

Article

A Determination of Free Energy Changes from a Gas Phase Study of Equilibria $[(C_2H_2)_m(N_2)_{n-1}]^+ + N_2 = [(C_2H_2)_m(N_2)_n]^+$

Carlos V. Speller*^a and Marc Fitaire^b

^aDivisão de Plasmas/LABMAT, Departamento de Engenharia Mecânica,
Universidade Federal de Santa Catarina, 88040-900 Florianópolis - SC, Brazil

^bLaboratoire de Physique des Plasmas[#], Université de Paris-Sud,
91405 Orsay Cedex, France

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O equilíbrio de reações íon-molécula de agregação (“clustering”) entre íons $(C_2H_2)_m^+$ e moléculas N_2 em fase gasosa foi estudado por técnica de espectrometria de massa de alta pressão, em misturas N_2 - C_2H_2 irradiadas por partículas α . Valores de energia livre de agregação, $\Delta G_{n-1, n}^0$, foram determinados para reações $(C_2H_2)_m^+(n-1)N_2 + N_2 \rightleftharpoons (C_2H_2)_m^+nN_2$, para diferentes valores de m e n . Para $m=2$, i.e., para $(C_2H_2)_2^+$, os valores encontrados para $\Delta G_{n-1, n}^0$, quando $T = 129$ K, foram 0.87 ± 0.20 kcal/mol para $(n-1, n) = (2,3)$ e 0.88 ± 0.20 kcal/mol para $(n-1, n) = (3,4)$. Para $m = 3$ (“íon-nucleador” $(C_2H_2)_3^+$), as variações de energia livre encontradas foram 0.91 ± 0.30 kcal/mol para $(n-1, n) = (2,3)$; 0.73 ± 0.30 kcal/mol para $(n-1, n) = (3,4)$; 0.65 ± 0.30 kcal/mol para $(n-1, n) = (4,5)$; e 0.58 ± 0.30 para $(n-1, n) = (5,6)$.

Gas phase equilibria of ion-molecule clustering reactions between $(C_2H_2)_m^+$ ions and N_2 were investigated by high-pressure mass spectrometry in N_2 - C_2H_2 mixtures irradiated by α -particles. Free energy values of clustering, $\Delta G_{n-1, n}^0$, were obtained for reactions $(C_2H_2)_m^+(n-1)N_2 + N_2 \rightleftharpoons (C_2H_2)_m^+nN_2$, for different values of m and n . For $m = 2$, i.e., for the “core ion” $(C_2H_2)_2^+$, the values found for $\Delta G_{n-1, n}^0$ at $T = 129$ K are 0.87 ± 0.20 kcal/mol for $(n-1, n) = (2,3)$ and 0.88 ± 0.20 kcal/mol for $(n-1, n) = (3,4)$. For $m = 3$ (“core ion” $(C_2H_2)_3^+$), the free energy changes were found to be 0.91 ± 0.30 kcal/mol for $(n-1, n) = (2,3)$, 0.73 ± 0.30 kcal/mol for $(n-1, n) = (3,4)$; 0.65 ± 0.30 kcal/mol for $(n-1, n) = (4,5)$, and 0.58 ± 0.30 for $(n-1, n) = (5,6)$.

Keywords: ion-molecule reactions, mass spectrometry, Titan atmosphere

Introduction

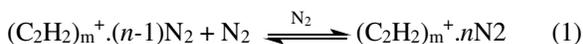
The atmosphere of Titan is mainly composed^{1,2} of nitrogen, with a few percent of methane, and acetylene as one of its minor components. In previous studies^{3,4} we reported the thermochemical data regarding the clustering of N_2/CH_4 on different core ions of interest in understanding Titan’s chemistry. Pure N_2 and CH_4 , as well as N_2 - CH_4 mixtures were used to obtain the data. In the present work, we have carried out studies on N_2 - C_2H_2 mixtures at high pressures (1-20 Torr). As in previous studies, the main purpose was to obtain thermochemical data on clustering

ion-molecule reactions pertinent to the ion chemistry of Titan’s atmosphere. Information of this type is fundamental to an understanding of the complex chemistry associated with planetary atmospheres for the following reasons, among others: (1) ions represent efficient nucleating agents, resulting in the formation of large cluster buildup and eventually droplet formation; (2) clustering modifies the chemistry associated with ion neutralization because the ligands can act both as heat “sinks” for energy released in the neutralization as well as nearest-neighbor partners in chemical reactions; (3) planetary atmospheres contain both

[#] Associated to CNRS (URA73).

polar and non-polar components, which compete both as ligands and as candidates for the core ions within clusters, therefore dictating the terminal ion chemistry. This overall competition is ultimately controlled by the thermochemistry and kinetics associated with each individual clustering and association reaction expected to occur in any given atmosphere because of its composition, particle density, temperature, profile, etc.

The clustering of N_2 on the cluster ions $(C_2H_2)_m^+$ was investigated. Reaction-free energy changes, $\Delta G_{n-1, n}^0$, corresponding to:



were determined at one temperature, with N_2 acting as a third-body.

Very little data regarding clustering with acetylene ions have been reported to date. The formation of acetylene cluster ions, such as $(C_2H_2)_m^+$, or mixed clusters, such as[#] $[(C_2H_2)_m(N_2)_n]^+$ in N_2 - C_2H_2 -ionized mixtures, is to be expected.

An efficient charge transfer mechanism from N_i^+ ($i = 1-2$) ions assures^{5,6} the formation of $C_2H_2^+$ ions. This can be understood on the basis of the following considerations:

- In mass spectra obtained in nitrogen and in acetylene, respectively, with high energy alpha-particles, the primary ions N_2^+ and $C_2H_2^+$ are dominant (approximately 80% in each case)⁷. As the fraction of acetylene in the N_2 - C_2H_2 mixture is $\leq 2\%$ in the present experiment, the expected dominant primary ion is N_2^+ , followed by N^+ ;

- The first ionization energy (IE) of C_2H_2 , to form $(C_2H_2)^+$, is only 11.394 eV^{8,9}, which is low in comparison to those associated with nitrogen (IE[N_2] = 15.5812 eV for N_2^+ , and 24.3 for N^+). Since the residence time of the reaction chamber is on the order of ms, and IP[C_2H_2] is relatively low, N_2^+ and N^+ will lead to the formation of $C_2H_2^+$ by fast charge transfer;

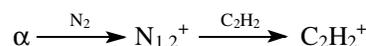
- Moreover, the appearance energy (AE) of C_2H_2 to form C_2H^+ is 17.36 eV. So, even if this minor ion is formed, charge transfer between C_2H^+ and N_2 will occur, thus also indirectly contributing to the formation of $C_2H_2^+$ ($C_2H^+ \xrightarrow{N_2} N_2^+ \xrightarrow{C_2H_2} C_2H_2^+$).

- Finally, it is easily verified that under the present experimental conditions, the formation of N_3^+ and N_4^+ by the ternary reactions:

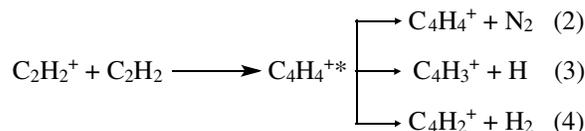


is expected to be insignificant in comparison to the bimolecular transfer charge from N_2^+ and N^+ to C_2H_2 . The ex-

pected primary ion in the α -particle radiolysis of nitrogen containing trace amounts of acetylene, such as in the present experiment, is thus essentially $C_2H_2^+$, which follows the reaction:



This is consistent with the observation of Lind and Bardwell¹⁰, who have shown that irradiation of N_2 - C_2H_2 mixtures by α -particles from radon does not lead to the synthesis of nitrogen compounds, the final product being the same as that which is formed in the absence of nitrogen. Nevertheless, they observed that the energy absorbed by the nitrogen contributed to the polymerization of C_2H_2 to form the solid cuprene, $[(C_2H_2)_m]$. Once formed, $C_2H_2^+$ can react with C_2H_2 to give⁵ $C_4H_4^{+*}$, an excited complex, which in turn will be either stabilized by collision with a third body (N_2) at higher pressures, or dissociated into the condensation ions $C_4H_3^+$ and $C_4H_2^+$:



The formation of $C_4H_4^+$ (or $(C_2H_2)_2^+$) via channel (2) can be represented by the three-body ion-molecule association reaction



where k stands for the effective reaction constant.

These ions can then undergo subsequent clustering reactions with C_2H_2 or N_2 . In the present study only reactions corresponding to equilibrium (1) were investigated.

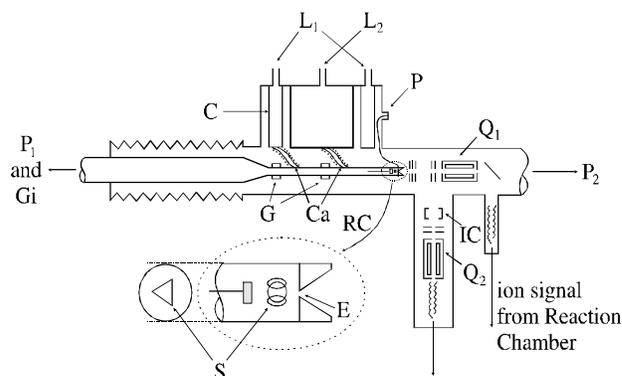


Figure 1. The schematic of the apparatus: C-cryostat; Ca-calorific conductor surrounded by heaters for temperature regulation; E-extraction hole; G-glass; Gi-gas inlet; L1-liquid N_2 inlet; L2-liquid N_2 or He inlet; P-polarization electrode for extraction hole; P₁, P₂-pumps; Q₁-quadrupole mass filter for ion analysis; Q₂ quadrupole mass filter for neutral gas analysis; RC-reaction chamber; IC-ionization chamber; S-alpha sources; T-temperature probe.

Since no protonation is involved in the formation of the clusters, we will not consider structural formula or charge localization, even though the first clustering step starts with the primary reactant ion $C_2H_2^+$; *i.e.*, $C_2H_2^+ \cdot (C_2H_2)_{m-1} \cdot (N_2)_n = [(C_2H_2)_m(N_2)_n]^+$.

Experimental

The measurements were performed with the High-Pressure Mass Spectrometer at the Université de Paris-Sud/LPGP, where ionization is initiated by alpha-particle bombardment. The experimental system is the same as previously described^{4,11}. Figure 1 illustrates the overall geometry of the mass spectrometer sampling system. Ions are generated in a field-free stainless steel source, by 5.4 Mev α -particles from three enclosed ²⁴¹Am (40 μ Ci cm⁻²) radioactive sources fixed on the source walls. Ions exit the source through a 50 μ m diameter hole into a low pressure ($P \leq 10^{-5}$ Torr) analysis chamber. These ions are accelerated and focused by electrostatic lenses, mass analyzed by a quadrupole mass filter, and detected by a 17-dynode electron multiplier. The highest mass to charge ratio (mass/z) value studied was 246. Since it is known¹² that the transmission in a quadrupole decreases as the value of the ion mass increases, corrections were applied for variations in the mass spectrometer transmission with respect to the selected mass. The neutral gas is pumped by a 600 l/s cryogenic pump which maintains the pressure inside the mass spectrometer at values less than 10^{-5} Torr. The reaction chamber is pumped by a 140 l/s turbomolecular pump, yielding a background pressure on the order of 10^{-7} - 10^{-8} Torr. A second quadrupole mass spectrometer, Q₂, downstream from the ion-extraction hole was used as a neutral gas analyser, permitting continuous monitoring of the partial pressures of the minority gases. In order to reduce water impurities, the gases flowed through a cold trap at 77 K before being introduced into the reaction chamber.

The gases were supplied by L'Air Liquide and were used as purchased. A N₂-C₂H₂ (98:2) mixture, which according to the supplier contained < 3 ppm O₂, < 2 ppm H₂O, < 2 ppm CO, < 1 ppm CO₂, and 1 ppm PH₃, was used as the initial mixture. Pure N₂ (< 0.1 ppm and < 1 ppm H₂O) was added to the N₂-C₂H₂ mixture to change the concentration of acetylene. Nitrogen (N₂) was used both as the bath and the ligand gas, and acetylene (C₂H₂) was 0.05 to 2% of the total N₂-C₂H₂ gas mixture. Experiments were performed under a total pressure ranging from 5 to 50 Torr, and at temperature values of 129, 132 and 273 \pm 2 K. The temperature was measured using a diode, inserted directly in the reaction chamber (see Fig. 1), close to the sample region, and calibrated[#] at ambient and liquid nitrogen temperatures. In this range, deviation from linearity can be considered negligible, and so $I \propto V$ is assumed. A combination of technical difficulties, related to the simultaneous

control of temperature and mixture composition, prevented us from obtaining enough data at different temperatures to determine enthalpy changes. Ionization at the source results in rapid primary ion-neutral reactions that generate C₂H₂⁺. Clustering reactions between C₂H₂⁺, C₂H₂, and N₂ then take place, resulting in the equilibrium (1). Under the conditions of the present study, the clustering neutrals (ligands) and the third body necessary for collisional stabilization of the intermediate complex are the same (N₂). Equilibrium constants $K_{n-1, n}$ are calculated as usual

$$K_{n-1, n} = \frac{I^+ \cdot nL}{[I^+ \cdot (n-1)L] \times P_L}$$

where $[I^+ \cdot (n-1)L]$ and $(I^+ \cdot nL)$ correspond, respectively, to the measured ion intensities of the reactant and product ions of the studied equilibrium (1), and P_L is the pressure of the ligand L in atmospheres. Free energy changes $\Delta G_{n-1, n}^0$, were obtained from the thermodynamic relation $\Delta G_{n-1, n}^0 = -RT \ln K_{n-1, n}$, connecting the equilibrium constant $K_{n-1, n}$ and the free energy change $\Delta G_{n-1, n}^0$; R is the perfect gas constant. Equilibrium conditions are discussed in Refs. 4 and 11. Furthermore, as will be shown in the next sections, the equilibrium constants were verified to be independent of the ligand (N₂) pressure between 10 and 50 Torr, as well as of the C₂H₂ partial pressure.

The estimated errors associated with the equilibrium constant measurements were 10-20% for $m = 2$, and 20-30% for $m = 3$. These errors are mainly related to noise, which often appeared during the peak intensity measurements at low temperatures (in general below 150 K), and for which no explanation could be found in our experiment. As a consequence, a relatively large dispersion of the points was observed in the equilibrium constant plots. Nevertheless, the uncertainties in $\Delta G_{n-1, n}^0$ are often reported to be in the range of ± 0.2 - 0.5 kcal/mol, and the present results lie within this range.

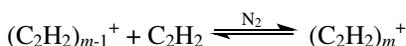
Results

Figure 2 presents the mass spectra of a N₂-C₂H₂ mixture for $P(\text{C}_2\text{H}_2) = 3$ mTorr and two different nitrogen pressures (5 and 30 Torr, respectively) at a temperature of 132 K. At the lower N₂ pressure, the most obvious feature is the grouping of the mass pattern into subpatterns which repeat themselves with a periodicity of 26 mass units. We can reasonably ascribe these peaks to (C₂H₂)_m⁺ ions, with $m = 2$ to 10 (the peak at $m = 1$, C₂H₂⁺, *i.e.*, corresponding to mass/z = 26, was observed only at higher temperatures, *e.g.* at 273

Although the accuracy inferred from the calibration curve is higher than 2 K, the ability to state that the temperature in the source is defined within this value comes from our previous measurements, followed by a comparison with the results reported by other authors (see "Comment on the Errors" at the end). However, as regards the free energy uncertainty, the errors associated with the equilibrium constants predominate over those of the temperature.

K). At higher N_2 pressures, the shifting of these peaks to higher mass values is obvious. Low intensity peak groups at intermediary mass values also showed an increase in their intensities as the nitrogen pressure was increased. A proposed scheme showing the formation of $[(C_2H_2)_m(N_2)_n]^+$ clusters from the primary ion $C_2H_2^+$ is given in Fig. 3, where we have also included exchange reactions of N_2 for C_2H_2 . Given the greater well depth for C_2H_2 as a ligand (see next paragraph), this exothermic displacement seems to be an essential feature of the schematic of the cluster formation, as observed in other composite cluster systems^{13,14}.

Although $(C_2H_2)_m^+$ ions were clearly predominant at the lower N_2 pressures, as shown in Fig. 2, attempts to investigate the equilibrium



under the experimental conditions used in our experiment were not successful. The ligand (C_2H_2) pressure investigated ranged from 5 to approximately 260 mTorr. For $P(N_2) = 10$ Torr, it was observed that at the lowest C_2H_2 pressures (between 5 and 40 mTorr, approximately) the ratio between the product and the reactant ion intensities, $[(C_2H_2)_m^+]/[(C_2H_2)_{m-1}^+]$, tended to increase slightly with pressure, but not directly proportional to pressure as required under equilibrium conditions ($I_{m+1}/I_m = KP_L$). Above 40 mTorr, the ratio tended toward a constant value. The reason for this is not clear. The results suggest that at 132 K, lower C_2H_2 pressures might be one of the necessary

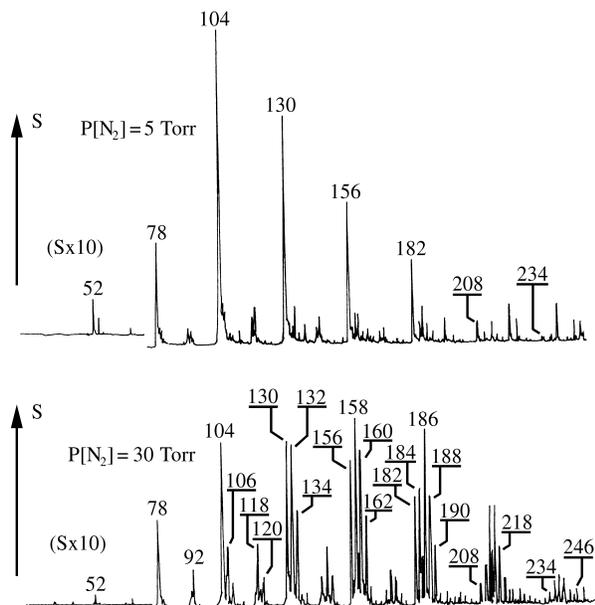


Figure 2. The mass spectra (signal intensity S in arbitrary units) of a N_2 - C_2H_2 mixture for $P(C_2H_2) = 3$ mTorr and $T = 132$ K. The spectra show the effect of nitrogen pressure variation for $P(N_2) = 5$ and 30 Torr. Mixed clusters with N_2 and C_2H_2 ligands are clearly more abundant at the higher nitrogen pressure.

conditions to achieve equilibrium for the above reactions. We also see that in both spectra of Fig. 2, at 5 and 30 Torr, a series of clusters starting at mass/ $z = 66$ (which possibly corresponds to $[X(C_2H_2)_r(N_2)_s]^+$, X being a unknown compound), probably formed in the discharge from impurities or from the gases under study. Nevertheless, this series is out of the scope of the present study.

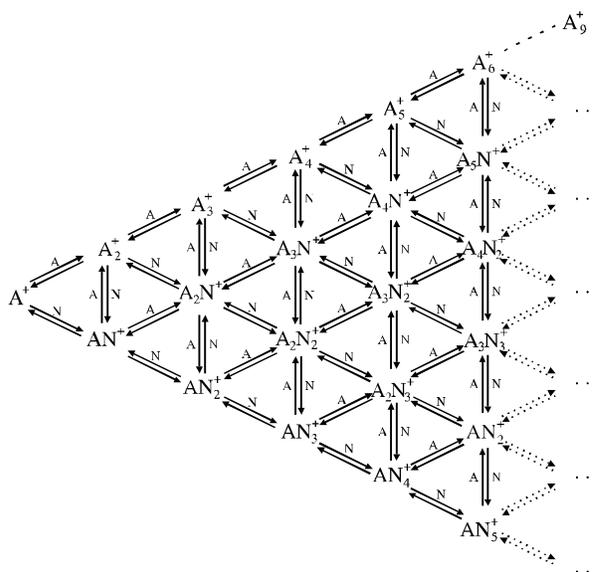


Figure 3. A schematic showing the formation of $[(C_2H_2)_m(N_2)_n]^+$ clusters from the primary ion $C_2H_2^+$ in a N_2 - C_2H_2 mixture ($A = C_2H_2$ and $N = N_2$). The complete set of reactions starts with reaction 1, $(C_2H_2)_m^+ \cdot (n-1)N_2 + 2N_2 \rightleftharpoons (C_2H_2)_m^+ nN_2$ for each combination of the variables $m = 1-9$ and $n = 1-6$ (ranges seen in the spectrum of Fig. 2). For the sake of simplicity, only part of the scheme is shown in the figure.

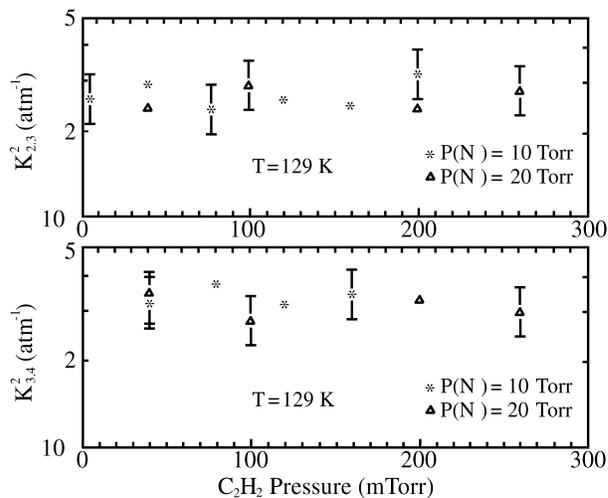


Figure 4. Reaction $(C_2H_2)_m^+ \cdot (n-1)N_2 + 2N_2 \rightleftharpoons (C_2H_2)_m^+ nN_2 + N_2$. Equilibrium constants $K^2_{2,3}$ and $K^2_{3,4}$ vs. acetylene pressure, for $P(N_2) = 10$ and 20 Torr at $T = 129$ K. The equilibrium constant is given as $K^{m}_{n-1, n}$, where the superscript m stands for the number of acetylene molecules in the reactant and in the product ion.

Figure 4 shows the equilibrium constants $K_{n-1,n}^m$ ($m = 2$; $n = 3-4$) for reaction (1) versus the partial pressure of acetylene (5-260 mTorr), for two different values of the nitrogen pressure (10 and 20 Torr). The values of $K_{n-1,n}^2$ remain constant as a function of the acetylene pressure over the entire range studied, for both values of the nitrogen pressure. This result is consistent with the attainment of equilibrium in the reaction chamber.

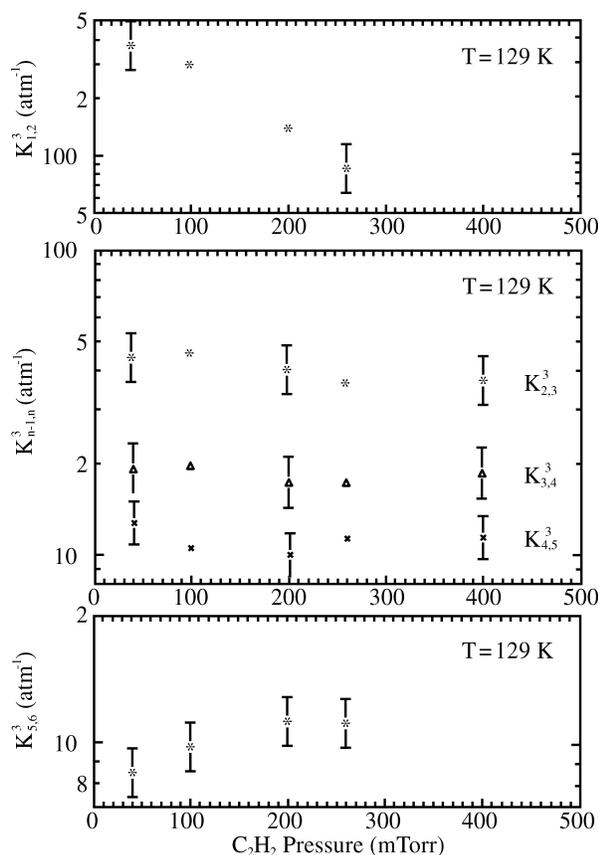


Figure 5. The reaction $(C_2H_2)_m^+ \cdot (n-1)N_2 + 2N_2 \rightleftharpoons (C_2H_2)_m^+ nN_2 + N_2$. Equilibrium constants $K_{1,2}^3$, $K_{2,3}^3$, $K_{3,4}^3$ and $K_{5,6}^3$ ($m=3$; $n=2-6$) vs. acetylene pressure, for $P(N_2) = 20$ Torr at $T = 129$ K. We see that $K_{1,2}^3$ does not correspond to equilibrium over the pressure range studied; $K_{5,6}^3$ appears to correspond to equilibrium above ~ 150 mTorr.

The same checks were made for the $K_{n-1,n}^3$ ($m = 3$; $n = 2-6$) constants, shown in Fig. 5. Except for $K_{1,2}^3$ and $K_{5,6}^3$, they can be considered independent of the C_2H_2 partial pressure within the pressure range 5 to 400 mTorr, for a N_2 pressure of 20 Torr. However, the results for $K_{5,6}^3$ suggest a tendency towards a constant value for acetylene pressures

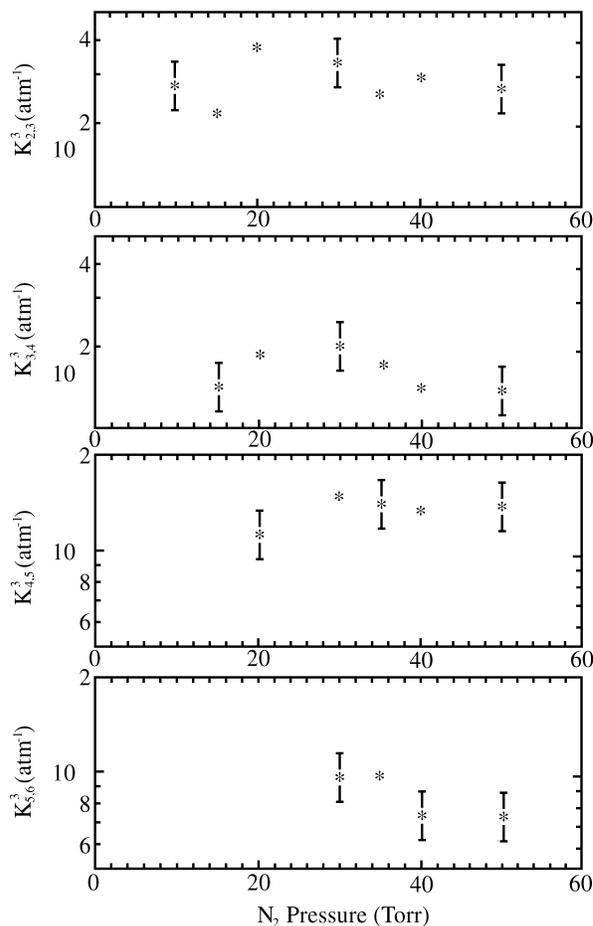


Figure 6. The reaction $(C_2H_2)_m^+ \cdot (n-1)N_2 + 2N_2 \rightleftharpoons (C_2H_2)_m^+ nN_2 + N_2$. Equilibrium constants $K_{2,3}^3$, $K_{3,4}^3$, $K_{4,5}^3$ and $K_{5,6}^3$ ($m = 3$; $n = 3-6$) vs. nitrogen pressure, over the pressure range 10-50 Torr, for $T = 129$ K. $K_{1,2}^3$ (not shown) does not correspond to equilibrium over the studied pressure range; although $K_{5,6}^3$ is constant within the error bars, more measurements (or a larger pressure range) are desirable in this case.

Table 1. Free energy changes^a and log of equilibrium constants K for equilibria $[(C_2H_2)_m(N_2)_{n-1}]^+ + N_2 = [(C_2H_2)_m(N_2)_n]^+$, at $T = 129$ K. Standard state 1 atmosphere.

	reaction	$\ln K_{129K} (\text{atm}^{-1})$	$-\Delta G_{129K}^0$ (kcal/mol)
$m = 2$	$(C_2H_2)_2(N_2)_2]^+ + N_2 = [(C_2H_2)_2(N_2)_3]^+$	3.40	0.87 ± 0.20
	$[(C_2H_2)_2(N_2)_3]^+ + N_2 = [(C_2H_2)_2(N_2)_4]^+$	3.45	0.88 ± 0.20
$m = 3$	$[(C_2H_2)_3(N_2)_2]^+ + N_2 = [(C_2H_2)_3(N_2)_3]^+$	3.55	0.91 ± 0.30
	$[(C_2H_2)_3(N_2)_3]^+ + N_2 = [(C_2H_2)_3(N_2)_4]^+$	2.85	0.73 ± 0.3
	$[(C_2H_2)_3(N_2)_4]^+ + N_2 = [(C_2H_2)_3(N_2)_5]^+$	2.55	0.65 ± 0.3
	$[(C_2H_2)_3(N_2)_5]^+ + N_2 = [(C_2H_2)_3(N_2)_6]^+$	2.25	0.58 ± 0.30

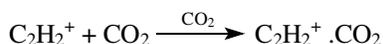
^aThe signals given correspond to the forward reactions.

higher than approximately 200 mTorr. We therefore assume the equilibrium for pressures above 200 mTorr. For practical reasons, the study of the $K^3_{n-1,n}$ dependence on the ligand pressure N_2 (Fig. 6) was done at a constant ratio of $P(C_2H_2)/P(N_2) = 2 \cdot 10^{-2}$ (the available initial mixture). In view of their observed independence (again, only $K^3_{1,2}$, not shown, is not found in equilibrium conditions) as a function of the C_2H_2 concentration, this should not affect our conclusions regarding equilibrium. Both sets of measurements, varying either N_2 or C_2H_2 , show the same trend, *i.e.*, the $K^m_{n-1,n}$ ($m = 3; n = 3-6$) are independent of the partial pressures of N_2 and C_2H_2 within the experimental accuracy of $\pm 30-40\%$ for the equilibrium constants.

The determinations inferred from the experimental results are summarized in Table 1, where the log of the equilibrium constants for reaction (1), as well as the free energy changes for the corresponding forward reactions are shown.

Discussion

McCrumb *et al.*⁵ have investigated reaction (5). At 2.8 Torr and 300 K, the stabilization of $C_4H_4^{+*}$ (channel 2) was dominant, channels (3) and (4) being unimportant in their experiment. The formation of $(C_2H_2)_2^+$ was also investigated by Rakshit and Warneck¹⁵, using CO_2 as a third body. They also studied the formation of the clusters $(C_2H_2)_3^+$ and $C_2H_2^+ \cdot CO_2$, as well as the association of C_2H_2 with $C_4H_2^+$ and $C_4H_3^+$, also with CO_2 as a third body. The measured reaction constants for all these clustering reactions where C_2H_2 was the ligand molecule were very high, whether in N_2 or CO_2 , and on the order of $10^{-26}-10^{-27} \text{ cm}^6 \text{ s}^{-1}$. However, for the clustering of CO_2 with $C_2H_2^+$,



they found a much lower value for the corresponding reaction constant, $k \leq 4 \cdot 10^{-30} \text{ cm}^6 \text{ s}^{-1}$. In other words, the clustering of C_2H_2 with $C_2H_2^+$ leads to the formation of $(C_2H_2)_n^+$ clusters at least 10^4 times faster than the association of CO_2 with $C_2H_2^+$. As a general trend, it is observed that N_2 displays a slower reaction constant than CO_2 as regards its clustering on the same ion. Moreover N_2 is observed to be less efficient than CO_2 as a third body. For example, in the case of the formation of $(C_2H_2)_2^+$, the literature gives $k = 1.6 \cdot 10^{-26} \text{ cm}^6 \text{ s}^{-1}$ and $0.6 \cdot 10^{-26} \text{ cm}^6 \text{ s}^{-1}$ for CO_2 and N_2 , respectively^{5,15}. This probably reflects the lower number of degrees of freedom in N_2 ¹⁶. The relative reactivity of the ligands CO_2, N_2, C_2H_2 is thus seen to increase in the order $N_2 < CO_2 < C_2H_2$. This is quite reasonable in terms of the basicity of these ligands, which is a function of their polarizability, α ($\alpha(N_2) = 1.76 \text{ \AA}^3$, $\alpha(CO_2) = 2.59 \text{ \AA}^3$ and $\alpha(C_2H_2) = 3.33 \text{ \AA}^3$). The greater stability of the $C_2H_2 \cdot C_2H_2^+$ complex, relative to $C_2H_2 \cdot CO_2$ and $C_2H_2 \cdot N_2$ also follows from this order of basicity, and is stressed by

our failure to observe equilibria once the $(C_2H_2)_m^+$ complexes are formed.

Therefore, it is plausible to expect that in order to have reaction rates on the same order as those leading to the formation of $(C_2H_2)_m^+$ clusters, the partial pressure ratio $P(N_2)/P(C_2H_2)$ must be at least 10^4 . This is consistent with the spectra shown in Fig. 2 for $P(N_2)/P(C_2H_2) \sim 10^3$, where $(C_2H_2)_m^+$ clusters are predominant; however, when the pressure ratio is increased to 10^4 , $[(C_2H_2)_m(N_2)_n]^+$ clusters are clearly observed.

It should be remembered that the spectra shown in Fig. 2 were obtained at a different temperature than that used by Rakshit (132 K in this work and 300 K for Rakshit with CO_2). The much lower temperature in our work should favor clustering reactions by increasing the corresponding equilibrium constants.

Regarding Table 1, we see that at 129 K all reactions studied are spontaneous. For $[(C_2H_2)_3(N_2)_n]^+$ ($m = 3$), the stability of the clusters increases monotonically with the number of N_2 molecules attached, *i.e.*, in the order $A^+(N_2)_2 < A^+(N_2)_3 < A^+(N_2)_4 < A^+(N_2)_5 < A^+(N_2)_6$, where $A = C_2H_2$. As for $[(C_2H_2)_2(N_2)_n]^+$ ($m = 2$), the stabilities are found to be roughly the same, whether for $n = 3$ or $n = 4$.

Studies involving composite clusters have been reported in the literature (see for ex., Refs. 13 and 14). In these studies, the ligands under investigation were polar (HCN, H_2O, NH_3, H_2S), thus involving ligand-ligand bonds stronger than those in the present case where the ligands are non-polar. Nitrogen and acetylene clusters are much more fragile, raising the questions as to whether changes in the nitrogen pressure also affect the acetylene equilibrium. Even though the estimated values of enthalpy changes are consistent with the expected numbers (see below), we believe that further investigation is needed in order to clarify this point.

The temperature dependence of the equilibrium constants was not investigated in the present study, and so enthalpy changes, $\Delta H^0_{n-1,n}$, could not be determined. However, an estimation of $\Delta H^0_{n-1,n}$ can be made if we attribute the estimated values for the corresponding entropy changes, $\Delta S^0_{n-1,n}$. If we estimate $\Delta S^0_{n-1,n}$ as $-20 \pm 3 \text{ cal/mol K}$, a range in which most of the values determined for cluster ions of the $X^+(N_2)_n$ -type fall^{14,17,18}, then $\Delta H^0_{n-1,n}$ can be estimated from the thermodynamic relation $\ln K = \Delta S^0/R - \Delta H^0/RT$, which connects the equilibrium constant K and the entropy and enthalpy changes. This yields enthalpy changes in the range of -3.4 to $-3.1 \pm 0.4 \text{ kcal/mol}$, which are roughly the same as those found for other clustering reactions with nitrogen for the same number of clustered molecules. These estimates are merely speculative and are to be used with caution.

To explain the possible formation of organic-nitrogen molecules in the atmosphere of Titan, Capone *et al.*¹⁹ pro-

Table 2. Free energy changes^a for different equilibria $[(X)_m(N_2)_{n-1}]^+ + N_2 = [(X)_m(N_2)_n]^+$, at T = 129 K. Standard state 1 atmosphere.

reaction	$-\Delta G^0_{129K}$ (kcal/mol)
a) $CH_5^+ + N_2 = CH_5^+(N_2)$	4.3 ^a
b) $CH_5^+(N_2) + N_2 = CH_5^+(N_2)_2$	3.3 ^a
c) $C_2H_5^+ + N_2 = C_2H_5^+(N_2)$	4.6 ^a
d) $C_2D_5^+(N_2) + N_2 = C_2D_5^+(N_2)_2$	1.9 ^a
e) $C_2D_5^+(N_2)_2 + N_2 = C_2D_5^+(N_2)_3$	1.4 ^a
f) $C_2D_5^+(N_2)_3 + N_2 = C_2D_5^+(N_2)_4$	1.1 ^a
g) $H_2CN^+ + N_2 = H_2CN^+(N_2)$	4.7 ^b
h) $H_2CN^+(N_2) + N_2 = H_2CN^+(N_2)_2$	2.5 ^b
i) $H_2CN^+(N_2)_2 + N_2 = H_2CN^+(N_2)_3$	1.5 ^b
j) $H_2CN^+(N_2)_3 + N_2 = H_2CN^+(N_2)_4$	1.3 ^b
k) $H_2CN^+(N_2)_4 + N_2 = H_2CN^+(N_2)_5$	1.2 ^b
l) $CH_5^+ + CH_4 = CH_5^+(CH_4)$	4.7 ^c
m) $CH_5^+(CH_4) + CH_4 = CH_5^+(CH_4)_2$	3.1 ^c
n) $CH_5^+(CH_4)_2 + CH_4 = CH_5^+(CH_4)_3$	0.7 ^c
o) $CH_5^+(CH_4)_3 + CH_4 = CH_5^+(CH_4)_4$	0.5 ^c

posed a mechanism involving exchange reactions between N_2 , CH_4 and C_2H_2 in $HCNH^+(L)_n$ clusters ($L = \text{ligand}$). Later, $HCNH^+(N_2)_n$, as well as $C_pH_q^+(N_2)_n$ and $C_pH_q^+.CH_4$ formation in the alpha-particle radiolysis of N_2 - CH_4 mixtures was observed at Orsay by these authors^{3,4}. Hiraoka and Kebarle²¹ studied $C_pH_q^+(CH_4)_{n-1-4}$. Table 2 shows the estimated ΔG^0 values corresponding to the formation of these ions at 129 K (the same as in Table 1). This temperature is close to that of the region of maximum cosmic ray-activated chemistry in the atmosphere of Titan, estimated^{1,19} as 150-160 K. The comparison of the stabilities found for these clusters and those of the acetylene-nitrogen clusters investigated in the present study show that clusters with the same number of clustered molecules around the core ion present comparable ΔG^0 . If present in the atmosphere of Titan they could probably all interact by exchange reactions, ultimately leading to the formation of $[(C_2H_2)_m(N_2)_n]^+$.

Comments on the errors

In determining the enthalpy and entropy changes in some of our previous work, the temperature ranges for the different reactions studied were relatively small. This is a common feature among previous studies involving ion clustering with N_2 reported by several laboratories. In our earlier studies on the $O_2^+(N_2)_n$ and $NO^+(N_2)_n$ ¹¹, and $HCNH^+(N_2)_n$ ³ clusters, small ranges of T were also used. Later, good agreement was obtained by Hiraoka and Nakajima¹⁸ between their thermochemical data and our data for $O_2^+(N_2)_2$; good agreement was also found between the theoretical results obtained by Ha and Nguyen²⁰ and our experimen-

tal determinations for ΔH^0 regarding $HCNH^+(N_2)_n$. However, the absolute values of our equilibrium constants were much larger than those measured by Hiraoka and Nakajima, resulting in smaller values for ΔG^0 . This was particularly true for the larger clusters ($n > 1$), where the ΔS^0 values did not lie within the expected range (20 ± 3 cal/mol.K), but rather were lower. Since then, however, in order to avoid collisional induced dissociation when sampling the fragile clusters, more precautions have been taken⁴ regarding the magnitude of the ratio between the product and reactant ions $I^+ nL$ and $I^+ (n-1)L$. The results recently obtained⁴ for the clustering of CH_5^+ and $C_2H_5^+$ with CH_4 provide a basis for comparison with the measurements of K made by Hiraoka and Kebarle²¹. The equilibrium constants (and therefore of ΔG^0) for these association reactions are in very good agreement. Furthermore, the corresponding ΔS^0 values also are within the expected range mentioned above.

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