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The reactions of atomic oxygen with unsaturated hydrocarbons in planetary atmospheres

N. BALUCANI

The observation in hydrocarbon-rich planetary atmospheres of highly unsaturated organic molecules (such as acetylene) poses the question of how these molecules can survive in the upper atmospheres where atomic and radical species are relatively abundant. From a chemical point of view, indeed, each unsaturated C-C bond is a potential site for addition reactions especially when radicals are involved. Part of this puzzle is actually explained by the fact that the reactions of small alkynes, alkenes and dienes with several atomic and radical species (such as atomic carbon or CH, C_2H, C_2 and CN radicals) do not destroy the C-atom skeleton of unsaturated species, but rather elongate it. Notable examples are the reactions between C, C_2, C_2H, CH, CN with acetylene (HCCH) and diacetylene (HCCCCH) which, in laboratory experiments, have been verified to generate the products C_3, C_3H, C_3H_2, C_4H, C_5H, C_6H, C_6H_2, HC_3N and HC_5N [1]. Some of these species have been identified in hydrocarbon-rich atmospheres, including the atmosphere of Titan. Quite interestingly, analogous oxygen-containing highly unsaturated species have not been identified in planetary atmospheres. Oxygen in C-rich atmospheres appears, instead, to be mostly locked in CO_2, H_2CO and CO.

In our laboratory we have started a systematic investigation of several reactions involving atomic oxygen and unsaturated hydrocarbons (C_2H_2, C_2H_4, CH_3CCH, $CH_2{=}C{=}CH_2$) by means of the crossed molecular beam technique with mass spectrometric detection and time-of-flight analysis [2-5]. Quite interestingly, we have observed that C-C bond fission channels are always relevant or dominant reaction pathways. The most illustrative case is the reaction between O and allene ($CH_2{=}C{=}CH_2$) where ˜ 90% of the reaction leads directly to the stable products $CO+C_2H_4$ [5], but also significant fractions of the reactions $O+C_2H_2$and $O+C_2H_4$ lead to the products $CO+CH_2$ and $HCO+CH_3$, respectively [2,3]. In other words, the reactions of unsaturated hydrocarbons with atomic oxygen are not only terminating the hydrocarbon growth in oxygen-rich environments, but are also able to convert relatively abundant and widely spread small unsaturated hydrocarbons directly into CO or its precursor HCO. Implications for the chemistry of the planetary atmospheres will be noted.

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Reactions of state-selected $O^+(^4S, ^2D, ^2P)$ oxygen ions relevant to the chemistry of Titan's ionosphere

B. CUNHA DE MIRANDA, C. ROMANZIN,
S. CHEFDEVILLE, V. VUITTON, J. ZABKA,
M. POLASEK, C. ALCARAZ

The objectives of this work are derived from the very recent debate on the role of oxygen species in the chemistry of Titan atmosphere [1]. It appears that these species could be initiated by O^+ cations that are injected on Titan from another Saturn satellite, Enceladus, as confirmed by the observation of precipitating O^+ flux by the Cassini Plasma Spectrometer [2]. The charge transfer (CT) of O^+ ions producing neutral O atoms would be the starting point of the chemistry of oxygen in Titan neutral atmosphere. Thus, it appears very important to caracterize as well as possible the reactions of O^+ with the two most abundant neutrals of Titan's atmosphere, N_2 and CH_4.

In this work, the reactions of state-selected $O^+(^4S, ^2D, ^2P)$ atomic ions ($^{16}O^+$ and $^{18}O^+$) with methane (CH_4 and CD_4) have been studied on the guided ion beam apparatus CERISES [3] using VUV radiation at the synchrotron SOLEIL. Absolute cross sections for the ionic product formations have been measured as a function of electronic excitation of O^+ and collision energy. With electronic excitation of the O^+ parent ion from the ground state ^4S to the long lived excited states ^2D and ^2P, a reduction of the total cross section and a complete inversion of the branching ratio between the main products ($CH_4{}^+$ and $CH_3{}^+$) are observed.

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Dissociation of the CO_2 dications in the upper atmospheres of planets - a new route of CO^+ and O^+ formation

M. ALAGIA[a], P. CANDORI[b], S. FALCINELLI[b]
F. PIRANI[c], R. RICHTER[d],
S. STRANGES[e], [a], F. VECCHIOCATTIVI[b]
[a]IOM-CNR, Laboratorio TASC, I-34149 Basovizza, Trieste, Italy
[b]Dipartimento di Ingegneria Civile ed Ambientale,
Università di Perugia, 06125 Perugia, Italy
[c]Dipartimento di Chimica, Università di Perugia,
06123 Perugia, Italy
[d]Sincrotrone Trieste, Area Science Park,
34149 Basovizza, Trieste, Italy
[e]Dipartimento di Chimica, Universit di Roma "La Sapienza",
00185 Rome, Italy

The first observation of the CO_2^{2+}dication formed by electron impact ionization of carbon dioxide was reported in1961 [1]. Since that experiment, the double ionization of CO_2has been studied in several laboratories [2-5]. These kinds of processes are of great interest because of the involvementof CO_2 in several atmospheric phenomena of the Earth andof other planets and in plasma environments. In Mars' atmosphere, where CO_2 is the main component, the importance ofthe CO_2^{2+} dication and its dissociation has been recently demonstrated [6]. In this contribution we present a double photoionization of CO_2 molecules studied in the 34-50 eV photon energy range, by the use of synchrotron radiation and detecting electron-ion and electron-ion-ion coincidences. The experiment has been carried out at the synchrotron light laboratory ELETTRA (Trieste, Italy) by the use of the ARPES end station of the Gas Phase Beamline [7,8]. The CO_2 molecular beam and the vuv light beam cross at right angles, with the light polarization vector being parallel to the synchrotron ring plane and perpendicular to the time-of-flight direction of detected ions. Three processes have been observed: (i) the formation of the CO_2^{2+} molecular dication, (ii) the production of a metastable $(CO_2^{2+})^*$ that dissociates, with an apparent lifetime of 3.1 μs, giving rise to CO^+ and O^+ ions, and (iii) the dissociation leading to the same products, but occurring with a lifetime shorter than 0.05 μs. In the photon energy range investigated, the double dissociative photoionization reaction of CO_2 leads to an isotropic distribution of CO^+ and O^+ product ions with respect to the polarization vectorof the light. When the photon energy increases, the distribution of products becomes anisotropic, with the two ions preferentially emitted along the direction of the light polarization vector. This implies that the molecule photoionizes when oriented parallel to that direction and also that the ${CO_2}^{2+}$ dication just formed dissociates in a time shorter than its typical rotational period. At low photon energy, the CO^+ and O^+ product ions separate predominantly with a total kinetic energy between 3 and 4 eV. This mechanism becomes gradually less important when the photon energy increases and, at 49 eV, a process where the two products separate with a kinetic energy between 5 and 6 eV is dominant.

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Implantation of reactive ions in oxygen rich ices

G. Strazzulla

I will describe some results recently obtained from laboratory experiments of implantation of reactive (H, C, N, O, S) ions in water ice and mixtures with molecular oxygen and nitrogen. Experiments have been conducted with ions at different charge states and energies, bombarding ices at different temperatures. The results arediscussed in the light of their relevance in astrophysical environments. In particular the results demonstrated that CO_2 is formed after C implantation in all of the investigated targets (water ice and mixtures with molecular oxygen and nitrogen). Sulfuric acid dissolved in water ice is formed with an high yield after S implantation. H implantation in sulfur dioxide produces poly-SO_3.

Potential O-organic chemistry in Titan's environment

F. RAULIN, C. BRASSÉ, P. COLL
Laboratoire Interuniversitaire des Systèmes Atmosphériques,
Universités Paris Est Créteil & Paris Diderot, UMR CNRS 7583,
IPSL, 61 Avenue Général de Gaulle, 94010 Créteil Cedex France

With its unique dense dinitrogen-methane atmosphere, Titan, the largest satellite of Saturn, exhibits a chemically reduced environment where an active, complex and quasi prebiotic organic chemistry is going on[1]. This chemistry mainly involves C-H-N atoms, since O-containing gaseous compounds are only present as trace components in the atmosphere.

The only O-compounds so far detected in gas phase in Titan atmosphere are CO, CO_2 and H_2O, CO being the most abundant with a concentration of about 50 ppm in the stratosphere[2], instead of some 14 ppb[3] for CO_2 and 0.4 ppb[4] for H_2O. In spite of its low atmospheric concentration, CO may be the source of O-organics produced during the chemical evolution of the atmosphere. Laboratory simulation experiments starting from N_2-CH_4 gas mixtures including a small fraction of CO, submitted to plasma discharge, have shown the formation of oxirane as the main O-product, although at low concentration[5,6].

However, the main involvement of oxygen atoms in Titan's organic chemistry should be in the internal ocean of the satellite, the presence of which looks more and more likely[7,8]. This liquid water phase is supposed to include up to several percents of ammonia. It is also likely that it initially included some organic matter coming from chondritic materials which were present in the early history of the satellite and participated in its formation9. Consequently, part of this organic matter could have chemically evolved in such a polar solvent and Titan's early ocean may have experienced an active prebiotic chemistry. However, Titan's ocean today is located below a 50-80 km thick ice layers and its organic content cannot be explored easily.

Nevertheless, there are other places in Titan's environment where an active organic O-chemistry could occur, and could be much more easily looked at. Indeed, Titan's surface could episodically experience the presence of liquid water. Models show that large cometary impacts could melt Titan's surface water ice and provide liquid water bodies allowing, although for short time periods10, further chemical evolution of the organic aerosols accumulating on the surface. Similarly, the release of water-ammonia slush coming from the deep surface layers, during cryovolcanism episodes11 could also permit the chemical evolution of the aerosols. These surface processes, could be the source of an important incorporation of O-atoms in the resulting products, through hydrolysis processes.

During the past few years, many experimental works have been carried out in the laboratory to study those processes, using Titan's tholins (laboratory analogues of Titan's aerosols12) within conditions trying to mimic these Titan's surface conditions[13-15]. Their results show the formation of several organic O-compounds of biological interest, which could be present on Titan's surface and detectable in the frame of future mission of exploration of Titan.

We will present these different aspects of the O-organic chemistry of Titan, including the most recent laboratory results.

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Formation of negative ions from water group positive ions at high collision energies: Implications for the ionosphere of Titan.

M. Polášek[a], J. abka[a],
C. Alcaraz[b], V. Vuitton[c]
[a]J. Heyrovský Institute of Physical Chemistry of the ASCR,
Dolejškova 3, Praha 8, 182 23 Czech Republic
[b]Laboratoire de Chimie Physique, UMR 8000 CNRS - Univ.
Paris Sud 11, - Bât. 350, 91405 Orsay cedex, France
[c]Laboratoire de Planétologie de Grenoble, Bâtiment D
de Physique BP53, 38041, Grenoble, France

The Saturnian magnetosphere is dominated by neutrals originating from the icy satellites and ring system. These neutrals are ionised in the inner and middle magnetosphere producing a plasma composed of protons, H2+, and so-called "water group" ions O^+, HO^+, H_2O^+ and H_3O^+ [1]. Saturn is a rapidly rotating planet so that the resulting velocity of the plasma is quite rapid, varying from ˜ 30 km s1 near Enceladus at 4 RS to 170 km s1 near Titan at 20 RS [1]. A precipitation of O^+ ions with energies of 1-4 keV was found at Titan by the Cassini CAPS spectrometer.[2] It has been speculated [3] that a few percent of the oxygen ion flux is converted to O ions that may play a role in the Titan's negative ion chemistry, which was found unexpectedly rich, [4] but is still rather poorly understood [5].

Absolute cross-sections have already been measured for the O+ O [6] and O O [7] processes at high energies, however no data are available for the other "water group" ions.

The objective of this study was to measure the absolute total cross-sections for the formation of O and HO ions by charge reversal processes of O^+, HO^+, H_2O^+ and H_3O^+ ions in collisions with Xe, N_2 and CH_4.

The experiments have been done on the ZAB2-SEQ sector type mass spectrometer consisting of magnetic (B) and electrostatic (E) analysers. The ions were formed from water vapours by the electron- or chemical ionization. They were accelerated to 8 keV and mass-selected by the magnetic sector (B). The electron transfer processes occurred in the collision cell located between B and E, in which the collision gas was admitted. The negative ions formed in the cell were analyzed by E and detected.

In case of HO^+, H_2O^+ and H_3O^+ ions, only O and HO were detected. The cross-section values decrease for the studied targets in the order Xe > CH_4 > N_2. Moreover, certain differences in the [O]/[HO] ratios were observed for the different targets.

Our results show that the oxygen containing negative ions as well as the neutral species can be formed by the high-energy collisions of positive "water group" ions impacting the Titan's upper atmosphere. These species may interact with the components of the Titans atmosphere in many ways and can, for example, initiate numerous ion/neutral-, neutral/neutral-, and collision-induced unimolecular reactions.

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Oxygen chemistry in star forming-regions

A. OCCHIOGROSSO

Known as PAH's precursors, aliphatic hydrocarbons (with formula C_nH_{2n+2}, C_nH_{2n-2}, C_nH_{2n}) play an important role in the star-forming region chemistry. They have been identified towards different astrochemical environments and their column densities are in the range 1015 to 1017 cm-2 (Lahuis and van Dishoeck 2000, Hinkleet al. 2008, van Dishoeck et al. 1995). Presently, there is no generally accepted explanation of the formation mechanisms for hydrocarbons but their abundances seem to be linked to the availability of atomic oxygen (Fortney 2012).

Here, we present a revised chemistry for the reactions between oxygen and different hydrocarbons based on the new experimental results obtained by Leonori et al. (2012). In particular, we focused on the reactions listed below

Ψ O+ C_2H_2
Ψ O+ C_2H_4
Ψ O+ CH_3CCH
Ψ O+ CH_2CCH_2

and we model various astrochemical environments looking at the effects that these interactions produce on the molecular abundances for the species involved. Particular attention is given to star forming region for the possible implications on the content of oxygen compounds in newly formed planets.

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Solid oxygen on the icy satellites

RAUL BARAGIOLA

I will discuss the formation of O_2, H_2O_2 and ozone from the radiolysis of ice by UV photons and magnetospheric ions, trapping of exospheric O_2 enhanced by irradiation, and the ususpected thermal staibility of cold traps with pools of solid oxygen. The results and new paradigms result from multiple simulations at our laboratory at the University of Virginia.

Influence of CO on the N_2-CH_4 Titan atmospheric reactivity

NATHALIE CARRASCO

The atmosphere of Titan is mainly made of N_2 and CH_4, and the subsequent $C_xH_yN_z$ volatile species produced by photochemistry. Most of the laboratory studies simulating Titan's atmospheric reactivity focus on the highly complex carbon and nitrogen organic chemistry leading to a production of laboratory analogues of Titan's aerosols, called Tholins.

However, Titan's atmosphere contains traces of oxygen-bearing compounds, among them carbon monoxyde CO. Carbon monoxyde is actually the most abundant oxygenated volatile, with a 47 ppmv concentration measured in high stratosphere.

In this work we investigate the influence of CO on the N_2-CH_4 reactivity. We simulate the whole reaction chains with a laboratory Radio Frequency Capacitively Coupled plasma discharge (RF CCP) gas mixture of in a nitrogen, methane and carbon monoxyde. We find that CO introdution modifies significantly the kinetics and the chemical composition of the gas products, and involves inclusion of oxygen in the dust.

As a conclusion, we show that carbon monoxyde is effectively coupled with N_2-CH_4 chemistry and that it impacts even the solid organic aerosols production.

Barrierless ionic pathways in the synthesis of methyl esters of small carboxylic acids

D. ASCENZI, P. TOSI, G. GUELLA
Department of Physics, University of Trento,
Via Sommarive 14, I-38123 Povo Trento (Italy)

Oxygen bearing complex organic molecules have long been detected in the interstellar medium especially in hot cores and molecular clouds [1]. Among them, the esters of small carboxylic acids such as methyl and ethyl formate play a key role in understanding the origin of life since they can act as the building block of bio-polymers. Despite its detection in various sources, the path leading to methyl formate still remains a question of debate [2]. When only gas-phase mechanisms are considered the observed abundance of methyl formate is under-predicted, hence the contribution of surface and grain chemistry has been introduced [3, 4, 5]. Recent chemical imaging studies of methyl formate and its precursors suggest a new gas-phase route to its formation involving ion-molecule reactions [6] and the gas/grain chemical networkmodel has been recently modified to account for ion-molecule reactions between protonated methanol and formic acid as well as protonated formic acid and neutral methanol [7].

The reactivity of protonated methanol and formic acid has been recently reinvestigated and found to give, in addition to the adduct ion, protonated methyl formate plus water via a barrierless methyl cation transfer process [8]. On the other side, the reaction between a neutral alcohol (methanol) and a protonated carboxylic acid (formic acid) is well-known in organic chemistry as acid-catalyzed Fischer esterification. The traditional Fisher mechanism, although having a stable entrance channel complex, evolves via a tetrahedral intermediate hampered by large barriers and therefore is not viable under the low temperatures of the ISM. However a recent theoretical investigation on the closely related reaction of protonated acetic acid with methanol proposes an alternative proton-shuttle mechanism proceeding without barriers [9] at energies above that of reagents.

Stimulated by such findings we have investigated the reaction of protonated acetic acid with methanol, to give protonated methyl acetate, using the technique of guided ion beam tandem mass spectrometry, which permits to measure reactive cross sections as a function of collision energy and pressure. We have experimental evidence that the reaction leading to the protonated ester:

$$CH_3COOH_2{}^+ + CH_3OH \quad CH_3C(OH)OCH_3{}^+ + H_2O$$

proceeds even below the energy required for the formation of the tetrahedral intermediate (a barrier of ˜ 14.6 kcal/mol is calculated in [9]), hence an alternative mechanism should be operative in this gas-phase esterification reaction. Finally, we note that, although methyl acetate has not yet been detected in the ISM, both its precursors methanol and acetic acid are known to be present, hence the possible chemical routes leading to its formation maybe of interest for the astrochemical community.

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Carbon dioxide dynamics in earth and planetary atmospheres: vibrational energy transfer in CO_2 + CO_2 collisions

A. LOMBARDI[a], A. LAGANÀ[a], F. PIRANI[a],
M. BARTOLOMEI[b]
[a]Department of Chemistry, University of Perugia,
Via Elce di Sotto 8, 06123, Perugia, Italy
[b]Instituto de Fisica Fundamental, CSIC,
Serrano 123, 28006, Madrid, Spain

The vibrational energy exchange occurring in collisions involving small molecules is largely responsible for energy relaxation and state population of gas phase, and therefore plays a key role in determining the energy balance of planetary atmospheres (see e.g. [1]). Carbon dioxide is an important component of planetary atmospheres. Being a triatomic molecule, the exchange of internal energy upon collision can be relevant and is a key step in its contribution to the energy balance of the atmospheres. Therefore the behaviour of CO_2 in inelastic collisions with itself or other species such as N_2 and CO deserves considerable interest and finds interesting applications in plasma chemistry and hypersonic aerodynamics.

The first step of the study has been concerned with the assemblage of an appropriate Force Field. To this end electronic structure calculations have been performed at a CCSD(T) level to integrate previous MP2 results [2]. Related information has been used to build a semiempirical potential energy surface (PES) that makes use of a recently introduced bond-bond approach [3,4]. Due to the important effects of long range interactions on vibrational relaxation and excitation, intermolecular interactions have been formulated using a well tested bond-bond interaction model [3], which reproduces with accuracy short and log range parts of the intermolecular interactions. The resulting PES has been exported into the VENUS [5] program, and extended ensembles of quasi-classical trajectories (QCT) have been run for the CO_2 + CO_2 collisions in a wide range of energies. Results are targeted to calculate state-to-state vibrational exchange cross sections and thermal rate coefficients. These quantities are the necessary input of kinetic models of use in gas dynamics, aircraft re-entry studies, and many other technological applications.

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N+O associative ionization with formation of NO^+

D. SKOUTERIS, F. PIRANI, A. LAGANÀ
Dipartimento di Chimica, Università degli Studi di Perugia, Italia

Atomic nitrogen and oxygen, as well as the NO^+ ion, are important species of upper planetary atmospheres. The dissociative recombination of the NO^+ ion has been extensively studied, while much less is known on the reverse process $N + O \rightarrow NO^+ + e^-$. Its potential role in the ionospheres of planets or interstellar clouds has still to be assessed.

To characterize associative ionization of N+O, we have used a time-dependent quantum wavepacket method. This study furnishes also complementary information on the dissociative ionization of NO^+. Boltzmann averaging enables us to derive thermal rate constants for the process which will allow assessing the possible relevance of this process in planetary atmospheres rich of nitrogen and oxygen species.

Ion reactions as pathways to complex organic molecules

W. D. GEPPERT[a], M. HAMBERG[a], E. VIGREN[a]
R. D. THOMAS[a], V. ZHAUNERCHYK[a], E. S. WIRSTRÖM[b]
C. M. PERSSON[b], T. J. MILLAR[c], J. SEMANIAK[d]
M. KAMIÑSKA[d], F. ÖSTERDAHL[a], J. H. BLACK[b]
Å. HJALMARSON[b], P. BERGMAN[b], M. HOLMGREN[b]
F. HELLBERG[e], M. LARSSON[a],
[a]Stockholm University, Department of Physics,
Roslagstullbacken 21, SE-10691 Stockholm, Sweden
[b]Onsala Space Observatory, SE-439 92 Onsala,Sweden
[c]Queen's University Belfast, University Road,
Belfast, BT7 1NN, UK
[d]Institute of Physics, wiłtokrzyska Academy,
PL-25406, Kielce, Poland
[e]Manne Siegbahn Laboratory, Frescativgen 24,
SE-104 05 Stockholm, Sweden

One of the crucial questions in interstellar chemistry is the one if methanol, ethanol, dimethyl ether and formic acid are produced in the gas-phase or on grain surfaces. As gas-gas production pathways very often ion-neutral reactions leading to the protonated form of the species followed by dissociative recombination to yield the final product have been invoked.

In the case of methanol, a feasible gas-phase production process is unlikely. The rate of radiative association of CH_3^+ and H_2O leading to $CH_3OH_2^+$ has been found to be far to low to explain the observed methanol abundances [1] and, on top of that, only a minor fraction of methanol (3 %) is produced in the dissociative recombination of the latter ion [2]. Introduction of these new findings into state-of-the art model calculations of dark clouds yielded that the proposed gas-phase mechanism is by far insufficient to explain the observed methanol abundances. On the other hand, successive hydrogenation of CO on icy grain surface by H atoms has been found to produce methanol [3].

It now remains to be proven by direct observation that interstellar methanol really originates from grain surfaces. This can be done by the so-called, isotope labelling a posteriori, which was first suggested by Charnley et al. [4].

The method is based on the fact that ^{13}C is preferably accumulated in CO at low temperature, which in turn results in a ^{13}C deficiency in other molecules forming from ion-neutral reactions in the gas-phase [5]). Assuming that this selective fractionation remains unaltered by the processes of adsorption and desorption, the ^{12}C/^{13}C ratio in various molecules could be used to distinguish between formation from CO on cold grains and gas-phase formation.

We therefore performed observations of the ^{12}C/^{13}C ratio for C^{18}O and methanol in several massive young stellar objects, one pair of compact HII regions and one source hosting several young stellar objects. The 2-1 rotational line groups of the 2 isotopomers around 96 GHz were observed using the 20m telescope at Onsala Space Observatory. (see Fig. 1). With one exception (where the ^{12}C molecule lines are very probably optically thick) the agreement of the ^{12}C/^{13}C ratio on the two compounds is excellent. This points to a surface origin of interstellar methanol, which is also corroborated by the fact that a strong correlation of abundances between methanol and formaldehyde has been found in several star-forming regions [6].

Furthermore, the role of dissociative recombination in the formation of other, more complex molecules detected in star-forming regions like ethanol, dimethyl ether and ethanol will be discussed.

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Do chiral organic molecules survive extraterrestrial delivery?

Y. KEHEYAN
ISMN-CNR, INAF, c/o Dept. of Chem.,
University of Rome "La Sapienza"

Extraterrestrial delivery of organic matter played an important role in prebiotic evolution. It depends on the capability of the biomolecules to survive at high temperatures, because to reach the earth the space bodies can be exposed to a significant heat up. It has also been suggested that the chiral molecules of extraterrestrial origin might have initiated the biological homochirality, thus also the chiral properties must be preserved. The survivability of the molecules on the space bodies who reach the earth can be influenced by different factors, one of this is the chemical composition of the space body because minerals can act as catalysts for the molecule decomposition and racemization. The aim of the present study is to evaluate the behavior of chiral molecules to preserve their optical activity during extraterrestrial delivery. Indeed, besides the decomposition, high temperatures may cause chiral molecules to isomerize forming racemates. The kinetic of racemization has been studied at various temperatures, on various minerals and on two meteorites The experiments have been performed by pyrolysis gas chromatography mass spectrometry: a technique that is receiving considerable attention in various space missions .

Temperature effects on the ozone abundance in terrestrial exoplanets’ atmospheres

ERIC HÉBRARD

The search for extrasolar terrestrial planets raises currently a considerable scientific interest. The first one to be discovered are on close-in orbits around their parent stars. Known terrestrial exoplanets can therefore be as hot as a few thousand K, such as Corot-7b and Kepler-10b. The detectability of any spectral features in exoplanetary atmospheres depends mainly on two main parameters: their chemical composition and their temperature profile. However, the competition between photochemical kinetics and thermochemistry susceptible to exist in hot terrestrial atmospheres prevents us from generalizing the processes occurring in Earth’s atmosphere and initiating potential departures from equilibrium. It requires therefore detailed modelling in order to estimate the risk of false-positive and/or false-negative occurrences when seeking spectroscopic evidence of habitable conditions and life.

We apply here a one-dimensional model coupling photochemical and thermochemical kinetics and vertical diffusion to study the effects of disequilibrium chemistry on the atmospheric composition of hot terrestrial exoplanets.

We will show that the ozone abundance is very sensitive to the temperature profile and is consequently a source of notable uncertainties when modelling hot terrestrial atmospheres. Indeed, high atmospheric temperatures seem to inhibit very efficiently the production of an ozone O3 layer when considering thermochemical kinetics and when fully reversing kinetic reaction rates. In the Earth’s atmosphere, the destruction of ozone O3 occurs through a large number of reactions, among which are some catalytic cycles involving mainly hydrogenous compounds (H, OH, HO2) and competiting efficiently with the regular Chapman cycle. Globally, the higher the atmospheric temperatures, the larger the increase in some of these active compounds abundances over equilibrium predictions.

Exploring super-Earth atmospheres

Y. MIGUEL

The search for extrasolar planets has resulted in the discovery of super-Earths, with masses between 1 and 10 Earth masses. Interior models suggest that some of these exoplanets might be potentially rocky in nature, with outgassed atmospheres. Since no such planets exist in our solar system, the atmospheric composition and structure of these potentially rocky super-Earths remains largely unknown.

These planets are interesting targets for future observations, therefore, addressing their composition and atmospheric structure is a major issue and the aim of our work. We explore the composition and possible atmospheric structure of super-Earths with outgassed atmospheres and how this structure changes according to the planetary observable data: mass or radius, semimajor axis and stellar type, to get a better understanding and characterization of extrasolar rocky planets.

In order to explore such planetary atmospheres and find out what we expect to find in these worlds, we model potential outgassing and atmospheric profiles. In this work we show our results, exploring how different initial conditions lead to different atmospheres for the planets. "

Spectrometric detection of molecular oxygen in the atmospheres of terrestrial planets

MARIA BLECKA
Space Research Centre, Polish Academy of Sciences

Short review of our knowledge on the abundance of oxygen compounds in the atmospheres of terrestrial planets in particular on Mars and Venus will be done. The recent results from present missions MARS-EXPRESS, VENUS-EXPRESS and HERSCHEL will be discussed.

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List of participants

Dr. Christian Alcaraz, LCP-CNRS-Univ. Paris Sud, France
christian.alcaraz@u-psud.fr
Dr. Daniela Ascenzi, Department of Physics, University of Trento, Italy
ascenzi@science.unitn.it
Prof. Nadia Balucani, Dipartimento di Chimica, Universita' degli Studi di Perugia, Italy
nadia.balucani@unipg.it
Maria Blecka, SRC PAS, Poland
mib@cbk.waw.pl
Dr. Nathalie Carrasco, LATMOS, France
nathalie.carrasco@latmos.ipsl.fr
Dr. Wolf Geppert Stockholm University, Sweden
wgeppert@hotmail.com
Dr. Eric Hébrard, Laboratoire d'Astrophysique de Bordeaux, France
hebrard@obs.u-bordeaux1.fr
Dr. Yeghis Keheyan, CNR, Italy
yeghis.keheyan@uniroma1.it
Dr. Andrea Lombardi, Dipartimento di Chimica, Università degli Studi di Perugia, Italy
abulafia@dyn.unipg.it
Dr. Yamila Miguel, Max Planck Institute fur Astronomie, Germany
yami.miguel@gmail.com
Dr. Christian Muller, BUSOC, Bruxelles, Belgium
christian.muller@busoc.be
Angela Occhiogrosso, University College London, UK
ao@star.ucl.ac.uk
Dr. Miroslav Polášek, J. Heyrovsky Institute of Physical Chemistry, Prague, Czech Republic
miroslav.polasek@jh-inst.cas.cz
Prof. François Raulin, LISA/IPSL CNRS & UPEC-Univ. Paris Diderot, France
francois.raulin@lisa.univ-paris12.fr
Dr. Dimitrios Skouteris, Dipartimento di Chimica, Università degli Studi di Perugia, Italy

dimitris@dyn.unipg.it

Dr. Stefano Stranges, Dipartimento di Chimica, Università La Sapienza, Italy

stefano.stranges@uniroma1.it

Dr. Giovanni Strazzulla, INAF-Osservatorio Astrofisico di Catania, Italy

gianni@oact.inaf.it