

LABORATORY INVESTIGATION OF THE O(³P,¹D) + SMALL AROMATICS REACTIONS: THE ROLE OF OXYGEN ATOMS IN SPACE ORGANIC CHEMISTRY

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Atomic oxygen (AO), both in its ground (³P) and excited (¹D) electronic state, is an important player in the chemistry of Universe due to its capability to oxidize organic molecules in various terrestrial and extraterrestrial environments.[1-3]

The electrophilic character of oxygen atoms means that they can easily react with electron-rich sites of organic molecules, such as double or triple bond of unsaturated aliphatic and aromatic hydrocarbons. The reactions result either in forming O-rich organic compounds or in the degradation of the organics. In the latter case, acting as a hydrocarbon-degrading agent, AO causes the destruction of the substrate with which it reacts leading ultimately to the formation of CO or CO₂.

In this context, AO-induced degradation is a reason for major concern for materials for aerospace applications and especially for C-based materials like polymers.[4-7] In particular, AO erosion has been recognized to be the most critical hazard for polymers exposed to the specific conditions of the Low Earth Orbit (LEO, the region that extends up to 2000 km above the Earth surface), where most satellites orbit. At these altitudes, AO, mainly formed *via* VUV photo-dissociation of O₂, represents 80% of the residual atmosphere (the remaining 20% is mainly constituted by nitrogen molecules) and its interaction with polymers causes material degradation and alterations in its chemical composition, surface morphology, and optical properties. Similar processes can also occur in the Low Mars Orbit (LMO), where a significant quantity of AO is generated through the photo-dissociation of carbon dioxide.[8]

O atoms and OH radicals are also considered the possible chemical agents for the depletion of organics in the Martian regolith, along with other oxidizing agents [9,10]. This could explain the failure to detect volatile organic molecules on the Martian surface during the Viking 1976 mission,[11] even those expected from the impacts of asteroids, comets, and interplanetary dust particles.[12-14] Notably, only some chlorinated aromatic hydrocarbons, chlorobenzene and dichlorobenzene, have recently been detected on the Martian surface by Curiosity.[15]

In this context, we have started a systematic experimental investigation of the gas-phase reactions involving oxygen atoms and aromatic hydrocarbons, with the aim to unveil the primary products, their relative yields, and the reaction mechanism at the

microscopic level. This goal is made more difficult by the fact that, typically, these are multichannel reactions in which the nonadiabatic transition (*intersystem crossing*, ISC) from the entrance triplet to the underlying singlet potential energy surface (PES) plays a central role by opening new competing reaction channels.[16]

In this contribution, we focused on the reactions between O(³P,¹D) and three small aromatic molecules, namely benzene (C₆H₆),[17] pyridine (C₅H₅N),[18] and toluene (C₆H₅CH₃), that can serve as prototype of more complex compounds, such as polycyclic aromatic hydrocarbons (PAHs) and some polymeric units.

We have used the crossed molecular beam (CMB) scattering technique, equipped with universal electron-impact ionization mass-spectrometric detection and time-of-flight (TOF) analysis.[19] The synergy with electronic structure and RRKM (Rice-Ramsperger-Kassel-Marcus) computations has allowed us to complete the picture of the reaction dynamics of the systems under investigation. Remarkably, we have found that the presence of a N atom in the aromatic ring increases the probability of a ring contraction with respect to the reactions involving benzene. In fact, the spin forbidden CO-forming channel, leading to cyclopentadiene + CO, accounts for ~30% of the total reactive flux of the O(³P) + benzene reaction.[17] Instead, in the case of O(³P) + pyridine, the ring-contraction channel, leading to pyrrole + CO *via* ISC, is dominant (BF ≈ 98%). This unexpected behavior of the O(³P) + pyridine reaction was rationalized by invoking an efficient ISC occurring before the high entrance barrier for O-addition to the N-atom lone pair (the so-called *ipso* addition). This is the first detection of ISC in the entrance channel in the absence of heavy atoms.[18]

Instead, the CH₃ group of toluene seems to preserve the product aromaticity reducing the yield of the ring-contraction mechanism.

This work can contribute to shed light on the aforementioned destruction processes triggered by O atoms and the role of oxygen in determining the chemical evolution of different extraterrestrial environments.

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