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Crossed molecular beam experiments on bimolecular reactions of relevance in astrochemistry: the case of atomic oxygen reactions with small unsaturated hydrocarbons

Abstract – The presence of atomic oxygen in the interstellar medium is one of the factors that limit the growth of the carbon skeleton of organic molecules, as it easily degrades organic molecules into CO or one of its precursors (e.g. HCO). Yet, its reactions can actually lead to the formation of O-rich organic molecules like esters or carboxylic acids. In this contribution, we summarize recent experimental work on the reactions between atomic oxygen and small unsaturated hydrocarbons performed in our laboratory by means of the crossed molecular beam techniques with mass spectrometric detection. Our results show that, even if C-C bond fission dominates the reaction mechanism in most cases, interesting O-bearing radicals are formed that can further foster the chemical complexity of interstellar organic molecules.

1. Introduction

Oxygen is an important player in the chemistry of the Universe, being the third most abundant element. Even though its mole fraction is only 477 ppm, it is more abundant than carbon (326 ppm) and nitrogen (102 ppm) and exhibits a rich chemistry, contrarily to the two most abundant elements, hydrogen and helium, characterized by mole fractions of 90.9964% and 8.8714%, respectively. Among the various extraterrestrial environments, interstellar clouds (that is, the regions of the

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interstellar medium where most of matter outside solar systems gathers, with number densities as low as 10⁴ molecules/cm³ and temperatures ranging from 10 to 100 K) are the subject of great interest, because these are the regions of galaxies where new stars, and their solar systems, are formed (Caselli and Ceccarelli, 2012). Since we cannot directly reconstruct the evolution of our own star and solar system, neither can we observe the birth of a new star in real time because the timescale is outside the human range, the best approach to understand how Sun and its Solar System were formed is to analyze different interstellar objects in different evolutionary stages and try to recreate the sequence of steps that leads from a diffuse cloud to a Sunlike star and its planets (Caselli and Ceccarelli, 2012). The observation of relatively complex organic molecules (McGuire, 2018) in all the stages that are believed to lead to star formation seems to suggest that interstellar clouds can be the chemical factories where massive synthesis of organic molecules occurs, thus providing the newly formed solar systems with the inventory of the simple organic molecules necessary to trigger (if the planet conditions are favorable) the emergence of life (Caselli and Ceccarelli, 2012; Balucani, 2009). This vision gains support from the observation of plenty of complex chemicals (including aminoacids and other prebiotic molecules) in the small bodies of our solar systems (asteroids, meteorites, comets and even interplanetary dust particles) that are supposed to be the carriers that bring interstellar molecules (and the products of their chemical evolution) to the newly formed planets (Ehrenfreund et al., 2002).

Given the predominance of hydrogen, oxygen is mainly sequestered as water. In cold objects, it is assumed to be strongly depleted from the gas-phase being the main constituent of the water-ice mantles that cover interstellar dust particles (Occhiogrosso *et al.*, 2013). Also, a significant fraction is segregated into CO, a very abundant interstellar molecule. Yet, the presence of residual oxygen in atomic form can have a strong influence in the formation and destruction of interstellar complex organic molecules (Occhiogrosso *et al.*, 2013). In particular, because of its capability of reacting with organic molecules in a destructive way, the presence of atomic oxygen can severely reduce the chemical complexity of the available organic species.

In this contribution, we will show several cases in which atomic oxygen degrades organic molecules. In particular, we will analyze several examples of reactions with unsaturated hydrocarbons. As we are going to see, oxygen atoms are even more effective than we thought in inducing the break-up of C-C bonds and in degrading them directly towards CO or CO precursors. However, at the same time the reactions of atomic oxygen with organic molecules allow for the formation of other complex molecular species (Balucani *et al.* 2015, Skouteris *et al.* 2018) that can, instead, foster the chemical growth of prebiotic molecules. Quite interestingly, indeed, among the so-called interstellar complex organic molecules (iCOMs), those which are by far the most abundant do contain oxygen, namely formaldehyde, methanol, dimethyl ether, methyl formate etc. (Ceccarelli *et al.*, 2017, McGuire, 2018). In this contribution, we will briefly summarize the main results obtained in

our laboratory by means of the crossed molecular beam technique with mass spectrometric detection on the reactions of atomic oxygen with unsaturated hydrocarbons (Casavecchia *et al.*, 2015). Among the results we have obtained, the focus will be on the product branching ratios. We will also analyze the effect of those revised branching ratios in the chemistry of interstellar clouds and the role of atomic oxygen in the organic chemistry of interstellar objects (Occhiogrosso *et al.*, 2013).

2. Experimental method

In our laboratory, we use the crossed molecular beam technique coupled to mass spectrometric detection. The basic scheme of our apparatus follows the classical design by Lee and coworkers (for a scheme of our apparatus in its recent version see Casavecchia *et al.* 2015, 2009; for the original work by Lee and coworkers, see Lee *et al.* 1969). Our machine features an efficient radio frequency discharge beam source for the production of intense supersonic beams of atomic or diatomic radicals (see Alagia *et al.* 1996 and Leonori *et al.* 2010). When applied to the production of beams of atomic oxygen, we obtain a very high degree of dissociation starting from a dilute mixture of molecular oxygen in helium or neon. Atomic oxygen is produced mainly in its ground ³P state, with a small percentage (around 5%, see Alagia *et al.* 1996) in the first electronically excited state ¹D.

The observables of this experimental technique are the product angular and time-of-flight distributions (Balucani *et al.*, 2006). From these quantities, we can gain insights into the reaction mechanism and product branching ratios. In particular, the product branching ratios are of interest in the context of applied chemistry, because the products of one elementary reaction are the reactants of subsequent ones in the intricate networks of elementary chemical reactions that account for the global transformation. Since most of the kinetics experimental techniques are designed to record the disappearance rate of one reactant, rather than determining the appearance rate of products, our experimental results nicely complement the results of kinetics experiments.

3. The reaction of atomic oxygen with hydrocarbon containing a triple bond

In our laboratory, we have investigated the reaction of atomic oxygen in its ground state with ethyne and propyne (Leonori *et al.*, 2014; Vanuzzo *et al.* 2016). No experimental evidence of the reactions involving O(¹D) was obtained at the mass-to-charge ratios investigated. In both cases, we have verified that the initiation of the reaction occurs with the addition of the electrophilic atomic oxygen to the π system of the alkyne. In the case of ethyne, because of its symmetric structure, only two sets of products have been observed, that is HCCO + H (O/H exchange channel) and CO + CH₂ (C-C bond breaking channel). The O/H exchange channel is dominant (accounting for *ca.* 80%) under all the experimental conditions investi-

gated. There is no experimental evidence of the occurring of intersystem crossing (ISC) to the underlying singlet potential energy surface. Several theoretical studies (Gimondi *et al.*, 2016; Rajak and Maiti, 2014; Nguyen *et al.*, 2006) confirm our data in this respect. In the case of the reaction with propyne, given that also in this case the initial attack is towards the π system of the molecule, the asymmetry of the molecule makes more channels possible. In addition, the occurrence of ISC is very important in this case. In Table 1 are reported the product branching ratios (B. R.) under the conditions of our experiments.

Reaction channel	O + HCCH	B. R.	O + CH ₃ CCH	B. R.
Н	H + HCCO	0.79	H + CH ₃ CCO	0.04
CH ₃	-		CH ₃ + HCCO	0.10
СО	$CH_2 + CO$	0.21	C ₂ H ₄ /CHCH ₃ +CO	0.74
НСО	-		$HCO + C_2H_3$	0.11
H ₂	-		$CHCCO + H_2$	0.01

Table 1. Experimental branching ratios of the two simplest O + alkyne reactions at $E_c \sim 10$ kcal/mol.

4. The reaction of atomic oxygen with hydrocarbons containing one double bond

In our laboratory, we have investigated the reaction of atomic oxygen in its ground state with ethene, propene and 1-butene (Fu *et al.*, 2012; Balucani *et al.* 2015b; Leonori *et al.*, 2015; Caracciolo *et al.*, 2017). In all cases, we have verified that the initiation of the reaction occurs with the addition of the electrophilic atomic oxygen to the π system of alkenes. The main result of our investigation is that there is a facile pathway leading directly to the formation of formaldehyde, accounting for 20%, 44% and 15% of the reaction involving ethene, propene and 1-butene, respectively (see Table 2 and Caracciolo *et al.*, 2017). This was unexpected for the reactions with propene and 1-butene. ISC is also important for these reactive systems, but its extent varies from system to system, as a result of the detailed characteristics of the associated triplet and singlet potential energy surfaces and their coupling terms. In the case of the reaction $O(^{3}P)+C_{2}H_{4}$, we have compared our detailed observables with the predictions of quasiclassical trajectories calculations on an accurate potential energy surface where the occurrence of ISC was explicitly considered. This comparison fully corroborates our experimental findings (Fu *et al.* 2012; Balucani *et al.* 2015b).

Reaction channel	$O + CH_2 = CH_2$	B. R.	O + CH ₃ -CH=CH ₂	B. R.
Н	$H + CH_2CHO$	0.30	Н + СН,СНСНО	0.07
Н	H + CH ₃ CO	0.03	$H + CH_3COCH_2$	0.05
CH3	CH ₃ + HCO	0.34	CH ₃ +CH ₂ CHO/CH ₃ CO	0.32
H ₂ CO	$CH_2 + H_2CO$	0.20	$CHCH_3/C_2H_4 + H_2CO$	0.44
H ₂	$H_2 + CH_2CO$	0.13	$CH_{3}CHCO + H_{2}$	0.03
C ₂ H ₅	-		$C_2H_5 + HCO$	0.09

Table 2. Experimental branching ratios of the two simplest O + alkene reactions at $E_c \sim 9$ kcal/mol.

5. Astrophysical implications

The new branching ratios derived in our laboratory for the reactions O+C₂H₂, CH₃CCH, C₂H₄ and CH₂CCH₂ have been tested in astrochemical models of interstellar clouds (Occhiogrosso et al. 2013) for four different scenarios corresponding to the conditions of *i*) diffuse clouds, *ii*) translucent clouds, *iii*) dark cores and *iv*) hot cores. Important differences were noted with respect to the previous models referring to the data set of UMIST 2006 (one of the most used databases for astrochemistry, now evolved in the more recent UMIST 2012, see Woodall et al. 2007 and McElroy et al., 2013). The new branching ratios affect the abundances of several observed species in the case of hot cores. The main differences have been highlighted in Figure 2 and Table 6 of the paper by Occhiogrosso et al. 2013. Apart from some interesting effects on the species which are already considered in the models (such as CH₂, CH₃, CH₂CO or C₂H₂ and C₂H₄ themselves), the inclusion of new species can have a profound influence in the outcome of astrochemical models. For instance, in Figure 2 the abundances of the newly inserted species CH₂CHO/CH₂CO and CH₄CCO reach very high, unrealistic values because no destruction pathways were included. This is a way to estimate the maximum impact of these species in different evolutionary stages of hot cores. In real cases, when chemical destruction routes will be included, their reactions with other constituents of hot cores (ion species, for instance, or other abundant reactive radicals) could lead to more complex molecules bearing an oxygen atom. We remind that several of the hot cores considered in Occhiogrosso et al. (2013) are the objects where a large number of molecular species, complex to some extent and rich in oxygen (e.g. methyl acetate, ethyl formate, methoxymethanol), have been detected (McGuire, 2018). In other words, even if the presence of atomic oxygen impedes the growing up of the skeleton of C-atoms, it might lead to the formation of O-rich organic molecules.

This suggestion is actually supported by two modelling studies, in which the reactions of atomic oxygen with organic radicals already bearing an oxygen atom were invoked to lead to the formation of methyl formate, glycolaldehyde and acetic acid. Methyl formate, indeed, results from the sequence of reactions (S1) (see Balucani *et al.*, 2015a), while glycolaldehyde and acetic acid result from the sequence of reactions (S2a,b) (see Skouteris *et al.*, 2018) in the gas phase, starting from saturated molecules which can well be formed by surface-induced hydrogenation on interstellar dust particles:

$$\begin{array}{c} CH_{3}OCH_{3} \xrightarrow{OH,Cl} CH_{3}O\dot{C}H_{2} \xrightarrow{O} CH_{3}OCHO \quad (S1) \\ CH_{3}CH_{2}OH \xrightarrow{OH,Cl} CH_{3}\dot{C}HOH \xrightarrow{O} CH_{3}COOH \quad (S2a) \\ CH_{3}CH_{2}OH \xrightarrow{OH,Cl} \dot{C}H_{2}CH_{2}OH \xrightarrow{O} HCOCH_{2}OH \quad (S2b) \end{array}$$

In this sense, the role of atomic oxygen is strategical in converting the saturated species possibly produced by heterogeneous processes on the dust surface into much more complex and variegated species.

In conclusion, as expected, the reactions of atomic oxygen with organic molecules have the capability of degrading them by inducing the fission of C-C bonds. At the same time, however, new radicals containing an O-atom are formed and they can, in turn, lead to the formation of O-rich organic molecules. Some of these species (glycolaldehyde, acetic acid) are widely detected in space and are considered to be prebiotic species, being potential precursors of sugars and aminoacids.

A more general conclusion is that only the detailed knowledge of the reactions leading to the formation of the most important prebiotic molecules will help us to understand if the chemistry that precedes life emergence is common in the Universe and, in turn, if life is possible outside our Solar System.

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REFERENCES

- Alagia M., Aquilanti V., Ascenzi D., Balucani N., Cappelletti D., Cartechini L., Casavecchia P., Pirani F., Sanchini G., Volpi G. G. (1997). Magnetic analysis of supersonic beams of atomic oxygen, nitrogen and chlorine generated from a radio-frequency discharge. Israel Journal of Chem. 37, 329.
- Balucani N. (2009). Elementary reactions and their role in gas-phase prebiotic chemistry. International Journal of Molecular Sciences 10, 2304.
- Balucani N., Capozza G., Leonori F., Segoloni E., Casavecchia P. (2006). Crossed molecular beam reactive scattering: from simple triatomic to multichannel polyatomic reactions. International Reviews in Physical Chemistry 25, 1952.
- Balucani N., Ceccarelli C., Taquet V. (2015a). Formation of complex organic molecules in cold objects: the role of gas-phase reactions. Monthly Notices of the Royal Astronomical Society 449, L16.
- Balucani N., Leonori F., Casavecchia P., Fu B., Bowman J. M. (2015b) Crossed molecular beams and quasiclassical trajectory surface hopping studies of the multichannel nonadiabatic O(³P)+ethylene reaction at high collision energy. The Journal of Physical Chemistry A 119, 12498.
- Caracciolo A., Vanuzzo G., Balucani N., Stranges D., Cavallotti C., Casavecchia P. (2017). Observation of H-displacement and H₂ elimination channels in the reaction of O(³P) with 1-butene from crossed beams and theoretical studies. Chemical Physics Letters 683, 105; and to be published.
- Casavecchia P., Leonori F., Balucani N., Petrucci R., Capozza G., Segoloni E. (2009). Probing the dynamics of polyatomic multichannel elementary reactions by crossed molecular beam experiments with soft electron-ionization mass spectrometric detection. Physical Chemistry Chemical Physics 11, 46.
- Casavecchia p., Leonori F., Balucani N. (2015). Reaction dynamics of oxygen atoms with unsaturated hydrocarbons from crossed molecular beam studies: primary products, branching ratios and role of intersystem crossing. International Reviews in Physical Chemistry 34, 161.
- Ceccarelli C., Caselli P., Fontani F., Neri R., López-Sepulcre A., Codella C., Feng S., Jiménez-Serra I., Lefloch B., Pineda J. E., Vastel C., Alves F., Bachiller R., Balucani N., Bianchi E., Bizzocchi L., Bottinelli S., Caux E., Chacón-Tanarro A., Choudhury R., Coutens A., Dulieu F., Favre C., Hily-Blant P., Holdship J., Kahane C., Jaber Al-Edhari A., Laas J., Ospina J., Oya Y., Podio L., Pon A., Punanova A., Quenard D., Rimola A., Sakai N., Sims I. R., Spezzano S., Taquet V., Testi L., Theulé P., Ugliengo P., Vasyunin A. I., Viti S., Wiesenfeld L., Yamamoto S. (2017). Seeds Of Life In Space (SOLIS): The organic composition diversity at 300–1000 au scale in solar-type star-forming regions. The Astrophysical Journal 850, 176.
- Ehrenfreund P., Irvine W., Becker L., Blank J., Brucato J. R., Colangeli L., Derenne S., Despois D., Dutrey A., Fraaije H., Lazcano A., Owen T., Robert F. (2002). Astrophysical and astrochemical insights into the origin of life. Reports on Progress in Physics 65, 1427.
- Fu B., Han Y.-C., Bowman J. M., Angelucci L., Balucani N., Leonori F., Casavecchia, P. (2012) Intersystem crossing and dynamics in O(³P) + C₂H₄ multichannel reaction: experiment validates theory. Proceedings of the National Academy of Sciences of the United States of America 109, 9733.
- Ilaria Gimondi, Carlo Cavallotti, Gianmarco Vanuzzo, Nadia Balucani, Piergiorgio Casavecchia (2016). Reaction dynamics of O(³P) + propyne: II. Primary products, branching ratios, and role of intersystem crossing from ab initio coupled triplet/singlet potential energy surfaces and statistical calculations. The Journal of Physical Chemistry A 120, 4619.

- Lee Y. T., McDonald J., LeBreton P., Herschbach D. (1969). Molecular beam reactive scattering apparatus with electron bombardment detector. Review of Scientific Instruments 40, 1402.
- Leonori F., Hickson K. H., Le Picard S., Wang X., Petrucci R., Foggi P., Balucani N., Casavecchia P. (2010). Crossed-beam universal-detection reactive scattering of radical beams characterized by laser-induced-fluorescence: the case of C, and CN. Molecular Physics 108, 1097.
- Leonori F., Balucani N., Capozza G., Segoloni E., Volpi G. G., Casavecchia P. (2014). Dynamics of the O(³P) + C₂H₂ reaction from crossed molecular beam experiments with soft electron ionization detection. Physical Chemistry Chemical Physics 16, 10008.
- Leonori F., Balucani N., Nevrly V., Bergeat A., Falcinelli S., Vanuzzo G., Casavecchia P., Cavallotti C. (2015). Experimental and theoretical studies on the dynamics of the O(³P) + propene reaction: primary products, branching ratios, and role of intersystem crossing. The Journal of Physical Chemistry C 119, 14632
- McGuire B. A. (2018). 2018 Census of interstellar, circumstellar, extragalactic, protoplanetary disk, and exoplanetary molecules. The Astrophysical Journal Supplement Series 239, 17.
- McElroy D., Walsh C., Markwick A.J., Cordiner M.A., Smith K., Millar T.J. (2013). The UMIST database for astrochemistry 2012. Astronomy and Astrophysics 550, A36.
- Nguyen T. L., Peeters J., Vereecken L. (2006). Quantum chemical and theoretical study of the O(³P) + C₂H₂ reaction: a multistate process. The Journal of Physical Chemistry 110, 6696.
- Occhiogrosso A., Viti S., Balucani N. (2013). An improved chemical scheme for the reactions of atomic oxygen and simple unsaturated hydrocarbons implications for star-forming regions. Monthly Notices of the Royal Astronomical Society 432, 3423.
- Rajak, K., Maiti, B. (2010). Trajectory surface hopping study of the O(³P) + C₂H₂ reaction dynamics: effect of collision energy on the extent of intersystem crossing. The Journal of Chemical Physics 140, 044314.
- Skouteris D., Balucani N., Ceccarelli C., Vazart F., Puzzarini C., Barone V., Codella C., Lefloch B. (2018). The genealogical tree of ethanol: gas-phase formation of glycolaldehyde, acetic acid and formic acid. The Astrophysical Journal 854, 135.
- Vanuzzo G., Balucani N., Leonori F., Stranges D., Nevrly V., Falcinelli S., Bergeat A., Casavecchia P., Cavallotti, C. (2016). Reaction dynamics of O(³P) + propyne: I. primary products, branching ratios, and role of intersystem crossing from crossed molecular beam experiments. The Journal of Physical Chemistry A 120, 4603.
- Woodall J., Agúndez M., Markwick-Kemper A. J., Millar T. J. (2007). The UMIST database for astrochemistry 2006. Astronomy and Astrophysics 466, 1197.