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Evidence of production of $\text{H}_2\text{CN}^+ \cdot \text{N}_2$. Application to the atmosphere of Titan (*)

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Résumé. — La molécule $\text{H}_2\text{CN}^+ \cdot \text{N}_2$ est mise en évidence dans un mélange $\text{N}_2\text{-CH}_4$ soumis au rayonnement alpha d'une source radioactive. La constante d'équilibre est mesurée et la valeur de l'enthalpie de la réaction a été déterminée ($|\Delta H^0| = 7,65 \pm 0,09 \text{ kcal.mole}^{-1}$).

Abstract. — The molecule $\text{H}_2\text{CN}^+ \cdot \text{N}_2$ has been observed in a mixture of $\text{N}_2\text{-CH}_4$ irradiated by alpha particles from a radioactive source. The equilibrium constant has been measured and the enthalpy of the reaction has been calculated ($|\Delta H^0| = 7.65 \pm 0.09 \text{ kcal.mole}^{-1}$).

1. **Introduction.** — Titan, the largest satellite of Saturn, is one of the smallest objects in the solar system to have an atmosphere. Evidence of complex chemical phenomena arising in this atmosphere is of great interest, both in cosmochemistry and in exobiology. This concerns particularly chemical processes involved in the formation of prebiotic molecules, probably similar to those which could have acted in the primitive earth's atmosphere.

Infrared measurements performed by VOYAGER I show that Titan's atmosphere is mainly composed of molecular nitrogen ($\approx 90\%$) [1] and methane ($\approx 5\%$). Small amounts of H_2 , C_2H_2 , C_2H_4 , C_2H_6 , C_3H_8 and C_4H_2 produced by photolysis of methane, have been detected, and also nitriles : HCN , C_2N_2 and HC_3N [2], which are able to play a fundamental role in the formation of other prebiotic molecules. Moreover, it is reasonable to presume that more complex organic compounds are also present in Titan's atmosphere, such as CH_3CN , $\text{C}_2\text{H}_3\text{CN}$, $\text{C}_2\text{H}_5\text{CN}$ and, may be, nitriles of higher order [3, 4].

Probably three-body association reactions are mainly involved in the synthesis of such nitriles [3, 5] in Titan's lower atmosphere : in fact, high pressures and low temperatures are propitious conditions, while ionization results from cosmic rays impinging on the atmosphere. Among all the ions able to play a role, H_2CN^+ is probably of great importance : it is assumed to be responsible for HCN formation [6], while further more it can be combined with molecules N_2 ,

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CH_4 and C_2H_2 to produce compounds such as CH_3CN , $\text{C}_2\text{H}_3\text{CN}$, ... through three-body reactions.

Until now, only little information is known about chemical reactions involving such ions. Figure 1 illustrates some possible schemes leading to H_2CN^+ formation in Titan's atmosphere [3, 6]. In the following, we shall present results of laboratory measurements concerning the formation of $\text{H}_2\text{CN}^+\text{-N}_2$ from H_2CN^+ .

Fig. 1. — Schematic diagram of N^+ ion-molecule reactions with CH_4 and N_2 leading to production of H_2CN^+ .

2. Experimental device. — An experimental set up has been designed to allow the observation of ions produced in variable, relatively high pressure and low temperature gas (1 to 700 torr, 10 to 300 K) from low activity alpha sources (^{241}Am , $40\ \mu\text{Ci}/\text{cm}^2$). Ions resulting from primary ionization are subjected to collisions with neutral species which lead to formation of several secondary ionic species. These are extracted from the gas chamber through a small hole (diameter $\varnothing = 50\ \mu\text{m}$), then driven to a quadrupole mass spectrometer (MS) acting as an ion analyser. A cryostat allows one to vary the gas temperature which is measured using an AsGa probe situated in the gas chamber. The neutral gas composition is determined by means of a second MS downstream from the extracting hole.

3. Experimental results and discussion. — Figure 2 shows an example of a recorded spectrum in the case of a $\text{N}_2\text{-CH}_4$ ($\sim 100 : 1$) mixture at a pressure $p = 40$ torr and a temperature $T = 262$ K. Amplitudes of $m/e = 28$ and 56 observed peaks are mainly due respectively to H_2CN^+ and $\text{H}_2\text{CN}^+\text{-N}_2$. This has been shown by substituting CD_4 for CH_4 in the same proportion mixture : the two previous peaks are then observed at $m/e = 30$ and 58 , and nothing remains at $m/e = 28$ and 56 but low amplitude peaks attributed to N_2^+ and N_4^+ . The identity of these last ions has been confirmed similarly by substituting for mass 14 nitrogen an isotopic mixture of equal quantity of mass 14 and mass 15 nitrogen : the peak corresponding to $m/e = 28$ is then splitted into two peaks of comparable amplitude at $m/e = 28$ and 29 ; the peak at $m/e = 56$, which implies three nitrogen atoms, then appears at $m/e = 56, 57, 58$ and 59 .

Such recorded spectra allow one to determine the equilibrium constant [3] K_1 corresponding to the reaction

In the following, we shall assume that reaction (1) is reversible. This will be verified later. K_1 is then determined [7, 8] using relation :

$$K_1 = \frac{[\text{H}_2\text{CN}^+\text{-N}_2]}{[\text{H}_2\text{CN}^+][\text{N}_2]}$$

Fig. 2. — Mass spectrum in a mixture of $\text{N}_2\text{-CH}_4$. Beyond H_2CN^+ and $\text{H}_2\text{CN}^+-\text{N}_2$ ions, the probable chemical formula attributed for other detected ionic species are indicated (traces of hydrogen and of hydrocarbons (C_2H_6 , C_3H_8 , ...) contribute for the production of some of the ionic species). With MS sensitivity chosen for spectrum clarity, the amplitude of the $\text{H}_2\text{CN}^+-\text{N}_2$ peak is out of scale; this peak is thus shown with a MS sensitivity divided by ten for comparison with the other peaks.

where brackets indicate densities of corresponding compounds. In our experiment, the ratio of ionic densities is equal to the ratio of peak amplitudes for masses 56 and 28, and nitrogen density is given by the pressure measured in the gas chamber.

Figure 3 shows variations of $\text{Log } K_1$ as a function of T^{-1} (Van't Hoff plot). These variations are deduced from measurements at several nitrogen pressures and several molar fraction of methane as well in the case of CD_4 or ^{15}N .

One can observe a linear variation, independent of nitrogen pressure in the region studied (20 to 80 torr) and independent of the methane proportion (1 to 5 %). This indicates that a thermodynamic equilibrium is reached and that the reversibility assumption is valid.

Points corresponding to measurements with CD_4 deviate notably from the drawn line. This is due to oxygen, present in small proportion in the gas, which leads to formation of NO^+ ions with mass $m/e = 30$. These ions contribute to the peak attributed to D_2CN^+ making the corresponding

Fig. 3. — Van't Hoff plot of the $\text{H}_2\text{CN}^+ + 2 \text{N}_2 \rightleftharpoons \text{H}_2\text{CN}^+-\text{N}_2 + \text{N}_2$ reaction for a N_2 - CH_4 mixture ($\approx 100 : 1$): $\times$, 20 torr; $\bullet$, 40 torr; $+$, 80 torr; $\circ$, measured in N_2 ($m = 14$ and 15)- CH_4 ; $\square$, measured in N_2 - CD_4 .

calculation of K_1 erroneous. Complementary measurements show that the proportion of NO^+ increases with decreasing temperatures and is negligible at room temperature. The point obtained for 300 K is thus the only one to be valid.

Another point can also be plotted on the K_1 curve, deduced from a recorded spectrum using ^{14}N and ^{15}N mixture. Nevertheless, its precision is also smaller because it was necessary to add the amplitudes of the four peaks of ions $\text{H}_2\text{CN}^+-\text{N}_2$ and the two peaks of ions H_2CN^+ to deduce the ionic densities of interest.

The standard enthalpy, ΔH^0 , of reaction (1) can be estimated, using the curve of K_1 as drawn on figure 3, and the relation

$$K_1 = \exp(\Delta S^0/R - \Delta H^0/RT)$$

R is the perfect gases constant and it is assumed that the variation in entropy, ΔS^0 , is small in the range of studied temperatures (200-300 K). We obtain $|\Delta H^0| = 7.65 \pm 0.09 \text{ kcal.mole}^{-1}$ (the relative error is determined using statistic deviation from Van't Hoff plot). Such a value of ΔH^0 implies that the $\text{H}_2\text{CN}^+-\text{N}_2$ ion is relatively stable in low temperature Titan's atmosphere.

K_1 value at 150 K can be deduced by extrapolating results of figure 3. We obtain $K_1 = 2.95 \times 10^3 \text{ torr}^{-1}$. If the value $k_+ = 10^{-28} \text{ cm}^6 \cdot \text{s}^{-1}$ is attributed [3] to the constant of the forward reaction, leading to the formation of $\text{H}_2\text{CN}^+\text{-N}_2$, it is then possible to calculate, using our K_1 value, the reaction constant, k_- , for the reverse process. We obtain $k_- = 1 \times 10^{-15} \text{ cm}^3 \cdot \text{s}^{-1}$ at 150 K.

Besides the results presented above, analysis of spectra obtained at low temperature ($T \approx 150 \text{ K}$) for pressures around 40 torr, suggest that the ion H_2CN^+ can be possibly associated with several nitrogen molecules. Association of other ionic species with N_2 or CH_4 is also evidenced in these spectra. Ions of global formula C_2H_7^+ , C_3H_7^+ , ... have been detected and identified using, as previously, isotopic methane or nitrogen.

4. Conclusion. — Our results indicate that the reaction $\text{H}_2\text{CN}^+ + 2 \text{N}_2 \rightleftharpoons \text{H}_2\text{CN}^+\text{-N}_2 + \text{N}_2$ is possible and can lead to formation of the ion $\text{H}_2\text{CN}^+\text{-N}_2$ in Titan's atmosphere.

Equilibrium constants of this reaction have been measured for temperature ranging from 200 to 300 K allowing one to deduce the enthalpy ($|\Delta H^0| = 7.65 \pm 0.09 \text{ kcal} \cdot \text{mole}^{-1}$). Furthermore, existence of other possible association reaction of H_2CN^+ ion with N_2 or with CH_4 has been shown. Such results are in agreement with some expectations pointed out in a recent study [3, 6].

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