addition to HCN, a large variety of nitriles are generated such as CH_3CN (Marten et al., 2002), HC_3N, C_2N_2 (see Coustenis et al., 2010, and references therein) and – in the condensed form – C_4N_2 inferred from earlier Voyager infrared observations (Coustenis et al., 1989). Even though nitriles and hydrocarbon molecules occur only in trace amounts, they are of particular importance because they are considered to be key ingredients and building blocks to form Titan's organic, aerosol-particle based haze layers which blacken the surface (Wilson and Atreya, 2003). The aerosol composition is yet unknown but Cassini's Composite Infrared Spectrometer (CIRS) far infrared observations uncovered a correlation between the haze and HC_3N abundance that could then represents a good tracer (Jennings et al., 2012).

According to the model proposed by Vuitton et al. (2009), CN^- and C_3N^- are the most abundant ions around 1000 km, while C_5N^- becomes prominent below 850 km. CN^- is mainly produced by dissociative attachment of supra-thermal electrons on HCN and HC_3N and is essentially destroyed by associative detachment with H and CH_3 and through reaction with HC_3N. Interestingly, HC_3N is assumed to play a role both in the production and the destruction of CN^-. Reactions between these charged species and neutral molecules are expected to be involved in the growth of anions by triggering a chain of polymerization reactions. It is therefore important to understand the mechanisms involved, which can be better inferred by comparing kinetics experimental measurements to theoretical predictions. Apart from recent studies focusing on the reactions of C_mN^- ($m = 1$–6) with H atoms (Snow et al., 2009; Yang et al., 2011) and of CN^- with cyanoacetylene (Carles et al., 2011; Zabka et al., 2012), little is known about the reactivity of CN-bearing anions, and to our knowledge, no kinetics measurements involving these compounds exist below room temperature. More generally, only a handful of laboratory studies have indeed investigated the temperature dependence of the rate coefficients of reactions involving anions below 200 K. Three different types of experiments can be distinguished. The first one is based on a temperature variable radiofrequency ion trap. This technique, capable of cooling molecular ions to below 10 K in all degrees of molecular freedom, was successfully used to measure the reaction of $NH_2^- + H_2$ down to 8 K (Otto et al., 2008). The second method employs a liquid nitrogen cooled selected ion flow tube (SIFT) and can measure reactions down to 88 K. It has been used to investigate the associative detachment reactions of $O^- + NO$, $S^- + CO$ and $S^- + O_2$ and the rate coefficients and branching ratios for the reactions of $O^- + C_2H_2$ and $O^- + C_2H_4$ (Viggiano and Paulson, 1983). The third approach makes use of supersonic uniform flows providing wall-less reactors down to very low temperatures, in which molecules can easily be introduced at very high degrees of supersaturation. The method hence called CRESU, a French acronym for Cinétique de Réaction en Ecoulement Supersonique Uniforme, was used to measure the kinetics of the reaction of Cl^- with CH_3Br down to 23 K (Le Garrec et al., 1997).

We present here the first low temperature kinetics study involving CN^-, reacting with HC_3N, one of the most abundant nitrogen-bearing molecule in Titan's ionosphere around 1000 km (Vuitton et al., 2009). The temperature dependence of the rate coefficient of this reaction was measured from 49 to 294 K using the CRESU technique. The temperature dependence of the reaction was well reproduced theoretically using the infinite-order sudden (IOS) approximation combined with the capture theory (Clary, 1990). Charged products were also experimentally identified, allowing us to provide some insights into the growth of anions in the cold upper atmosphere of Titan.

2. Laboratory experiments

2.1. Experimental apparatus

The kinetics of reaction of CN^- anions with cyanoacetylene, HC_3N, is explored using the CRESU technique, which has been described in details elsewhere (Rowe et al., 1984). Only specific features are provided hereafter. Fig. 1 displays a schematic diagram of the experimental setup. An axially and radially symmetric uniform supersonic beam is generated by the isentropic expansion of a buffer gas (helium in the present experiments) through a Laval nozzle. Upstream of this nozzle, helium is continuously introduced into a reservoir by a calibrated mass flow controller at a typical flow rate of 50–100 slm (standard $l\,\mathrm{min}^{-1}$). Downstream, in the main chamber, the supersonic expansion generated by the nozzle is maintained by a 24,000 $\mathrm{m}^3\,\mathrm{h}^{-1}$ capacity pumping system. The design of the nozzle, as well as the pressures in the reservoir (a few tens of mbar) and in the main chamber (a few tenths of mbar), set the temperature of the supersonic flow. The velocity (several $10^4\ \mathrm{cm\,s}^{-1}$), the density (typically 10^{16}–10^{17} molecule cm^{-3}) and the low temperature of the supersonic flow are kept uniform over several tens of centimeters corresponding to hydrodynamic times of about 100–1000 μs. All other neutral gases necessary for the study of the title reaction are introduced in small amount into the reservoir by means of calibrated mass flow controllers. Due to the relatively high density of the flow, frequent collisions occur ensuring thermal equilibrium for all the molecular species present in the supersonic expansion.

An electron beam, produced by an electron gun (12 kV, 200 μA), crosses the supersonic neutral flow at 90°, downstream of the nozzle, generating a low density plasma, consisting primarily of buffer gas cations (He^+ here) and electrons ($[e^-] \sim 10^8$–$10^9\ \mathrm{cm}^{-3}$). Downstream along the axis of the supersonic flow, a movable quadrupole mass spectrometer (0–200 amu/q) coupled with a Langmuir probe (a loop of 25 μm diameter gold plated tungsten wire and 8.84 ± 0.05 mm long) allows to measure the ion signal and the electron density in the supersonic flow by skimming out a central portion of the flow.

One of the main difficulties of the present experiments is to generate CN^- ions rapidly and abundantly. To achieve this, negative ions are produced by dissociative electron attachment of cyanogen bromide BrCN vapors (Sigma Aldrich) previously diluted in helium (2% mole fraction) and injected into the reservoir. The exit channels for this reaction are (Bruning et al., 1996):

$$\mathrm{BrCN} + e^-(\leqslant 0.5\mathrm{eV}) \rightarrow \mathrm{Br} + \mathrm{CN}^- \tag{1}$$

$$\rightarrow \mathrm{Br}^- + \mathrm{CN} \tag{2}$$

As one can see on a typical ion spectrum recorded at a reaction time of 75 μs in a 157.5 K supersonic He flow (Fig. 2), the first exit channel clearly dominates the reaction. This is consistent with low energy electron attachment studies which determined a large cross section of $5.05 \times 10^{-14}\ \mathrm{cm}^2$ for that exit channel at 0 eV (Alajajian et al., 1988).