HCN FORMATION UNDER ELECTRON IMPACT: EXPERIMENTAL STUDIES AND APPLICATION TO NEPTUNE'S ATMOSPHERE

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ABSTRACT

Laboratory experiments simulating organic synthesis in Neptune's atmosphere have been performed. We have submitted to a spark discharge gaseous mixtures containing 9 mbar of molecular nitrogen and 3 mbar of methane (the $p(N_2)/p(CH_4)$ ratio is compatible with upper limits in Neptune's stratosphere) with varying quantities of molecular hydrogen. The spark discharge is used to model the energetic electrons produced by the impact of cosmic rays on the high atmosphere of Neptune.

HCN is synthesized in the described experimental conditions, even with a low mixing ratio of molecular nitrogen. Studying the variation of HCN production with the initial composition of the gas mixture and extrapolating to high mixing ratio of molecular hydrogen allows to estimate HCN production in Neptune's atmosphere. The computed HCN production flux is 7×10^7 m^{-2} s^{-1}, which is two orders of magnitude lower than the value predicted by chemical models for an internal source of N atoms. The major uncertainty in our extrapolation is the energetic distribution of electrons, implicitly assumed comparable in the discharge and in Neptune's atmosphere. We note that this distribution is also a source of uncertainty in chemical models.

The chemical mechanism responsible for the local formation of HCN in the stratosphere probably occurs in the reactor too. We propose a simple characterization of the spark discharge. We thus link the molecular nitrogen dissociation cross section by electron impact to the measured parameters of the experiments (current, voltage, initial partial pressures) and to the resulting HCN partial pressures. However, other laboratory experiments with larger hydrogen pressures, requiring a more powerful electric source, have to be performed to yield a value of the cross section.
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INTRODUCTION

Neptune, like the other giant planets, has an atmosphere mainly composed of molecular hydrogen and helium. Other molecules are also present: the most abundant is methane, then come ethane and acetylene. Methane dissociation under solar radiation leads to the production of radicals which react to give complex organic compounds (Toublanc *et al.*, 1995). Methane and some of the photochemical products probably form the observed clouds. Recently, although they were totally unexpected, two new

molecules, carbon monoxide (CO) and hydrogen cyanide (HCN), have been detected in Neptune's stratosphere from ground-based observations (Marten *et al.,* 1991 ; Rosenqvist *et al.,* 1992 ; Lellouch *et al.,* 1994). The fundamental question is the origin of these two species on this giant planet. The presence of CO in the stratosphere is assumed to be due to an internal source, as the molecule has also been detected in the troposphere (Guilloteau *et al.,* 1993) and should be carried into the upper atmosphere by upwards convection. The presence of HCN is more difficult to explain because its formation implies chemical processes involving N atoms and the origin of these atoms is not well known. The source of N atoms may be either external (escape of nitrogen from Triton, Neptune's satellite) or internal (N_2, though it has not been detected, should be present in the deeper atmosphere). Theoretical studies in order to discriminate between these two hypotheses are still in progress.

This paper presents an experimental study which is part of a program that will allow a better understanding of HCN formation in Neptune's atmosphere. This program includes observations and theoretical modeling. The aim of this work is to provide information that can improve the current theoretical models, especially the quite complete one about the physical-chemistry of Neptune's atmosphere already built by Dobrijevic, 1996. Comparison between experimental and model results allows us to study or to test chemical schemes for HCN formation under electron impact. As a matter of fact, an important uncertainty is the value of the molecular nitrogen dissociation cross section after electron impact. We will show that our experiments should provide this value.

CHEMICAL COMPOSITION OF NEPTUNE'S ATMOSPHERE

Voyager radio occultation and infrared spectrometer measurements have been used by Conrath *et al.* (1991) to estimate the helium abundance. Their analysis yielded helium mole fractions of 0.19 ± 0.032. At that time, they assumed that only H_2 and He contributed significantly to the mean molecular weight, *m,* in the upper troposphere and lower stratosphere. The recent detection of HCN suggests that molecular nitrogen could be present at these atmospheric levels. If present in sufficient amount, N_2 could contribute significantly to *m*. That is the reason why Conrath *et al.* (1993) have re-analyzed the Voyager data and have established constraints on the nitrogen abundance and illustrated the possible influence of N_2 on the He determination. They found a maximum nitrogen mole fraction of 0.6 % confirming earlier work from Lindal *et al.* (1990) which also concludes that the mole fraction of molecular nitrogen can not exceed 0.6%.
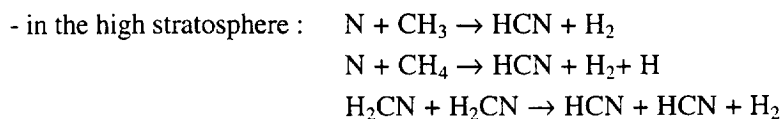
Hydrocarbons have also been detected in Neptune's atmosphere. Methane is the most abundant with a mixing ratio between 2×10^{-5} and 1.7×10^{-3} in the stratosphere (nominal value : 3.5×10^{-4}) (Baines *et al.,* 1994). Other hydrocarbons, like acetylene (C_2H_2) and ethane (C_2H_6), have been identified on Neptune from I.R. ground-based or Voyager (IRIS) data (Bézard *et al.,* 1991 ; Orton *et al.,* 1992 ; Kostiuk *et al.,* 1992 ; Yelle *et al.,* 1993).

Until the discovery of HCN , no nitrogen compound was thought to be present in appreciable amount in Neptune's stratosphere. Ammonia is cold-trapped at the tropopause, its mixing ratio in the stratosphere is then limited by saturation. The case of HCN is similar: if it is present in the troposphere, the hypothesis of a fast upward transport is ruled out because of the cold-trap. However, HCN has been detected in the millimeter range for the first time in 1991 by Marten *et al.* Since that time, the detection has been confirmed twice (Rosenqvist *et al.,* 1992 ; Lellouch *et al.,* 1994). This molecule is present in Neptune's stratosphere with a mixing ratio evaluated at $(1 +/- 0.3) \times 10^{-9}$ by Marten *et al.* (1993), (3 +/-
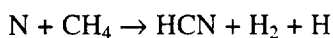
1.5)x10^{-10} by Rosenqvist *et al.* (1992) and (3.2 +/- 0.8)x10^{-10} by Lellouch *et al.* (1994). Thus, the proposed mechanism is a local formation of HCN in the stratosphere as discussed in the next paragraph.

ORIGIN OF HCN IN THE STRATOSPHERE OF NEPTUNE

The HCN formation results from an active organic chemistry involving methane and a nitrogen source. Considering the hypothesis of the internal source, Dobrijevic (1996) has determined the main reactions responsible of HCN's production. These are :

- in the high stratosphere : $N + CH_3 \rightarrow HCN + H_2$

$N + CH_4 \rightarrow HCN + H_2 + H$

$H_2CN + H_2CN \rightarrow HCN + HCN + H_2$

- in the low stratosphere:

$N + CH_4 \rightarrow HCN + H_2 + H$

Hypotheses for the origin of nitrogen atoms

The source of CH_3 is the photolysis of methane. The problem is to explain the origin of atomic nitrogen which initiates the nitrile production mechanism in the stratosphere. Several hypotheses can be examined (see figure 1). The theoretical models predict that nitrogen is in the form of ammonia in the external atmosphere of giant planets (Fegley and Prinn, 1986). Ammonia is present in Neptune's troposphere (Gautier *et al.*, 1995). However, this compound could not be a sufficient source for nitrogen atoms in the stratosphere because, as said previously, it should condense near the tropopause. Recently, Gautier et al. (1995) have shown from the interpretation of the centimeter wavelength spectrum of Neptune that the major part of nitrogen in the troposphere has to be in the form of N_2.

In 1993, for the first time, Marten has proposed that the source of stratospheric nitrogen atoms could be molecular nitrogen. N_2 could be present in the stratosphere with an upper limit of mixing ratio evaluated to 0.3 % or 0.6 %, depending on the authors.

Fig. 1 : Temperature profile and structure of Neptune's atmosphere. Hypotheses for the origin of N atoms : internal and external sources.

The dissociation of molecular nitrogen by solar EUV photons is limited by the large amount of H_2 which absorbs these radiations. The dissociation of molecular nitrogen as the result of charged particle impact is also limited because these particles are present only near the magnetic poles and are not energetic enough. For the hypothesis of an internal nitrogen source, only dissociation of N_2 by secondary electrons produced from cascading galactic cosmic rays is relevant. The scheme for
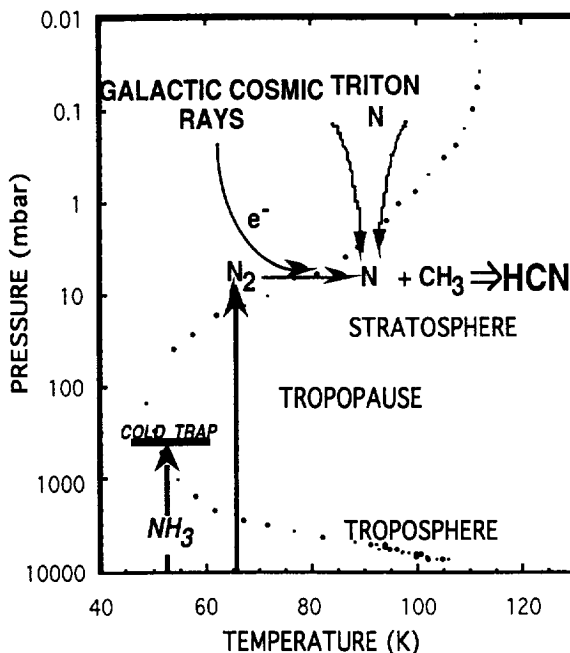
dissociation of N_2 by impact of galactic cosmic rays has been established by models (Capone *et al.*, 1976, 1977, 1979 ; Moses *et al.*, 1989, 1992 ; Lellouch *et al.*, 1994).

The hypothesis of an external source has been proposed by Rosenqvist *et al.* (1992). These authors have explained that nitrogen atoms can be supplied in sufficient amount by escape from the atmosphere of Triton, the largest satellite of Neptune.

LABORATORY EXPERIMENTS

Models have already been established in order to discriminate between the two hypotheses for the source of nitrogen atoms (internal or external). However, these models have to be better constrained. Consequently, laboratory measurements are very useful to understand the fate of nitrogen atoms and to properly model the HCN production rate on Neptune. In particular, to test the internal source, the molecular nitrogen cross section for dissociation by electron impact, σ, has to be known with better accuracy. Checking whether or not HCN can be synthesized under electronic impact with a low starting amount of nitrogen is of prime importance.

Thus, we have performed experimental studies which can allow us to determine the value of σ and to extrapolate to Neptune's atmosphere. Gas mixtures containing hydrogen, nitrogen and methane are submitted to a spark discharge as described in the experimental section. The spark discharge simulates the secondary electrons resulting from the impact of galactic cosmic rays in Neptune's stratosphere. We introduce in a reactor 9 mbar of nitrogen, 3 mbar of methane and we add a variable amount of hydrogen (from 0 to 150 mbar). The ratio CH_4 / N_2 is set to 1/3, compatible with the ratio of the maximum abundances of the two compounds in Neptune's stratosphere. We are not able to simulate Neptune's real composition (N_2, upper limit: 0.006, Conrath *et al.*, 1993 ; CH_4: 2 10^{-5}- 1.7 10^{-3}, Baines *et al.*, 1994 ; H_2: 0.81 +/- 0.032, Conrath *et al.*, 1991) because of two reasons. The first one is that we are not able to use a large amount of hydrogen for safety reasons and for the stability of the discharge. The second one is that we have to use sufficient amount of starting materials in order to obtain a detectable quantity of HCN. Still, from these experimental studies using varying quantities of hydrogen, we hoped to evaluate HCN production in Neptune's stratosphere by extrapolation to higher hydrogen pressures, in order to reach the same mixing ratios of nitrogen and methane than the ones expected in Neptune's stratosphere at the 10 mbar level.

EXPERIMENTAL

Reactor and Simulation

The reactor is a two liter glass vessel. The top part is equipped with a high vacuum stopcock and two tungsten electrodes. The two electrodes are linked to the reactor with two high vacuum O-rings (Rotulex, France), and are about 1 cm away from one another. The bottom part is equipped with a cold finger that can be immersed in liquid nitrogen during the sparking of the mixture. Thus, we consider that compounds other than H_2, CH_4, and N_2 are cold-trapped when they are synthesized. Before the experiment, the reactor is first washed with Decon (Prolabo, France), then carefully washed with water and dried, in order to remove all remaining organic residues. After each simulation, a secondary vacuum (about 10^{-5} mbar) is carried out in the reactor for one hour. The gas mixture (CH_4, N 45, Air Liquide, France; N_2, C, Aga and H_2, C, Aga, France) is introduced into the reactor through a vacuum line. Afterwards, the bottom of the reactor is immersed in liquid nitrogen 30 minutes before the beginning of

the discharge, in order to reach a thermodynamic equilibrium. The irradiation lasts one hour. Every ten minutes the intensity and the potential between the two electrodes are measured as detailed in the following paragraph in order to calculate the power of the discharge. After irradiation, the vessel is rapidly warmed up to room temperature and the resulting gas phase is quantitatively analyzed.

Energy quantification

The experimental set-up is described in figure 2. It is made up of a rheostat that allows us to set the inlet potential u_1. A ballast transforms the alternating current into direct current with an alternating high frequency part (25 kHz). The potential between the two electrodes is too high to be directly measured, but the power deposited in the gas mixture can be indirectly estimated. Indeed, the power $\mathcal{P}_1$ provided in the primary circuit (before the ballast) is equal (to within 10% because of loss in the ballast itself) to $\mathcal{P}_2$, the dissipated power in the secondary circuit (after the ballast). $\mathcal{P}_2$ is the sum of $\mathcal{P}_{2a}$, : joule effect in the resistors (R = 293 kW and r = 10 kW) and $\mathcal{P}_{2b}$: power deposited in the gas mixture. The resistor R is necessary to protect the electrodes from alteration. The currents are measured with two multimeters (Wavetek DM 15, and Wavetek RMS 225 for the high frequencies). The intensity in the primary circuit, i_1, is measured. The potential u_1 is known since it is set by the rheostat. So, we can calculate $\mathcal{P}_1$ ($\mathcal{P}_1 = i_1 \times u_1$). The potential u_{2eff}, measured at the limits of the resistor r, is split in two parts : a direct component $u_{2=}$ and an alternating component $u_{2\approx}$.

$$u_{2eff} = \sqrt{(u_{2=})^2 + (u_{2\approx})^2}$$

Then,

$$i_2 = u_{2eff} / r$$

and

$$\mathcal{P}_{2a} = (R+r)(i_2)^2$$

As seen earlier,

$$\mathcal{P}_1 = \mathcal{P}_2 \text{ and } \mathcal{P}_2 = \mathcal{P}_{2a} + \mathcal{P}_{2b}.$$

Thus, we can estimate the power $\mathcal{P}_{2b}$ provided to the gas mixture :

$$\mathcal{P}_{2b} = \mathcal{P}_1 - \mathcal{P}_{2a},$$

The calculated potential between the electrodes, u_2 ($u_2 = \mathcal{P}_{2b} / i_2$), is in the order of 1000 Volt.
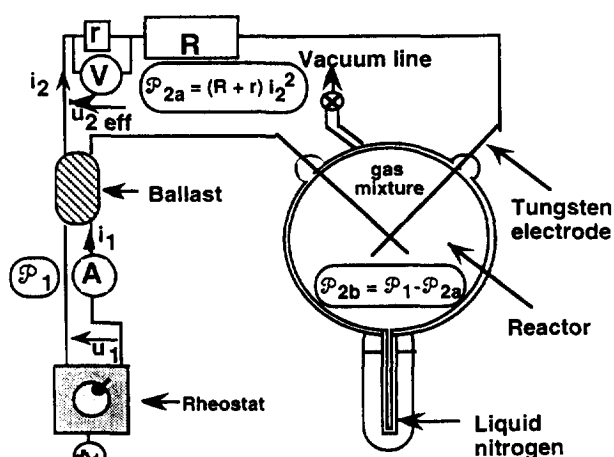

Fig. 2 : Schematic view of the experimental set-up used for the discharge and to evaluate the energy deposition.

HCN analysis

HCN synthesized after one hour of irradiation within the experimental conditions previously detailed is analyzed by IR spectroscopy. A 10 cm long gas cell equipped with CsI windows is used. IR spectra are collected with a Fourier Transform IR spectrometer (Perkin Elmer type 1710), with a 2 cm^{-1} resolution along 50 scans. Pressure broadening of the absorption band is produced each time by introducing about 800 mbar of nitrogen in the gas cell after admission of a resulting sample at a known partial pressure. A preliminary calibration of the IRTF is carried out with HCN synthesized at the laboratory in accordance with a classical protocol (Vogel, 1978). It gives us the partial pressure of HCN in the simulation sample from the measurement of the optical density at 712 cm^{-1}.

RESULTS AND DISCUSSION

Simulation experiments

Hydrogen cyanide is synthesized in noticeable amount with the described experimental conditions. We have especially studied the variation of the total quantity of HCN that is formed in the different experiments when the initial amount of hydrogen in the reactor increases.

To compare the results of the different experiments, we normalize the obtained partial pressure to the power of the discharge. Figure 3 shows the dependence of the inverse of the normalized HCN partial pressure, $\mathcal{P}_{2b}$ / p(HCN), as a function of the initial partial pressure of hydrogen, p(H$_2$). This dependence is quite linear. The extrapolation of this line to high hydrogen pressure allows us to estimate the amount of HCN that can be synthesized in Neptune's stratosphere.
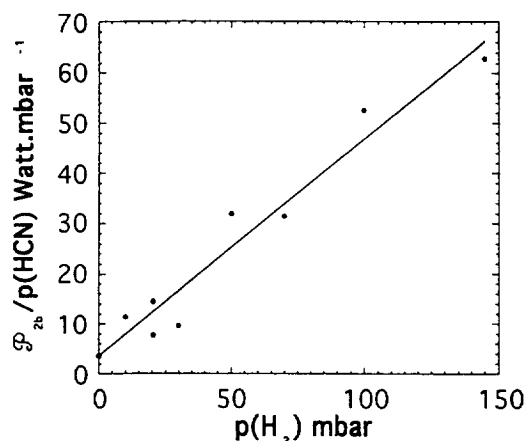

Fig. 3 : The inverse of HCN partial pressure after 1 hour of irradiation, normalized to the power of the discharge, ($\mathcal{P}_{2b}$/ p(HCN)) , is shown versus the initial partial pressure of hydrogen .

The atmosphere of the planet contains 0.3% nitrogen and 0.1% methane. The initial partial pressures used for the experiments are 9 mbar for nitrogen and 3 mbar for methane. Consequently, in order to extrapolate to the mixing ratios on Neptune of these two gases, we need to consider a total pressure of 3000 mbar, that is 2988 mbar of hydrogen. Fitting a straight line through the experimental points in figure 3, we extrapolate the value of $\mathcal{P}_{2b}$ / p(HCN) for this hydrogen partial pressure. Then, we can calculate n$_{HCN}$, the total number of HCN molecules synthesized in the reactor per unit of provided energy using the following equation :

$$n_{HCN} = \left(\frac{p(HCN)}{\mathcal{P}_{2b}} \right) \frac{V_{reactor}}{\Delta t \, k_B \, T} \tag{1}$$

where Δt is the duration of the experiment, $V_{reactor}$ is the total volume of the reactor, k_B is Boltzmann's constant and T is the mean temperature of the reactor.

From this experimental result, one can derive the HCN production flux φ_{HCN} (*Neptune*) in Neptune's atmosphere (molecules per cm^2 and per s) from the following equation :
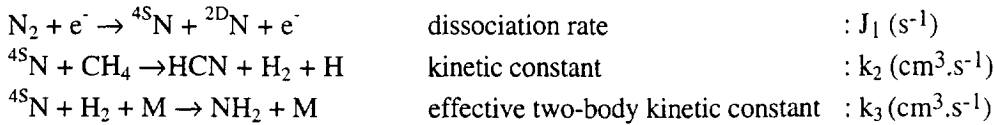
$$\varphi_{HCN}(Neptune) = n_{HCN}\, \Phi_e \qquad (2)$$

where Φ_e is the energy flux of secondary electrons produced by the collision of cosmic rays on atmospheric nuclei. The latter is assumed in our calculation equal to the energy flux of cosmic rays able to penetrate the atmosphere, Φ_{GCR}. We use the value 4.14×10^9 eV cm^{-2} s^{-1} given by Lellouch *et al.* (1994). We obtain $\varphi_{HCN}(Neptune) = 7 \times 10^7$ m^{-2} s^{-1}. This value is two orders of magnitude lower than the one predicted by photochemical models. Indeed, in the case of an internal source of N atoms, the HCN production flux has been estimated at 8×10^9 m^{-2} s^{-1} by Lellouch *et al.* (1994) and at 1.1×10^{10} m^{-2} s^{-1} by Dobrijevic (1996). The discrepancy between our experimental result and those obtained by models may be due to a different energetic distribution of the electrons in the reactor than the one assumed in models. We note that the energetic distribution of electrons in Neptune's atmosphere is not well known though it is an important piece of information in modeling HCN production. As a first conclusion, the knowledge of the energetic distribution of electrons in the discharge as well as in Neptune's atmosphere is essential to obtain the HCN production flux with a better accuracy.

Theoretical study

In our experimental simulation, when the quantity of hydrogen increases, one of the effects is of chemical nature : more nitrogen atoms react with H_2 rather than CH_4, so HCN is less synthesized (equation (3) below). The second effect is that the efficiency of the discharge decreases : part of the electrons can not be accelerated because of collisions with hydrogen, then they are not sufficiently energetic to dissociate molecular nitrogen (equation (8) below).

The hypothesis is that the following chemical scheme is responsible for HCN production in the reactor. It is in fact the one that occurs in Neptune's lower stratosphere corresponding approximately at the 10 mbar pressure level (Dobrijevic, 1996).

$N_2 + e^- \rightarrow {}^{4S}N + {}^{2D}N + e^-$ dissociation rate   : J_1 (s^{-1})

${}^{4S}N + CH_4 \rightarrow HCN + H_2 + H$ kinetic constant   : k_2 ($cm^3.s^{-1}$)

${}^{4S}N + H_2 + M \rightarrow NH_2 + M$ effective two-body kinetic constant : k_3 ($cm^3.s^{-1}$)

With this chemical scheme, and assuming a quick quenching of ${}^{2D}N$ to the ground state ${}^{4S}N$ (through NH, see discussion in Lellouch *et al.*, 1994), one obtains the following expression for the HCN production rate τ_{HCN} (cm^{-3} s^{-1}) as a function of methane, nitrogen and hydrogen initial densities, $[CH_4]$, $[N_2]$ and $[HCN]$ respectively :

$$\tau_{HCN} = \frac{2k_2\,[CH_4\,]J_1[N_2\,]}{k_3}\frac{1}{[H_2\,]} \qquad (3)$$

where J_1 is the molecular nitrogen dissociation coefficient (s^{-1}) which is a function of Φ, the flux density of "energetic" electrons (number of electrons with energy above the dissociation threshold, per cm^2 and per s and σ, the cross section (cm^2) for dissociation of molecular nitrogen by those energetic electrons:

$$J_1 = \Phi\, \sigma \qquad (4)$$

Let Δt be the duration of the experiment. The pressure of HCN in the reactor at the end of the experiment is:

$$p(HCN) = \tau_{HCN} \, \Delta t \, \frac{V_{spark}}{V_{reactor}} \, k_B T \tag{5}$$

where V_{spark} is the volume roamed by the electron beam.

Let us now write the electronic flux Φ as a function of hydrogen partial pressure, current i_2 and tension u_2 between the electrodes. Φ is equal to the total flux of electrons (which is proportional to the current i_2) multiplied by the probability for one electron to possess an energy E above the energy $E_{dissociation}$ needed to dissociate molecular nitrogen:

$$\Phi = A \, i_2 \, x \, probability(E > E_{dissociation}) \tag{6}$$

where A is independent of gas amounts and discharge power.

In order to gain the kinetic energy E, an electron must be accelerated by the electrical field for a distance:

$$x = \frac{E}{eu_2} d$$

with d and u_2 the distance and the tension between the two electrodes.

The probability for an electron to be allowed to travel a distance greater than x without making a collision is:

$$probability(free\ path > x) = exp\left(-\frac{x}{\lambda}\right)$$

where λ is the mean free path of an electron. Hence:

$$probability(E > E_{dissociation}) = exp\left(-\frac{E_{dissociation} d}{eu_2 \lambda}\right) \tag{7}$$

If there is a large amount of hydrogen then:

$$\lambda = \frac{k_B T}{\sigma_{coll} p(H_2) \sqrt{2}} \tag{8}$$

where σ_{coll} is the collision cross section of nitrogen molecules and electrons.

Using equations (3), (4), (6)-(8), one obtains from equation (3):

$$\ln\left[\frac{1}{i_2} \frac{p(HCN)p(H_2)}{p(CH_4)p(N_2)}\right] = B - C \, \frac{p(H_2)}{u_2} \tag{9}$$

where

$$B = \ln\left(2 \, \frac{k_2}{k_3} \, \sigma \, A \, \frac{V_{spark}}{V_{reactor}} \, \Delta t\right) \qquad and \qquad C = \frac{E_{dissociation}}{eu_2} \, d \, \frac{\sigma_{coll} \sqrt{2}}{k_B T}$$

Note that, as we consider large amounts of hydrogen, the effective two-body reaction rate k_3 for reaction 3 should be close to its high-density asymptotic value, $k_{3\infty}$, and therefore should not depend on $p(H_2)$. Thus, from one experiment to the other, we may change the gas amounts, and i_2 and u_2 may change, but neither B nor C vary, since they do not depend on gas amounts or discharge power.

Plotting the term written in the left side of equation (9) as a function of $[p(H_2)/u_2]$ should give a straight line. The interesting point is that we are able to determine the $k_2\sigma/k_3$ ratio which is the intersection of the line with the y axis. As k_2 and k_3 are known in the literature, the value of σ, the molecular nitrogen dissociation cross section, can be calculated. We are starting to use this expression for interpreting our experimental results but the study is still in progress. We have not carried out enough experiments to get a proper plot, in particular, we have to investigate higher hydrogen pressures. If we obtain a straight line, we will really confirm the hypotheses made and validate the proposed chemical scheme of HCN formation in the reactor.

CONCLUSION

From the measurement of the quantity of HCN produced in a gas mixture (containing CH_4, N_2 and varying quantities of hydrogen) submitted to a spark discharge, and the extrapolation to high hydrogen mixing ratio we have estimated the HCN production flux in Neptune's atmosphere. We find a value of 7×10^7 m^{-2} s^{-1}, two orders of magnitude lower that the previous determinations based on theoretical models (Lellouch et al., 1994 ; Dobrijevic, 1996). A better knowledge of the energetic distribution of the electrons both in Neptune's atmosphere and in the spark discharge would permit the determination of the HCN production flux with better accuracy. The theoretical and experimental approaches could then be reconciled. The characterization of our spark discharge can not be done without improving the experimental set up. This work is presently under development.

Besides, more experiments, involving higher amounts of hydrogen, have to be performed. The aim of this additional work is to validate equation (9). Increasing the range of hydrogen partial pressures would allow us to properly determine the coefficient B in that equation. The important value of σ, the molecular nitrogen dissociation cross section, could at last be reached.

We have already proved with our experiments that a low amount of molecular nitrogen is sufficient to synthesize HCN under electronic impact. This experimental result strengthens the hypothesis that an internal source of nitrogen atoms could explain the presence of hydrogen cyanide in Neptune's stratosphere.

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