EPSC Abstracts
Vol. 5, EPSC2010-117, 2010
European Planetary Science Congress 2010

Formation of nitriles and imines in the atmosphere of Titan: Combined crossed-beam and theoretical studies on the reactions of excited nitrogen atoms N(^{2}D) with methane, ethane and unsaturated hydrocarbons

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Abstract

Elementary reactions involving electronically excited atomic nitrogen in the metastable ^{2}D state with saturated (CH_4 and C_2H_6) and unsaturated (C_2H_2 and C_2H_4) hydrocarbons have been investigated by the crossed molecular beam technique with mass spectrometric detection. The nature of the primary products has been identified in all cases. Also, from the derived center-of-mass functions the reaction micromechanisms and the product energy partitioning have been obtained. The experimental results have been complemented by new electronic structure calculations of stationary points and product energetics for the relevant potential energy surfaces. In addition, statistical branching ratios have been derived at the temperatures relevant for the atmosphere of Titan. Interesting N-containing species (methanimine, ethanimine, ketenimine, acetonitrile etc.) have been identified as primary products. Implications for the atmospheric chemistry of Titan are discussed.

1. Introduction

Titan is the only body of our solar system characterized by a dense N_2 atmosphere like the Earth. The second most abundant component is CH_4 (~1.4% in the stratosphere), while larger hydrocarbons have been detected in trace amounts. The reactions of hydrocarbons or hydrocarbon radicals with active forms of nitrogen can account for the formation of the observed nitriles and other N-containing species. Nitrogen atoms in the first, metastable electronic ^{2}D state can be produced in the upper atmosphere of Titan by several processes involving N_2 (such as photodissociation, electron impact dissociation or dissociative photoionization) or the molecular ion N_2^+ (such as dissociative recombination) [1]. These processes lead to atomic nitrogen in the ground, ^{4}S, and electronically excited, $^2D_{5/2,3/2}$, states (energy content: 230.0 kJ mol^{-1}; radiative lifetimes of $^2D_{3/2}$ and $^2D_{5/2}$ are 6.1×10^4 and 1.4×10^5 s, respectively). Since collisional deactivation of N(^{2}D) by N_2 is a slow process, the main fate of N(^{2}D) above 800 km is chemical reaction with other constituents of Titan's atmosphere. The production of N atoms in the ^{2}D state is especially relevant, because ground state N atoms exhibit very low reactivity with closed shell molecules and the probability of collision with a radical is small. The paucity of detailed experimental information on the N(^{2}D)+hydrocarbon reactions has so far prevented to establish the actual role of those reactive systems in the N-chemistry of Titan. For instance, the reaction N(^{2}D)+C_2H_6 (ethane is the second most abundant hydrocarbon in the atmosphere of Titan) was not considered in the first photochemical models of the atmosphere of Titan, while in the models by Lara *et al*. [2] and Wilson and Atreya [3] it has been included with an estimated room temperature rate constant of 3.0×10^{-12} cm^3 s^{-1}. Nevertheless, the measured rate contant for N(^{2}D)+C_2H_6 is larger by one order of magnitude. In the most recent models by Lavvas *et al.* [4] and Krasnopolsky [5] the rate constant value has been corrected, but uncertainty about the nature of the reaction products remained. In particular, while in the models by Lara *et al*. [2], Wilson and Atreya [3] and Krasnopolsky [5] the only reaction channel considered is the one leading to NH+C_2H_5, Lavvas *et al*. [4] have put forward the suggestion that the main products are aziridine + H. The production of aziridine would have some interesting implications because this molecule is a possible precursor of ammonia via UV photolysis and therefore, N(^{2}D)+C_2H_6 reaction could account for the presence of ammonia in Titan's thermosphere (inferred from the analysis of the spectra recorded by INMS on board Cassini). Clearly, to establish the role of the $N(^2D)+C_2H_6$ reaction, as well as that of the reactions with the other hydrocarbons, in the chemical evolution of the atmosphere of Titan, the nature of the primary products has to be established in laboratory experiments.

2. Main results

The results of crossed molecular beam experiments have been complemented by electronic structure calculations of the stationary points on the relevant potential energy surfaces. The *ab initio* calculations have been also employed to determine the statistical (via a Rice-Ramsperger-Kassel-Marcus RRKM method) branching ratio (BR) of the products at the temperatures typical of the stratosphere of Titan. In the following subsections, the main results will be briefly summarized.

2.1 The reaction $N(^2D)+CH_4$

According to our experimental results [1], in addition to the channel leading to $NH+CH_3$ observed in a previous experiment, also methanimine ($CH_2=NH$) and methylnitrene (CH_3N) radical are formed as primary reaction products. An interesting conclusion of our study is that the $N(^2D)+CH_4$ reaction proceeds *via* the insertion of $N(^2D)$ into one of the methane C-H bonds thus forming a CH_3NH bound intermediate. The excess energy released during its formation causes the fragmentation into products. Interestingly, the experimental results indicate that there is a competition between the fragmentation of one of the two new bonds formed by $N(^2D)$ insertion and of one of the preexisting C-H bonds, not directly involved in the insertion process. As a result of this competition, the yield of the channels leading to the products $CH_2=NH+H$, CH_3N+H and $NH+CH_3$ has been observed to vary with the available energy. Notably, the RRKM BRs are not in line with the experimental ones. The conclusion of our study was that part of the reaction is dominated by dynamical effects (with the formation of the products CH_3N + H and $NH+CH_3$) and part by a statistical mechanism (leading to the formation of $CH_2=NH+H$) [1].

2.2 The reaction $N(^2D)+C_2H_6$

An important conclusion of the dynamical and theoretical investigation of this reaction is that it behaves statistically [6]. This implies that, for all purposes concerning the modelling of the atmosphere of Titan, we can refer to the RRKM BRs with confidence. The dominant reaction channel is the one leading to methanimine ($CH_2=NH$) + CH_3 (78.8%), followed by the one leading to ethanimine ($CH_3CH=NH$) + H (12.4%), with minor contributions from other channels [6]. Therefore, neither the assumption that $NH+C_2H_5$ is the sole reaction channel nor the recent suggestion that aziridine+H is the dominant reaction channel are correct. The models should be revised accordingly.

2.3 The reactions $N(^2D)+C_2H_4$, C_2H_2

The reactions of $N(^2D)$ with two relatively abundant unsaturated hydrocarbons have been reinvestigated with an improved crossed beam machine [7]. The analysis of the new data is still in progress. In the case of the reaction $N(^2D)+C_2H_4$ a new channel has been identified, which had not been observed in the previous crossed beam experiment [8].

3. Conclusion

The chemistry that controls the formation of nitriles and imines in the atmosphere of Titan, as well as nitrogen-rich aerosols, is slowly being unveiled. Nonetheless, much information on processes responsible for the nitrogen chemical budget is still missing. In particular, the reaction products of many reactions remain undetermined. Since the use in the models of unidentified products corresponds to an irreversible loss of the reactants, laboratory studies that identify the primary reaction products are crucial to building realistic models of the chemistry of planetary atmospheres. Future work on other relevant $N(^2D)$ reactions is being planned in our laboratory.

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