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Laboratory studies on the reactions of formation of nitriles and oxygenated compounds of relevance to the atmosphere of Titan

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Abstract. Accurate modeling of planetary atmospheres requires the knowledge of a series of chemical parameters, possibly determined in laboratory experiments. In particular, for gas-phase bimolecular reactions the kinetic rate constants and product branching ratios are desired. In our laboratory we have undertaken a systematic investigation of some bimolecular reactions, which are believed to form key steps in the models, with the aim of characterizing the reaction mechanism and product branching ratio. We have employed the crossed molecular beam scattering method with mass-spectrometric detection to study reactions involving atomic nitrogen in the first electronically excited state, $N(^2D)$, and ground state atomic oxygen, $O(^3P)$, with species relatively abundant in the atmospheres of Titan (as well as Mars and Triton). Results have been obtained for the reactions of $N(^2D)$ with H_2 and the hydrocarbons CH_4, C_2H_2 and C_2H_4, which are amongst the most abundant minor components of the atmosphere of Titan. In the cases of the reactions with hydrocarbons, molecular products containing a novel CN bond are formed, thus suggesting possible routes towards the production of gas-phase nitriles. Interestingly, most of the observed nitriles are either cyclic or unsaturated and could, therefore, be responsible for the building-up of the nitrogen-rich atmospheric aerosols of Titan. We have also investigated the reactions between $O(^3P)$ and unsaturated hydrocarbons, which might play a role in the conversion of oxygen to CO. Finally, we have extended the same approach to the study of radical-radical reactions, namely $O(^3P)$+CH_3 and C_3H_5. Molecular products other than those already considered in the modeling of planetary atmospheres have been identified and new routes of formation of CO can be envisaged.

1. Introduction

The atmospheres of planets – or satellites which possess one, like Titan – can be described as giant photoreactors, where the energy delivered by solar photons, cosmic rays and other energetic particles initiates a somewhat complex gas-phase chemistry. A detailed understanding of the chemical evolution of planetary atmospheres relies on a multidisciplinary approach. First of all, observations allow us to identify the molecules and their number densities. The chemistry which lies behind their formation starting from simple atoms or molecules is accounted for by complex reaction networks. To construct a realistic model, the important molecular processes

Send offprint requests to: Nadia Balucani should be identified and included with the appropriate parameters, possibly determined in laboratory experiments. As far as any bimolecular gas-phase reaction is concerned, given that it is thermodynamically feasible, the relevant parameters are (*i*) the kinetic rate constant and (*ii*) the product branching ratio. Reaction kinetics studies provide us with the reaction rate constants, but more rarely allow determining the nature of the products and their branching ratio. Nevertheless, this piece of information is fundamental to construct a correct model, because the products of one reaction are going to be the reagents of a subsequent one. In this respect a powerful approach is the one used in the research field of reaction dynamics. Such an approach can substantially contribute as it provides us with the most detailed knowledge of a gas-phase reaction and aims to verify whether a specific reaction pathway, and the related products, is easily accessible by the system. The main characteristic of a reaction dynamics experiment is that the reaction is investigated under single collision conditions. Several experimental techniques have been developed to achieve that (Casavecchia, 2000). In our laboratory we make use of the crossed molecular beam (CMB) technique with mass spectrometric (MS) detection. The benefits of the CMB technique strongly motivate its extension to the study of reactions of interest in astrochemistry. In the last few years the CMB method with MS detection has indeed been applied to the study of astronomically relevant reactions in different laboratories. In this way some reactions of atomic species such as oxygen (Balucani et al., 2006a), carbon (Costes et al., 2006; Kaiser, 2002; Casavecchia et al., 2001) and nitrogen atoms (Casavecchia et al., 2001; Balucani & Casavecchia, 2006a), simple radicals such as OH (Alagia et al., 1995), CN (Casavecchia et al., 2001; Kaiser & Balucani, 2001), C_2H (Kaiser et al., 2000b) and C_6H_5 (Kaiser et al., 2000a) radicals, and C_2/C_3 (Kaiser et al., 2001)) have been characterized. In the following paragraphs, after a brief introduction on the experimental method, we will summarize some of the results obtained in our laboratory which are of relevance to the atmosphere of Titan, as well as those of Mars and Triton. These studies have been carried out within the European Networks Molecular Universe (2004-2007) and Europlanet (2005-2008) funded by the European Commission.

2. The experimental technique

The CMB technique with MS detection − first developed in the late 60s to address fundamental aspects − has more recently achieved the capability of studying elementary reactions of relevance in astrochemistry, as a result of improvements in the production of beams of unstable species and vacuum technology (Balucani et al., 2006a; Kaiser & Balucani, 2001; Kaiser, 2002). In CMB experiments the reactants are confined into separate beams which cross each other at a specific angle; the species of each beam are characterized by a well defined velocity and are made to collide only with the molecules of the other beam, allowing us to observe the consequences of well defined molecular collisions. The products are therefore formed only at the collision center and fly undisturbed towards the detector because of the large mean free path achieved by operating at a very low pressure (10^{-5} Pa). In CMB experiments the product detection can be done by means of spectroscopic techniques, but it is the coupling with MS detection to make the method universal, that is, applicable to the study of (at least in principle) any reaction. Any species can be ionized in the ionizer which precedes the quadrupole mass filter and, therefore, it is possible to determine the mass (and in favorable cases the gross formula) of all the possible species produced in a reaction by ionizing the product and selecting different mass-to-charge ratios (m/e) in the mass filter. Some problems, such as dissociative ionization and background noise, have restricted the sensitivity of the method, but we have recently succeeded in overcoming most of those problems by means of the soft electron impact ionization (EII) approach (Balucani et al., 2006a). The use of MS detection is anyhow advantageous if compared to spectroscopic techniques, the applicability of which requires the knowledge of the optical properties of the products, while their nature

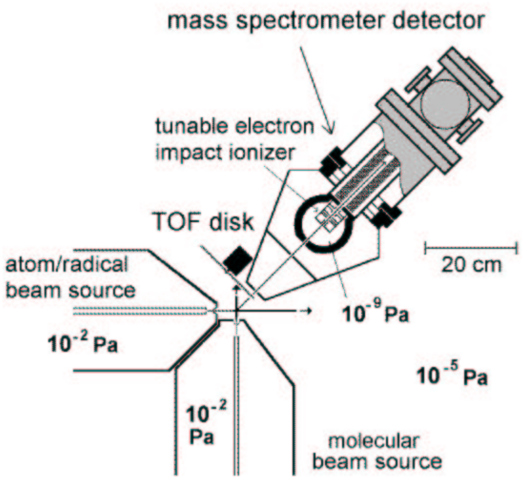

Fig. 1. Top-view of the crossed molecular beam apparatus with rotating MS detector and time-of-flight chopper operating in our laboratory.

itself can be unknown. An advantage with respect to common MS flow reactors is the possibility to measure product angular and velocity distributions, which allows one to directly derive the amount of the total energy available to the products and, therefore, the energetics of the reaction. This is crucial when more isomers with the same gross formula can be produced (Balucani & Casavecchia, 2006c). In general, the CMB technique allows one to determine (a) the nature of the primary reaction products, (b) the branching ratios of competing reaction channels, (c) the microscopic reaction mechanisms (d) the product energy partitioning. More generally, we can say that it is possible to obtain information on the underlying potential energy surfaces (PES) governing the transformation from reactants to products.

Perhaps the most difficult task in this kind of experiments is the production of beams of atomic or radical species with an intensity high enough to perform the experiment. In our laboratory we have achieved that by means of a versatile radio-frequency discharge beam source (Alagia et al., 1997): by using an appropriate molecular precursor seeded in He or Ne, we have been able to produce continuous supersonic beams of O, N and C atoms, OH and CN radicals, and C_2. More recently we have developed a flash pyrolytic beam source for the production of hydrocarbon radicals. The performance of the beam source, an adaptation to the production of continuous beams of the pulsed beam source originally developed by (Kohn et al., 1992), has been such as to allow the investigation of two radical-radical reactions, namely $O+CH_3$ and $O+C_3H_5$.

3. The reaction of $N(^2D)$ with simple hydrocarbons and H_2. Implications for the atmosphere of Titan

The chemical composition and evolution of the atmosphere of Titan has been the subject of numerous observations and extensive modeling. The still on-going Cassini-Huygens mission has been providing an unprecedented bulk of information on the "Earth-like moon". A series of detailed photochemical models have been developed over two decades (Yung et al., 1984; Toublanc et al., 1995; Lara et al., 1996; Wilson & Atreya, 2004) after the Voyager missions provided evidence that N_2 is the principal constituent of Titan's atmosphere. Those models succeeded in reproducing the bulk composition of the atmosphere of Titan and were able to explain (at least qualitatively) the presence of nitriles. In a gaseous environment dominated by molecular nitrogen with methane being the second most abundant molecule (in the order of few percent), it is intuitive that the formation of nitriles is initiated by the reactions of active forms of nitrogen - such as nitrogen atoms or ions, which are formed in the upper atmosphere. For instance, N_2 dissociation can be induced by electron impact, extreme-UV photolysis, galactic cosmic ray absorption. These processes, together with N_2^+ dissociative recombination and N_2 dissociative photoionization, lead to atomic nitrogen in the ground, ^4S, and metastable electronically excited, $^2D_{3/2,5/2}$, states (Carrasco et al., 2006). The radiative lifetimes of the metastable states $^2D_{3/2}$ and $^2D_{5/2}$ are quite long (12.3 and 48 hours), because the transition from a doublet to a quartet state is strongly forbidden. In addition, collisional deactivation of $N(^2D)$ by N_2 is a slow process (k_{298}=1.7×10^{-14} cm^3 molec^{-1} s^{-1}) (see Carrasco et al., 2006) and therefore the main fate of $N(^2D)$ above 800 km is chemical reaction with other constituents of Titan's atmosphere. The production of N atoms in the ^2D state is an important fact, because $N(^4S)$ atoms exhibit very low reactivity with closed-shell molecules and the probability of collision with an open-shell radical is small (Carrasco et al., 2006). On the contrary, the reactions of $N(^2D)$ with several molecules identified in the atmosphere of Titan (including the relatively abundant CH_4 and H_2) can give an important contribution to the chemical evolution of the atmosphere. CH_4 is the most abundant gas after N_2 and, therefore, reactive collisions of $N(^2D)$ with CH_4 can easily take place. Yung et al. (1984) suggested that the main products of the $N(^2D)+CH_4$ reaction are NH and CH_3 and, on this assumption, drew some reaction cycles, which ultimately lead to the formation of HCN. Also, Yung (1987) suggested that the reaction $N(^2D)+C_2H_2$ could be relevant in the case it leads to HCCN+H. The cyanomethylene radical was proposed, in fact, as an important intermediate towards the formation of C_2N_2 and C_4N_2. More recent photochemical models for calculating the vertical distribution of Titan's neutral atmosphere compounds rely on similar suggestions (Toublanc et al., 1995; Lara et al., 1996; Wilson & Atreya, 2004).

Laboratory experiments on the $N(^2D)$ reactions have become available only lately, because of the experimental difficulties in producing atomic species in electronically excited states in a controlled manner. The rate constants for the reactions $N(^2D)+CH_4$ (1), $N(^2D)+C_2H_2$ (2) and $N(^2D)+C_2H_4$ (3) have been measured in the late 90s and the room temperature values are slightly larger than those estimated and used in the models (for a critical review see Carrasco et al., 2006). As far as reaction (1) is concerned, however, the results of reaction dynamics studies do not sustain the assumptions of Yung et al. (1984) about the reaction mechanism and the nature of the products. According to the *ab initio* calculations of the NCH_4 PES (Kurosaki et al., 1998), the possible products – all formed after $N(^2D)$ has inserted into one of the C-H bonds of methane – are (1a) CH_3N+H, (1b) NH+CH_3, (1c) $CHNH_2$+H, and (1d) CH_2NH + H. A recent experimental study derived an absolute yield of 0.3±0.1 and 0.8±0.2 for NH (from channel 1b) and H (from channels 1a, 1c, 1d) production, respectively (Umemoto et al., 1998). Aiming to identify the CH_3N isomer(s) produced in channels (1a, 1c, 1d) we have performed a systematic study of the $N(^2D)+CH_4$ reaction as a function of collision energy, E_c (from 20 kJ mol^{-1} to 60 kJ mol^{-1}) (Casavecchia et al., 2001; Balucani & Casavecchia, 2006b). ¿From our experimental results, we have got experimental evidence that the channels leading to CH_2NH (methylenimine) and CH_3N (methylnitrene) are both open and the relative branching ratio varies considerably with the amount of energy available (Casavecchia et al., 2001; Balucani & Casavecchia, 2006b). Several implications for the atmospheric chemistry of Titan follow. The assumption that only NH and CH_3 are the products of reaction (1) is wrong since that reactive channel is minor in the laboratory experiments. Therefore, the nitrogen chemistry that relies on the dominance of channel (1b) in the photochemical models of the atmosphere of Titan should be reconsidered. Furthermore, our results suggest that the reaction (1) is an active route of formation of methylenimine, CH_2NH, a closed-shell molecule. Interestingly, CH_2NH contains a novel C-N bond, thus demonstrating that such a bond can be generated directly by a reaction involving an active form of N_2 and methane. The presence of an unsaturated CN bond renders CH_2NH a reactive molecule and is therefore possible that methylenimine further reacts in the relatively dense atmosphere of Titan, possibly contributing to the formation of larger nitrile molecules. In this respect, it is interesting to recall that the Titan's atmospheric aerosols were analyzed during the Huygens probe descent by the Aerosol Collector and Pyrolyser and were found to be rich in nitrogen (Israel et al., 2005). Alternatively, methylenimine could photodissociate after UV adsorption (CH_2NH has an absorption maximum near 250 nm) possibly generating HCN/HNC+H_2 or H_2CN/HCNH

+H. Interestingly, the presence of CH_2NH in the atmosphere of Titan has been recently inferred through the analysis of measurements of the ionospheric composition made by the Ion Neutral Mass Spectrometer (INMS) on the Cassini spacecraft (Vuitton et al., 2006).

We have also performed experiments on reaction (2) and the m/e=39 product (C_2HN) was found to be an important primary reaction product. According to the PES *ab initio* calculations (Balucani et al., 2000a), the addition of $N(^2D)$ to the π-system of C_2H_2 leads to a three-member cyclic HC(N)CH radical, which can either decompose to cyclic-HC(N)C+H or isomerize to HCCNH and/or H_2CCN (cyanomethyl). Both HCCNH and H_2CCN can dissociate into HCCN+H. Our experimental results are consistent with both HCCN+H and cyclic-HC(N)C+H formation (see Balucani et al., 2000a) and essentially confirm the potential role of the $N(^2D)+C_2H_2$ reaction as the first step in the formation of C_2N_2 and C_2N_4.

A final example is given, which is probably the case which fully represents the capability of the CMB technique, namely the reaction $N(^2D)+C_2H_4$ (3). Before our study, reaction (3) was not included in the models, even though ethylene is almost as abundant as acetylene. The only exception is the model by Lara et al. (1996) where, however, it was considered erroneously. Our experimental results clearly indicate that also this reaction proceeds through the formation of an addition intermediate and that products of general formula C_2H_3N are formed through a N/H exchange channel (Balucani et al., 2000b). Our findings are supported by the PES *ab initio* calculations by Takayanagi et al. (1998) and are consistent with the formation of ketenimine (CH_2=C=NH) and 2H-azirine (cyclic $CH(N)CH_2$). It is very interesting to note, however, that according to the energy release – an observable which can be obtained only from a reaction dynamics experiment – a consistent fraction of the 2H-azirine and ketenimine molecules are formed with enough internal energy to spontaneously tautomerize to the most stable isomer acetonitrile, even in a collision free environment. Therefore, reaction (3) can be considered an effective route which ultimately leads to the formation of CH_3CN. Our suggestion has been accepted and included in the model recently developed by Wilson & Atreya (2004) and it was seen to correctly predict the amount of acetonitrile observed in Titan's atmosphere. In addition to that, the 2H-azirine and ketenimine molecules which do not undergo tautomerization could contribute to the building-up of the nitrogen-rich aerosols of the atmosphere of Titan (this is especially true for ketenimine which contains two unsaturated bonds).

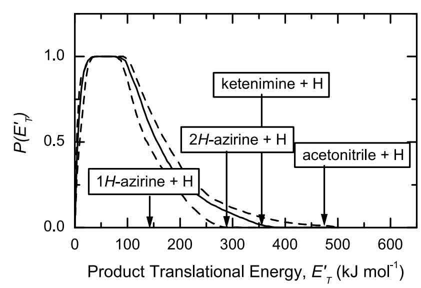

Fig. 2. Product translational energy distribution for the reaction $N(^2D)+C_2H_4$ as it was obtained in our CMB experiment at a collision energy of 33.3 kJ mol^{-1}. The arrows indicate the total available energy (given by $E_c - \Delta H^\circ_{rxn}$) for the channels leading to H+CH(NH)CH (1H-azirine), H+CH(N)CH_2 (2H-azirine), H+CH_2CNH (ketenimine), and H+CH_3CN (acetonitrile). For more details, see Balucani et al. Balucani et al. (2000b).

We have also investigated the reaction $N(^2D)+H_2$ (4), which is the best-characterized reaction involving the ^{2}D state of atomic nitrogen. The only exothermic reactive channel is the one leading to NH in its $X^3\Sigma^-$ electronic ground state and atomic hydrogen. Of relevance for the atmosphere of Titan is the product energy partitioning, that has been determined in those studies (Balucani & al., 2006b; Umemoto et al., 2000). In particular, the NH vibrational states are populated up to v'=3 (Umemoto et al., 2000); that should be accounted for in the modeling because the energy content of the vibrationally excited levels is sizeable and could significantly increase the capability of NH of undergoing subsequent reactions.

4. The reactions of atomic oxygen with unsaturated hydrocarbons and hydrocarbon radicals. Possible routes of CO formation in the atmosphere of Titan

Few oxygen containing molecules have been detected in the atmosphere of Titan, namely CO, CO_2, and, more recently, H_2O (Coustenis et al., 1998). In particular CO represents the major reservoir of oxygen and a long debate has concerned its origin, which can be primordial or photochemical. In all cases, since the upper atmosphere of Titan is quite rich in hydrocarbons, most of atomic oxygen will end up in CO or CO-containing molecules (Baines et al., 2006). To establish whether the external source of oxygen could account for the observed CO amount it is important to correctly include all the CO-forming reactions in the modeling. In our laboratory we have investigated the reaction of atomic oxygen with acetylene, ethylene, and methyl (CH_3, the main product of CH_4 photolysis) and allyl (C_3H_5) radicals. In all cases we have got evidence that CO, or CO-related molecules such as HCO, CH_2CO and acrolein, are formed.

As fas as the reaction $O(^3P)+C_2H_2$ (5) is concerned, while the rate constant has been well established the identity of the primary reaction products and their relative importance has been a subject of considerable controversy over the years. According to recent *ab initio* calculations, the reaction mechanism sees the initial electrophilic attack of the O atom to the triple bond of the C_2H_2 molecule with formation of a triplet diradical adduct that, under single collision conditions, undergoes CH bond cleavage to ketenyl(HCCO)+H (5a) or CC bond cleavage to CH_2+CO (5b). At the E_c of 52.7 kJ mol^{-1} we obtained the following branching ratio: 0.79±0.05 for the channel (5a) and 0.21±0.05 for channel (5b). The present estimate of the branching ratio is thought to be more accurate than previous ones (to be noted that the branching ratio for this system is essentially temperature-independent, Peeters et al. (1994)). The derived values are in excellent agreement with the most accurate kinetic determinations of Peeters et al. (1994).

If we move from the acetylene to the ethylene reaction, the presence of two additional hydrogen atoms (7-atom reactions) renders the PES much more complicated and opens up a larger variety of competing pathways. Five competing energetically allowed pathways are possible: (6a) CH_2CHO+H, (6b) CH_3CO+H, (6c) CH_2CO+H_2, (6d) $HCO+CH_3$, and (6e) $HCOH+CH_2$. Also in this case the overall rate constant of reaction (6) is well established (Nguyen et al., 2005), while the question of the identity of the primary reaction products and their relative importance has been controversial. In our laboratory we have determined the branching ratio for all possible channels with great accuracy at E_c=54.0 kJ mol^{-1}, thus obtaining for each of them: channel (6a) 0.27±0.06; channel (6b) 0.01±0.005; channel (6c) 0.13±0.03; channel (6d) 0.43±0.09; channel (6e) 0.16+0/−0.08. For this reaction as well, the branching ratio is essentially temperature-independent (Nguyen et al., 2005) and, therefore, should be valid for the modeling of the atmosphere of Titan.

More recently, we have started investigating the reactions involving atomic oxygen and hydrocarbon radicals. These experiments are quite challenging and, as a matter of fact, CMB studies on reactions involving two open-shell species are rare, mainly because of the difficulty in generating two chemically unstable species with a density high enough to perform a reactive scattering experiment. Nevertheless, the characterization of radical-radical reactions is certainly to be pursued because of the high reactivity of open-shell species, which renders their role in the chemistry of planetary atmospheres more important than their relative scarcity might suggest. The improvements of the CMB apparatus accomplished in our laboratory have been crucial to achieving that (Balucani et al., 2006a). Particularly the soft

EII approach has been essential to studying hydrocarbon radical reactions, because of the tendency of these species and their parent molecules to fragment into the ionizer. The first reactive systems we have looked at are those involving atomic oxygen and methyl, CH_3, and allyl, C_3H_5, radicals. As far as the reaction $O(^3P)+CH_3$ (7) is concerned, the only channel considered until recently was the one leading to formaldehyde (H_2CO) and H. The reaction has been included in the models accordingly (see, for instance, Wong et al., 2005). More recent experiments, however, have revealed that also CO is produced with a relatively large yield (see Marcy et al., 2001, and references therein), even though it is unclear how this channel proceeds. No feasible pathway leading to CO, in fact, was identified in the *ab initio* calculations of the relative PES (Marcy et al., 2001). In a first experiment, we have investigated reaction $O(^3P)+CH_3$ at E_c=57.3 kJ mol^{-1}; from the preliminary results we have got experimental evidence that the active channels are two: one leading to formaldehyde and atomic hydrogen, as generally accepted, and another one, leading to HCO and molecular hydrogen. Differently from H_2CO, HCO can easily fragment to CO and, therefore, the CO observed in the kinetic experiments can arise from a fast dissociation of the primary product HCO. We have also investigated reaction $O(^3P)+C_3H_5$ (8) at E_c=74.5 kJ mol^{-1} and found that, in addition to the only channel considered so far - the one leading to acrolein and atomic hydrogen - other products originated by C-C bond cleavage channels are open. Further measurements are, however, necessary to identify which of the possible channels ($CH_2O+C_2H_3$, $C_2H_2O+CH_3$, C_2H_4+HCO, C_2H_5+CO) are responsible for the signal observed.

5. Conclusions

We have investigated by the CMB technique the reactions of $N(^2D)$ with H_2 and the hydrocarbons CH_4, C_2H_2 and C_2H_4, which are amongst the most abundant minor components of the atmosphere of Titan. In the cases of the reactions with hydrocarbons, molecular products containing a novel CN bond are formed, thus suggesting possible routes towards the production of gas-phase nitriles. Remarkably, a variety of unsaturated nitriles (such as methylenimine and ketenimine) can be formed in those reactions. Those molecules could be responsible for the building-up of the atmospheric aerosols of Titan. We have also investigated the reactions between $O(^3P)$ and unsaturated hydrocarbons, which might be responsible for the conversion of oxygen to CO. Accurate branching ratios for the reaction with acetylene and ethylene have been given. Finally, we have extended the same approach to the study of radical-radical reactions, starting from the reactions of atomic oxygen with simple hydrocarbon radicals. Molecular products other than those already considered in the modeling of planetary atmospheres have been identified and new routes of formation of CO can be envisaged.

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