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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: $(3.9 \pm 0.5)\ 10^{-9}$ and $(1.0 \pm 0.2)\ 10^{-10}$ $cm^3.s^{-1}$ 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 to 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 is finally discussed.

Keywords

chemistry, reactivity, experiments, anions, cyanide, cyanoacetylide, ionosphere, Titan, kinetics, FTICR-MS

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 circumstellar envelopes (Agúndez et al., 2008; Agúndez et al., 2010; Brünken et al., 2007; Cernicharo et al., 2007; Cernicharo et al., 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).

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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 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; Botschwina and Oswald, 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; Garand et al., 2010; Sheehan et al., 2008a; Sheehan et al., 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; Yang et al., 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., 2014; Žabka et al., 2012). In the context of the ionospheric chemistry of Titan, though, recent experimental efforts have been made to study the

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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; 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 Lemon (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 synthetize. $C_3{}^{15}N^-$ parent anions is thus obtained from the reaction of C_3N^- with $HC_3{}^{15}N$ (see § 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 directs 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.

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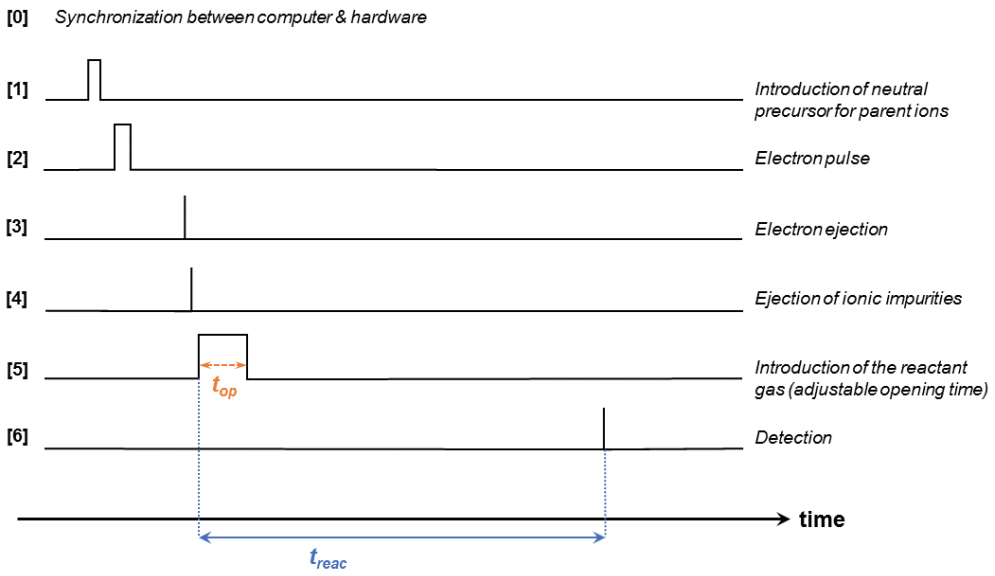


Fig. 1. Typical timing-diagram for a measurement sequence. **Typical durations for each sequence are: 100 ms for [1], 300 ms for [2], from 0 to 1500 ms for [5] and 2000 ms for [6].** Note that, if necessary, additional steps can be inserted to thermalize the primary ion with a pulse of He before the introduction of the reactant gas.

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 ($P \approx 6.7.10^{-7}$ 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 $I_p = \int_0^{t_{reac}} p.dt$ is thus equivalent to the real effective amount of cyanoacetylene introduced (see also § 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,

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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, Model 270B). The correcting factors extracted from the calibration for N_2 and HC_3N are 1.01 and 2.93 respectively. The close to one value obtained for N_2 was expected since Bayard Alpert gauges are factory calibrated for nitrogen. Note also that the result for HC_3N is close to the value calculated using the ratio of HC_3N to N_2 polarizabilities which is 3.33 (Woon and Herbst, 2009).

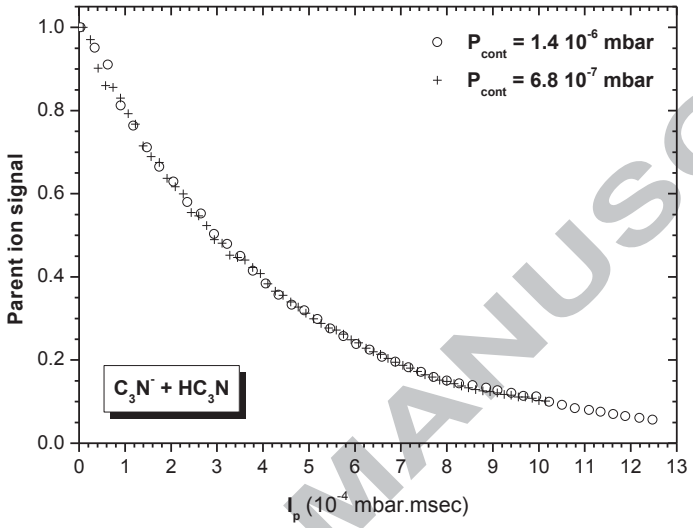


Fig. 2. Typical evolution of the C_3N^- primary ion signal for the reaction of C_3N^- with HC_3N using two different steady-state pressure (P_{cont}) conditions of the neutral reactant gas.

As an illustration, two series of measurements obtained for different HC_3N steady-state pressures are presented in Fig. 2. In this figure, the normalized intensity of the parent ion signal is plotted as a function of I_p so that, within the same series of measurements, each point corresponds to the ion signal for a given opening duration of the HC_3N admission valve t_{op}.

Note also that an additional sequence [4'] consisting in a 50 ms pulse of helium was inserted between [4] and [5] in order to thermalize the parent ions just formed to check to what extent kinetic energy and/or partial excitation of the parent ion could affect the rate constants. In the following, we will refer to the series of experiments performed without [4'] as "without thermalization" in opposition to the "with thermalization" ones.

3. Kinetic measurements

3.1. Data analysis and rate coefficient determination for CN^- + HC_3N

Fig. 3 presents a kinetic measurement relative to the CN^- + HC_3N reaction. As can be seen on this figure, the CN^- primary ion disappears and formation of the C_3N^- anion resulting from an efficient proton-transfer is observed:

$$CN^- + HC_3N \rightarrow HCN + C_3N^-$$

No other ionic product is observed as previously reported by several authors (Biennier et al., 2014; Carles et al., 2011; Žabka et al., 2012). Moreover, as, within experimental uncertainties, the C_3N^-

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production rate is found to be the same as the CN^- destruction rate over the range of I_p values probed here, it can be concluded that the proton transfer is the main channel for this reaction.

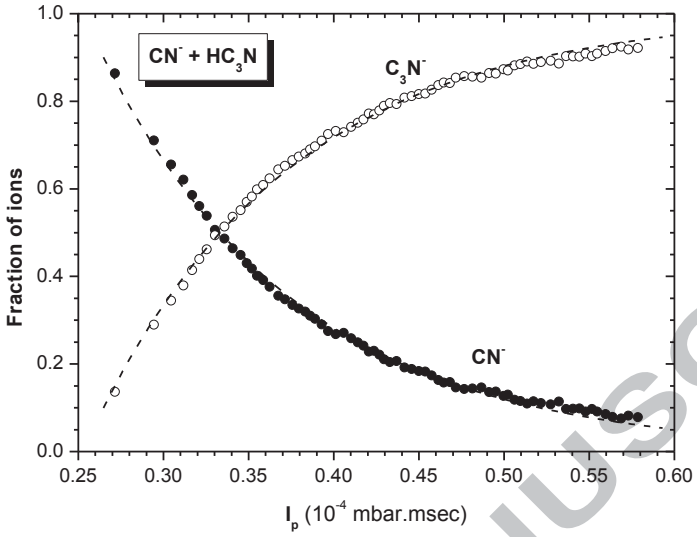


Fig. 3. Evolution of the normalized primary (CN^-) and product (C_3N^-) ion signals for the reaction of CN^- with HC_3N. Fits of the experimental data are indicated by dashed lines.

From these measurements, it is possible to retrieve the kinetic rate constant of the CN^- + HC_3N reaction considering that the decrease of the CN^- parent ion follows:

$$\frac{d[CN^-]}{dt} = -k.[CN^-].[HC_3N]$$

with $[X]$, the number of X molecules per unit of volume and k, the bimolecular rate constant in $cm^3.s^{-1}$. This expression indeed leads to:

$$[CN^-]_{t_{reac}} = [CN^-]_0.\exp\left(-k.\int_0^{t_{reac}}[HC_3N].dt\right)$$

which can also be written:

$$[CN^-]_{t_{reac}} = [CN^-]_0.\exp\left(-\frac{k}{k_b.T}.I_p\right)$$

since:

$$I_p = \int_0^{t_{reac}} p.dt = k_b.T\int_0^{t_{reac}}[HC_3N].dt$$

with k_b the Boltzmann's constant.

Fitting of the experimental data to an exponential leads to values of $(3.9 \pm 0.5)\ 10^{-9}$ $cm^3.s^{-1}$ and $(3.5 \pm 0.4)\ 10^{-9}$ $cm^3.s^{-1}$ for k, when the experiment is performed at 300 K, respectively with and without thermalization of the primary ion before reaction. The uncertainties presented here correspond to the quadratic sum of the statistical error on the fit and the uncertainty (10 %) on the absolute value of the target pressure. These two values are in excellent agreement with the value of $3.8^{+1.9}_{-0.8}\ 10^{-9}$ $cm^3.s^{-1}$ already reported in the literature by (Biennier et al., 2014) at 294 K in the CRESU apparatus (Reaction Kinetics in Uniform Supersonic Flow) and in good agreement, within error bars, with the

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larger value of (4.8 ± 1.4) 10^{-9} $cm^3.s^{-1}$ reported by (Carles et al., 2011) at room temperature in a Flowing Afterglow Langmuir Probe - Mass Spectrometer (FALP-MS). This also confirms that in our experiments CN^- is certainly formed with very little energy in excess as expected.

3.2. Investigation of the C_3N^- + HC_3N reaction

The reaction of C_3N^- with cyanoacetylene has been studied using the experimental protocol reported above for CN^- and HC_3N. As in the previous system, the occurrence of the proton-transfer channel:

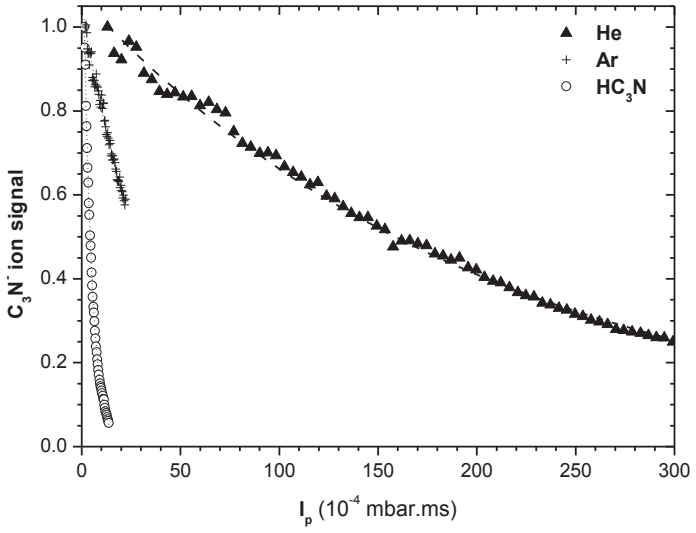
$$C_3N^- + HC_3N \rightarrow HC_3N + C_3N^-$$

was anticipated. However, it would lead to a C_3N^- product anion that cannot be distinguished from the primary ion. According to the experimental and theoretical results previously obtained (Žabka et al., 2014; Žabka et al., 2012), the formation of the heavier C_5N^- anion associated with the loss of a HCN molecule:

$$C_3N^- + HC_3N \rightarrow C_5N^- + HCN$$

was observed but in small quantities and only in a regime of multiple collisions at higher pressures of the target gas. Therefore, it was important to characterize its formation in a single collision regime.

In our work here, no ionic product different from the C_3N^- parent-ion was detected despite a clear decrease of the primary-ion signal (see Fig. 2). Note that, this C_3N^- loss is observed at much higher values of I_p than the ones used for the CN^- + HC_3N reaction, thus explaining why it is not visible in Fig. 3. The rate constant associated with the disappearance of the C_3N^- ion, when these experiments are performed at 300 K, was found to be equal to (1.0 ± 0.2) 10^{-10} $cm^3.s^{-1}$ and (1.0 ± 0.1) 10^{-10} $cm^3.s^{-1}$ respectively with and without thermalization of the primary ion by He before reaction. This rate constant being quite low and in absence of any ionic product, a series of control experiments in which the reactant gas HC_3N was replaced by rare-gas of different masses (He and Ar) has been carried out to check whether the observed decrease could be due to the diffusion of C_3N^- out of the cell because of non-reactive collisions or to direct collisional detachment although rather unlikely given the high electron affinity of C_3N^-. Results from these experiments are presented in Fig. 4.



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Fig. 4. Decrease of the C_3N^- primary ion signal resulting from collisions of C_3N^- with: (a) the reactant gas HC_3N (open circle), P_{cont} = 1.4 10^{-6} mbar; (b) Ar (cross), P_{cont} = 2.1 10^{-6} mbar; (c) He (solid triangle) P_{cont} = 3.3 10^{-6} mbar. Fits of the experimental data are indicated by dashed lines.

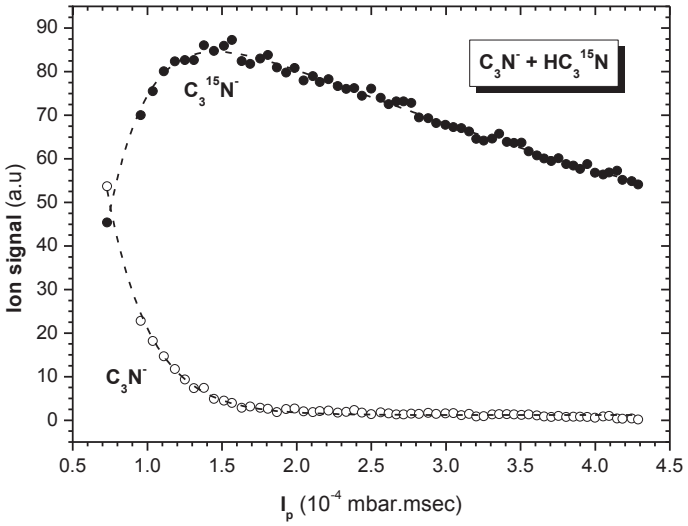
As can be seen from this figure, the decrease observed for the primary ion in presence of cyanoacetylene is of no comparison with the ones observed with rare-gas. The bimolecular rate constants retrieved from the exponential fit of these data lead indeed to much lower values than the ones observed with HC_3N (2 10^{-12} and 1 10^{-11} $cm^3.s^{-1}$ for He and Ar respectively). The observed behaviour is therefore likely attributable to a reactive process leading to one or several neutral products known respectively as associative detachment (AD) or reactive detachment (RD). In our case, a straightforward AD process would lead to a stable neutral product of molecular formula HC_6N_2. The energetics and the structure of this neutral product will be discussed later (see Section 4.1.) as well as the implications such a process may have on the hypothesis of a growth mechanism of $C_{2p+1}N^-$ species by ion-molecule reaction (see Section 4.3.).

3.3. Investigation of the C_3N^- + $HC_3{}^{15}N$ reaction

In order to further investigate the proton transfer channel, the first way to differentiate the parent and product anions, is to use an isotopic labelled target, $HC_3{}^{15}N$. The synthesis of the labelled cyanoacetylene follows the same scheme except that one starts from the ^{15}N labelled ammonium chloride ($^{15}NH_4Cl$) (99% ^{15}N from Cortecnet Europe) to produce ammonia, $^{15}NH_3$. A rapid conversion of the parent ion into its isotopic homologue is observed:

$$C_3N^- + HC_3{}^{15}N \rightarrow HC_3N + C_3{}^{15}N^-$$

together with a moderately rapid loss of the ionic product as shown in Fig. 5. This evolution is consistent with the existence of a competing AD or RD channel and can be accounted for by the reaction scheme proposed in Fig. 6. The ionic product, $C_3{}^{15}N^-$, resulting from the proton transfer can indeed react itself with the surrounding neutral reactant $HC_3{}^{15}N$ leading, either to an ion of same nature ($C_3{}^{15}N^-$) *via* proton-transfer (transparent for the kinetics as for the C_3N^- + HC_3N reaction), or to a neutral product through a slower AD/RD process. This latter channel would thus be responsible for the partial loss of the ionic product observed.



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Fig. 5. Evolution of the primary (C_3N^-) and product ($C_3{}^{15}N^-$) ion signals for the reaction of C_3N^- with $HC_3{}^{15}N$. Fits of the experimental data are indicated by dashed lines.

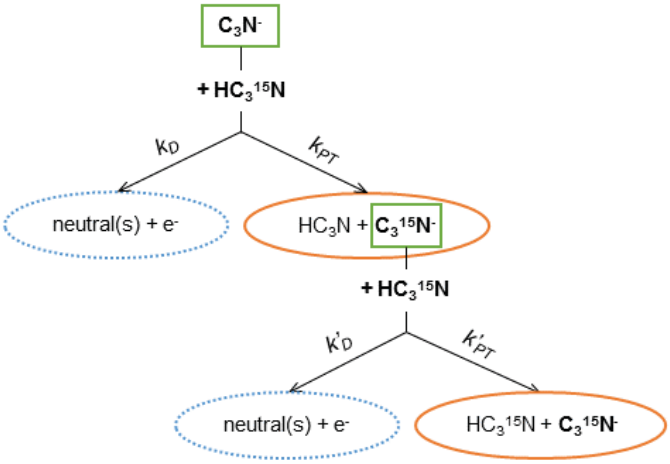


Fig. 6. Chemical scheme for the reaction of C_3N^- with $HC_3{}^{15}N$. The D and PT subscripts refer respectively to detachment (either associative or reactive) and proton transfer while the *k'* refers to subsequent reactions of the $C_3{}^{15}N^-$ ionic product.

Assuming this hypothesis, a global fit of the primary and product ions data set shown on Fig. 5 (dashed lines) has allowed us to retrieve the global rate constant $k = k_D + k_{PT}$ and k'_D for each reaction. The values obtained are summarized in Table 1. As k_D and k_{PT} cannot be determined separately, it has been assumed that $k_D \simeq k'_D$, which is reasonable according to the fact that all the measured k_D values for the C_3N^- + HC_3N, C_3N^- + $HC_3{}^{15}N$ and $C_3{}^{15}N^-$ + HC_3N reactions have been found to be very similar. An estimate for k_{PT} can thus be retrieved from: $k_{PT} \simeq k - k'_D$ and is also given in Table 1.

Reactive system	**Products of reaction**	**Kinetic rate constants[a] ($cm^3.s^{-1}$)**		
			without thermalization	*with thermalization*
CN^- + HC_3N	HCN + C_3N^-	k_{PT}	$(3.5 \pm 0.4)\ 10^{-9}$	$(3.9 \pm 0.5)\ 10^{-9}$
C_3N^- + HC_3N	neutral(s) + e^-	k_D	$(1.0 \pm 0.1)\ 10^{-10}$	$(1.0 \pm 0.2)\ 10^{-10}$
C_3N^- + $HC_3{}^{15}N$		k	$(1.4 \pm 0.2)\ 10^{-9}$	$(1.5 \pm 0.2)\ 10^{-9}$
	neutral(s) + e^-	k'_D	$(7 \pm 2)\ 10^{-11}$	$(7.0 \pm 0.9)\ 10^{-11}$
	HC_3N + $C_3{}^{15}N^-$	k_{PT}[b]	$(1.3 \pm 0.3)\ 10^{-9}$	$(1.4 \pm 0.3)\ 10^{-9}$
$C_3{}^{15}N^-$ + HC_3N		k	$(1.2 \pm 0.2)\ 10^{-9}$	
	neutral(s) + e^-	k'_D	$(8.0 \pm 0.9)\ 10^{-11}$	
	$HC_3{}^{15}N$ + C_3N^-	k_{PT}[b]	$(1.1 \pm 0.3)\ 10^{-9}$	

Table 1. Kinetic data for the reactions of CN^- and C_3N^- with HC_3N.

[a] The values presented here result from the average of several independent measurements performed for different steady-state pressure conditions of cyanoacetylene.

[b] k_{PT} is obtained from $k = k_D + k_{PT}$ assuming that $k_D \approx k'_D$.

3.4. Investigation of the $C_3{}^{15}N^-$ + HC_3N reaction

Using ^{15}N labelled parent **anions** is a second way to characterize the proton-transfer:

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$$C_3{}^{15}N^- + HC_3N \rightarrow HC_3{}^{15}N + C_3N^-$$

Similar observations have been made for the reaction of $C_3{}^{15}N^-$ with HC_3N as for the previous reaction in section 3.3 and the same chemical scheme as the one described in Figure 6 (replacing all C_3N^- and HC_3N by $C_3{}^{15}N^-$ and $HC_3{}^{15}N$, and *vice-versa*) is therefore assumed. Results from these experiments are presented in Figure 7 while the corresponding rate constants $k = k_D + k_{PT}$ and k'_D are summarized in Table 1.

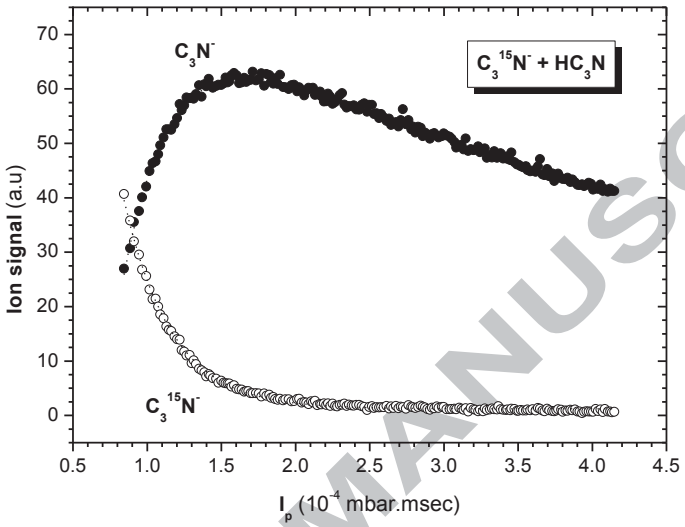


Fig. 7. Evolution of the primary ($C_3{}^{15}N^-$) and product (C_3N^-) ion signals for the reaction of $C_3{}^{15}N^-$ with HC_3N. Fits of the experimental data are indicated by dashed lines.

Before concluding this Results section, it is worth noting that the decrease of the (total) rate constant observed when going from CN^- + HC_3N to C_3N^- + $HC_3{}^{15}N$ and $C_3{}^{15}N^-$ + HC_3N cannot be accounted for by the sole change in the reduced mass of the reactive system. It would indeed lead to a more moderate decrease (see Section 4.2.). It is also important to note that the kinetic rate constants measured for the proposed associative/reactive detachment process are well within the order of magnitude reported in the literature for such reactions e.g. (Fehsenfeld et al., 1967; Ferguson, 1970), see also the 5.4 10^{-10} $cm^3.s^{-1}$ value measured by (Snow et al., 2009; Yang et al., 2011) for the AD reaction of C_3N^- with H.

4. Discussion

4.1. Reactivity of CN^- and C_3N^- with HC_3N

From our experimental results, it appears first that the proton transfer (PT) from CN^- to HC_3N is by far the dominant reactive pathway for the CN^- + HC_3N system as no other channels have been observed within our detection limits. So, if any, the rate constant associated to potential RD/AD channels would be much lower than the one obtained for PT. The PT transfer is also found to be 11 $kJ.mol^{-1}$ exothermic according to related quantum chemistry calculations by (Žabka et al., 2014) in good agreement with values obtained by (Biennier et al., 2014; Yang et al., 2011). This is not the case for RD/AD channels for which no exothermic pathways have been found (Biennier et al., 2014; Maergoiz et al., 1996; Yang et al., 2011), (see Table 2 for data on the energetics of the different pathways). Note however, that, for what concerns a possible AD process leading to a neutral $NC_2(H)C_2N$ species, the detachment step from the $NC_2(H)C_2N^-$ reactive intermediate is not the limiting

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one since it has been estimated as slightly exothermic (Δ_rH = -1.2 kJ.mol^{-1}) (Yang et al., 2011). HNC_4N^- and $NC(H)C_3N^-$ reactive intermediates have also been considered by these authors and they have been found to lie above the entrance channel.

Reactive system	Products of reaction		Δ_rH (kJ.mol^{-1})	Refs
$CN^- + HC_3N$	$HCN + C_3N^-$	PT	-11	a
	$HNC + C_3N^-$	**ISO1**	**≥ 42**	**b, g, h, i**
	$NCC(H)C_2N + e^-$	AD	133	b
	$CN^- + HNC_3$	**ISO2**	**≃ 200**	**b**
	$CN + HC_3N + e^-$	DD	372.6	c
	$HCN + C_3N + e^-$	RD	404.4	a, d
$C_3N^- + HC_3N$	$HC_3N + C_3N^-$	PT	0	
	$HCN + C_5N^-$	RC1	-36	a
	$HC_5N + CN^-$	RC2	-7	a, b
	$HNC + C_5N^-$	RC3	22.1	a, b
	$NC_4(H)C_2N + e^-$	AD	150	a, e, f
	$HNC_3 + C_3N^-$	**ISO3**	**≃ 200**	**b**
	$HNC_5 + CN^-$	**ISO4**	**≥ 236**	**b**
	$C_6N_2 + H + e^-$	**RD1**	**≥ 255**	**j, k, l, m**
	$HCN + C_5N + e^-$	**RD2**	393	a, d
	$HC_5N + CN + e^-$	**RD3**	366	a, b, d
	$HC_3N + C_3N + e^-$	DD	415.3	d

Table 2. Energetics of some selected pathways for the reactions of CN^- and C_3N^- with HC_3N.
a: (Žabka et al., 2014), b: (Yang et al., 2011), c: (Bradforth et al., 1993), d: (Yen et al., 2009), e: this paper, f: (Loison), g: (Chase, 1998), h: (Hansel et al., 1998), i: (Nguyen et al., 2015), j: (Francisco and Richardson, 1994), k: (Moffat and Knowles, 1969), l: (Harland, 1986), m: (Halpern et al., 1988)
The abbreviations refer to the type of process involved; *i.e.* PT stands for Proton Transfer, **ISO for isomerisation**, AD for Associative Detachment, DD for Direct detachment, RC for Reactive Channel, and RD for Reactive Detachment.

The situation is less clear for the reaction of the C_3N^- anion with cyanoacetylene. Apart from the **thermoneutral** PT channel, two reactive exothermic pathways are opened (RC1 and RC2) (Loison; Yang et al., 2011; Žabka et al., 2014). Yet, neither CN^- nor C_5N^- have been observed in our experiments. This is nevertheless consistent with the existence of one or more transition states whose energy would lie close to (Žabka et al., 2014) or above (Loison) the entrance channel and thus preclude the formation of the products. What is more puzzling is the experimental pieces of evidence in favour of a competitive detachment pathway although estimated as highly endothermic by calculations. Among the different channels considered in Table 2, the AD channel leading to $NC_4(H)C_2N + e^-$ seems however more likely given the large electron affinities of CN, C_3N and C_5N discarding the DD, **RD2 and RD3** channels. Moreover, two independent theoretical calculations (Loison; Žabka et al., 2014) indicate that the $NC_4(H)C_2N^-$ reactive intermediate is associated to a deep well (Δ_rH = -166 kJ.mol^{-1}). So, unlike for the $NC_2(H)C_2N^-$ case discussed above, here the endothermicity of the AD channel would rather stem from the detachment step, since the estimation of the EA for $NC_4(H)C_2N$ leads to an adiabatic value of 3.28 eV (CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level of theory, see Fig. 8 for the optimized geometries) suggesting that the electron is quite tightly bound.

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Fig. 8. Optimized geometries for the $NC_4(H)C_2N^-$ reactive intermediate and its neutral $NC_4(H)C_2N$ counterpart.

The hypothetical neutral compound whose molecular formula would be HC_6N_2 might indeed not be really stable. To our knowledge, the only experimental evidence for the existence of such a compound has been reported by Zwier in 2010 (Zwier, 2010) as a product of the reaction of HC_3N^* + HC_3N where HC_3N^* refers to cyanoacetylene in a metastable state. Note however, that an additional RD path likely involving $NC_4(H)C_2N^-$ **(path RD1)** could have been considered as well: C_6N_2 + H + e^-, since dicyanodiacetylene (C_6N_2) has been found to form quite efficiently from C_3N + HC_3N^* both in the gas and in the solid phase (Crepin et al., 2011; Seki et al., 1996). Yet the estimated heat of reaction for this alternative RD channel is again endothermic by more than 255 kJ.mol^{-1} (and up to 400 kJ.mol^{-1} depending on the values taken for the heats of formation of C_3N, HC_3N and C_6N_2) (Francisco and Richardson, 1994; Halpern et al., 1988; Harland, 1986; Moffat and Knowles, 1969).

To conclude, the reaction of CN^- with HC_3N proceeds dominantly through the exothermic PT pathway while the reaction of C_3N^- with HC_3N is more complicated than expected. In the latter case, PT does occur but at a lower rate and has no effect on the amount of C_3N^- ions as long as the ^{14}N species are concerned. The RC3 pathway associated with the growth of the parent anion into the following member of the $C_{2p+1}N^-$ series is not observed though exothermic, but a competitive AD channel does open. Theoretical calculations suggest that the $NC_4(H)C_2N^-$ reactive intermediate is implied but the molecular structure of the possibly neutral compound formed cannot be safely inferred and other reactive intermediates may be at play. The potential surface is indeed rather complicated and some less energetic paths leading to the detachment of the electron cannot be ruled out. It should also be pointed out that, among the $C_{2p+1}N/C_{2p+1}N^-$ radical/anion series, the C_3N/C_3N^- pair seems to mark a frontier in the evolution of molecular properties. Several theoretical studies have indeed underlined that when p goes from 1 to 2, both the electronic ground state and the dipole moment sign of the radicals switch respectively from $^2\Sigma$ to $^2\Pi$ and from minus to plus (Botschwina and Oswald, 2008a; Carelli et al., 2014; Pauzat et al., 1991). This change in molecular properties might somehow also affect reactivity. It is nevertheless clear that, according to our results, a residual excitation of the parent ion cannot be invoked to explain the detachment of the electron.

4.2. Comparison to models of capture

It is always useful to compare measured experimental rate constants to model calculations. In particular, for exothermic ion-molecule reactions governed by long range interactions such as ion – induced dipole and ion – permanent dipole, various methods have been used to evaluate the capture cross sections or rate constants and their thermally averaged values. They are extensions of the Langevin-Gioumousis-Stevenson (LGS) model (Gioumousis and Stevenson, 1958; Langevin, 1905) to non-central interactions with either approximations of the θ dependence (where θ is the angle between the directions of the permanent dipole and the vector connecting the two collision partners) (Barker and Ridge, 1976; Bass et al., 1975; Bates, 1981; Bates, 1983; Dugan Jr, 1973; Gupta

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et al., 1967; Moran and Hamill, 1963; Su and Bowers, 1973; Su and Bowers, 1975; Su et al., 1978) or semi-classical approaches to treat the rotational dependence (Sakimoto, 1981; Sakimoto, 1984), classical trajectory (CT) (Chesnavich et al., 1980; Dugan and Magee, 1967; Maergoiz et al., 1996; Su, 1988; Su, 1994; Su and Chesnavich, 1982), statistical (Barker and Ridge, 1976; Celli et al., 1980; Chesnavich et al., 1980; Quack and Troe, 1975; Troe, 1985; Troe, 1987; Troe, 1996) and quantum scattering (Clary, 1984; Clary, 1985; Clary, 1990; Clary and Henshaw, 1987) calculations. It is important to note that the general idea followed in these models is that once the capture is reached, the reaction is supposed to occur with unit probability. Therefore, if the reaction mechanism is really going only through an intimate complex, the values derived from the model are usually upper bound values of the reaction cross sections or rate constants as the complex can partially decompose back towards the reactant channel.

Model	$CN^- + HC_3N$		$C_3N^- + HC_3N$ [i]		Refs
	k/k_{LGS}	k (10^{-9} $cm^3.s^{-1}$)	k/k_{LGS}	k (10^{-9} $cm^3.s^{-1}$)	
LGS (C = 0)	1	1.36	1	1.13	a
Locked Dipole (C = 1)	7.05	9.62	7.05	7.94	b
CT 1982	3.18	4.33	3.18	3.58	c
CT 1988	3.42	4.66	3.42	3.85	d
CT 1996	3.252	4.44	3.249	3.66	e
SACM 1996	3.253	4.44	3.253	3.66	f
AC-IOSA (C = 0.25)	2.51	3.43	2.51	2.83	g
Experiment with He	2.88 [h]	3.93 ± 0.46 [h]	1.36 [j]	1.53 ± 0.18 [j]	
Experiment without He	2.54 [h]	3.46 ± 0.37 [h]	1.23 [j]	1.39 ± 0.17 [j]	
			1.07 [k]	1.21 ± 0.17 [k]	

a: Langevin-Gioumousis-Stevenson (Gioumousis and Stevenson, 1958; Langevin, 1905)
b: Locked Dipole (Gupta et al., 1967; Moran and Hamill, 1963)
c: Classical Trajectories (Su and Chesnavich, 1982);
d: Classical Trajectories (Su, 1988);
e: Classical Trajectories (Maergoiz et al., 1996);
f: Statistical Adiabatic Channel Model (Troe, 1996);
g: Combined Adiabatic Capture – Infinite Order Sudden Approximation (Clary, 1990);
h: PT channel for the CN^- + HC_3N reaction
i: The same reduced mass, calculated for C_3N^- + HC_3N, has been used in all the column but the differences on k values relative to ^{15}N labelled reactions which scales as $\mu^{1/2}$ is about 0.5 % only, hence lower than experimental uncertainties.
j: Sum of the PT and AD channels for the C_3N^- + $HC_3{}^{15}N$ reaction
k: Sum of the PT and AD channels for the $C_3{}^{15}N^-$ + HC_3N reaction

Table 3. Calculated and experimental rate constants at 300 K for the CN^- + HC_3N, C_3N^- + $HC_3{}^{15}N$ and $C_3{}^{15}N^-$ + HC_3N reactions. The values of HC_3N polarizability and permanent dipole moment used in the calculations are taken from (Woon and Herbst, 2009) and (DeLeon and Muenter, 1985) respectively and are $\alpha/4\pi\varepsilon_0$ = 5.848 $Å^3$ and μ_D = 3.73172 Debye.

We have first compared our results to the two extreme models, the LGS model (Gioumousis and Stevenson, 1958; Langevin, 1905) which consider only the ion-induced dipole interaction and the locked-dipole model (LD) (Gupta et al., 1967; Moran and Hamill, 1963) which also takes into account the ion – permanent dipole interaction at its maximal value by considering only θ = 0. The LGS rate constant is:

$$k_{LGS} = 2\pi . e . \sqrt{\frac{\alpha}{(4\pi\varepsilon_0)^2 . \mu}} \qquad \text{(Eq. 1)}$$

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with α the polarizability of the neutral molecule and μ the reduced mass of the two collision partners, and the LD rate constant is:

$$k_{LD} = k_{LGS} + 2\pi . e . \mu_D \sqrt{\frac{2}{\pi . \mu . k_b . T}} \quad \text{(Eq. 2)}$$

If one uses the form often taken for various models:

$$k = k_{LGS} . \left(1 + C . \frac{2x}{\sqrt{\pi}}\right) \quad \text{(Eq. 3)}$$

with:

$$x = \frac{\mu_D}{\sqrt{2 k_b . T . \frac{\alpha}{4\pi\varepsilon_0}}} \quad \text{(Eq. 4)}$$

k_{LD} corresponds to C = 1. As visible in Table 3, the experimental rates are all above the LGS values which situate these reactions as very efficient and well below the LD ones as expected.

In the eighties and later, several models have been found to predict better values for the capture cross sections and rate constants for ion – dipole systems, using either classical trajectory calculations by Su et al (Chesnavich et al., 1980; Su, 1988; Su, 1994; Su and Chesnavich, 1982) and Maergoiz et al (Maergoiz et al., 1996), statistical models: derived from the variational transition state theory (Chesnavich et al., 1980) or the statistical adiabatic channel model (SACM) (Troe, 1996), or close-coupling (CC) calculations combined with various approximations such as the adiabatic capture (AC), the centrifugal sudden approximation (CSA) or the infinite order sudden approximation (IOSA) (Clary, 1984; Clary, 1985; Clary, 1990; Clary and Henshaw, 1987). The results of these models for which a parametrization is given (Clary, 1990; Maergoiz et al., 1996; Su, 1988; Su and Chesnavich, 1982; Troe, 1996) have been used to calculate the rate constant for the two reactions of this work and are displayed in Table 3. The AC-IOSA approximation of the CC calculation corresponds to neglecting $\mathbf{j}^2$ terms in the Hamiltonian and is equivalent in fixing θ and doing averages over θ at the end (Clary, 1984; Clary, 1985; Clary, 1990; Clary and Henshaw, 1987). It leads to the Eq. 3 formula with C = 0.25 for the ion-dipole case (Clary, 1990). However, Clary claims that contrary to the dipole-dipole or quadrupole-dipole cases where it works quite well, it is not very accurate for ion-dipole interactions where the potential is highly anisotropic (Clary, 1985; Clary, 1990). This is probably why for the two reactions here where the HC_3N neutral has a strong permanent dipole (3.73 Debye) (DeLeon and Muenter, 1985), the values calculated with the AC-IOSA model in Table 3 are somehow smaller than the ones calculated with CT and SACM models. The AC-CSA approximation would probably give better estimates, similar to the CT and SACM values, however they cannot be calculated here as no easy parametrization exists for such complex calculations. The values calculated with the CT and SACM models are all quite close for each reaction leading to k/k_{LGS} ratios between 3.18 and 3.42, corresponding to C values ranging from 0.36 to 0.4 if Eq. 3 is used. Considering the convergence of these methods, it seems more reasonable to compare the experimental values with it.

For the CN^- + HC_3N reaction, the experimental rate constant is slightly higher, though within error bars, when a pulse of He is applied to help in the thermalization of the CN^- parent anions, and corresponds to k/k_{LGS} ratio of 2.88 which is about 11 % lower than the CT and SACM calculated values of Maergoiz (Maergoiz et al., 1996) and Troe (Troe, 1996).

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For the C_3N^- + $HC_3{}^{15}N$ reaction, the experimental rate constant, which is here the sum of the proton transfer (PT) and associative detachment (AD) channels, is also slightly higher when using a pulse of He to thermalize the C_3N^- parent anions. As the reduced mass is larger than for the previous reaction (25.3 instead of 17.2 Da), it is expected that the capture rate constants are smaller by about 18 % as it scales with $\mu^{-1/2}$. The *k* value is however much lower and the k/k_{LGS} ratio which takes into account the $\mu^{-1/2}$ dependence is 1.36 which is about 58 % (more than a factor 2) lower than the CT and SACM calculated values.

For the $C_3{}^{15}N^-$ + HC_3N reaction, the $C_3{}^{15}N^-$ parent anions have been produced by proton transfer in the C_3N^- + $HC_3{}^{15}N$ reaction. The experimental rate constant, which is also here the sum of the PT and AD channels, is even lower, about 30 % less than the C_3N^- + $HC_3{}^{15}N$ reaction, for almost the same value of the reduced mass μ, and the k/k_{LGS} ratio is only slightly larger than 1.

As mentioned above, the models calculate only capture rate constants and reaction rate constants could be lower if the efficiency of the reaction is less than one after the capture process. Moreover, the anions are considered as point charge in the models and the only variations between the CN^- and C_3N^- reactions should stem from the different reduced mass. However, it could be possible, that the proton transfer, which is here the major product channel, has a different efficiency on CN^- and C_3N^- to form HCN and HC_3N respectively. With the very small size of CN^-, it might be easier for the proton to be transferred to the preferred side of the anion, than for C_3N^- which is a longer chain. With the assumption that the PT would depend on the orientation of the C_3N^- chain relative to the HC_3N target, one could expect that only a reduced number of collisions lead to the proton transfer. **Geometric orientation of the reactants** would **thus** partly explain why the measured rate for the PT in the C_3N^- reaction is less efficient than for the CN^- reaction after considering the reduced mass dependence. For longer chains, *i.e.* for increasing size of $C_{2p+1}N^-$ reactants, it would be interesting to know if the PT is even less efficient or if it has already reached a minimal value. There is however an important consideration that should be made specifically for the C_3N^- + HC_3N reaction that arises from the symmetric character of the parent and product channels. Indeed, the reactants and the products are identical - HC_3N and C_3N^- on both sides - implying that, once the complex is formed, two iso-energetic exit channels leading to identical products are accessible with the same probability. There should thus be a 50 % decrease of the probability for the proton transfer and this would constitute the major contribution to the observed difference (-58 % as discussed in the section 4.2.) between the measured and calculated rates for the C_3N^- + $HC_3{}^{15}N$ reaction.

4.3. Implications for Titan's ionosphere

So far, this is the first measurement of the kinetic rate constants for the C_3N^- + HC_3N reaction reported in the literature. The measurements have been performed at room-temperature which is of course different from the temperatures encountered in the upper atmosphere of Titan where the ion and neutral temperature ranges are 125 - 200 K and 145 - 160 K, respectively (Crary et al., 2009). However, if one assumes a temperature-dependence for this reaction, similar to the very weak one found by (Biennier et al., 2014) for the PT in CN^- + HC_3N; then, in Titan's conditions, the order of magnitude of the rate constant associated to the RD/AD channel for the C_3N^- + HC_3N reaction, is expected to lie **around 10^{-10} $cm^3.s^{-1}$. Note that, up to now, this reaction is not considered in models and that a 10^{-9} $cm^3.s^{-1}$ value is assumed for detachment pathways involving radicals (Vuitton et al., 2009).** Measurements at low-temperature are needed to confirm this trend but this might have an effect on the amount of thermal electrons globally released.

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From the present results and the ones presented in (Žabka et al., 2014), an attempt to give a trend concerning the reactivity of the $C_{2p+1}N^-$ species with cyanoacetylene can also be made. Indeed, as p increases, the reactivity **changes**.

First, the PT channel seems to become less and less efficient as the length of the anion chain increases. As discussed earlier, a privileged orientation of the anion with respect to the neutral reactant molecule could also play a role. The energetics of the reaction itself seems to evolve unfavourably with p, since, according to the computed reaction enthalpies from (Yang et al., 2011), the $C_5N^- + HC_3N$ reaction would be endothermic ($\simeq$ +17 kJ.mol^{-1}).

Another important point is that the elimination of HCN coupled to the addition of a C_2 unit to the anion C-chain following:

$$C_{2p+1}N^- + HC_3N \rightarrow [HC_3N.C_{2p+1}N^-] \rightarrow HCN + C_{2p+3}N^-$$

does not seem to evolve favourably with p as well. Indeed, unlike for p = 0, no anionic product is observed for p = 1 (*i.e.* no C_5N^- observed) although supposedly formed through an exothermic process. This probably reflects the evolution of the electronic affinity throughout the $C_{2p+1}N^-$ series which increases by less than 0.05 eV when going from C_5N^- to $C_{11}N^-$ according to (Botschwina and Oswald, 2008a) while it increases by at least 0.5 eV when going from CN^- to C_5N^- according to (Yen et al., 2009). The gain in energy when increasing the C-chain length is thus greatly reduced for heavier species, *i.e.* for larger p values. As a consequence if we consider that reactivity towards HC_3N is directly related to the EA of the $C_{2p+1}N^-$ species, for what concerns the anion growth, then this pathway should become unlikely for p ≥ 1, at least in single-collision conditions. It has indeed been observed that in pressure conditions allowing for multiple collisions with HC_3N (Žabka et al., 2014), this growth takes place, showing that solvation energy by a spectator HC_3N molecule can, to some extent, balance the energetic cost of the elimination of a HCN molecule. As discussed in this latter paper, a solvation-process cannot be excluded in Titan's ionosphere especially if **one considers the anions likely present in the cosmic ray layer, close to the surface, where pressure is sufficient to enable three-body reactions.**

To conclude, we should also discuss the likely opening of a new reactive channel as p increases. No detachment processes (either AD or RD) - at least of any importance relative to the strong PT - have indeed been observed for the $CN^- + HC_3N$ reaction, but, though weak, detachment appears as not negligible for the larger C_3N^- anion. One could thus wonder whether this channel would somehow prevail over the different reactive paths for p ≥ 2. However, great caution needs to be made. In fact, no trend is observed in the kinetic constants measured by (Yang et al., 2011) for AD reactions of $C_{2p+1}N^-$ with H atoms (p = 0-2) (values around 5-6 10^{-10} cm^3.s^{-1}). So, no clear conclusions can be drawn without knowledge on the nature of the resulting neutral product(s) or new measurements. This is nevertheless likely that the AD or RD process at play in this reaction, ultimately leads to heavier molecules which could contribute to the so-called macromolecules that will further grow to aerosols through chemistry and coagulation as modelled by (Lavvas et al., 2013).

5. Conclusions

The well-known production of CN^- from BrCN and the extension of this approach to the production of C_3N^- from BrC_3N have allowed kinetic studies of these anions with the cyanoacetylene. Given their potential role in the growth of anionic species in the ionosphere of Titan and the confirmed presence of polycyanoacetylenic negative species throughout the interstellar medium, the reactions of CN^- and C_3N^- with HC_3N have been investigated by means of FT-ICR mass spectrometry.

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Global kinetic rate constants have been measured for both reactions at 300 K. The main reaction channel for these reactive systems is proton transfer between the primary ion and the cyanoacetylene molecule, although a slower competitive detachment pathway opens for the reaction of C_3N^- with HC_3N. A rate constant for this detachment process k_D has also been retrieved but the nature and energetics of the neutral product(s) formed through this process remain unknown. More theoretical effort is needed in order to elucidate these points. Additional experiments with larger anions, other neutral reactant such as HCN and HC_5N, or exploring the role of collision energy might also be of great interest to achieve a better understanding of the reactivity of $C_{2p+1}N^-$ ions with cyanoacetylene and to reveal if the transition from p = 1 to p = 2, is kind of a bottleneck in the reactivity of such anions.

Another key point for these reactions is their temperature dependence as they are expected to take place in astrophysical environments where the temperature is quite low. Experimental data are available over the 49 – 294 K temperature range for the CN^- + HC_3N reactive system (Biennier et al., 2014) but the determination of low temperature rate constants for the reaction of C_3N^- with HC_3N would also be useful on a more fundamental point of view since the dependence to temperature for AD/RD processes is still poorly known (Phelps, 1969; Viggiano et al., 1990; Viggiano and Paulson, 1983; Viggiano and Paulson, 1984). These experimental and theoretical efforts on the reactivity of the $C_{2p+1}N^-$ anions, combined with those more focused on their destruction processes, in particular through photodetachment (Kumar et al., 2013), should lead to significant improvements in the description of the ionospheric chemistry of Titan.

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

- Proton transfer is the main reaction channel for both reactive systems
- Slower competitive detachment pathway opens for C_3N^-: $(1.0 \pm 0.2)\ 10^{-10}\ cm^3.s^{-1}$
- Discussion of results on the basis of statistical models

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