Destruction of interstellar COMs by collisions with He⁺: the case of dimethyl ether and methylformate

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Collisions with He⁺ are an important pathway for the decomposition of complex organic molecules in the interstellar medium (ISM). Using a Guided-Ion Beam Mass Spectrometer we have explored the reactions of He⁺ with two O-bearing organic molecules, ubiquitous in star-forming regions, but whose kinetics has never been studied experimentally: dimethyl ether CH₃OCH₃ (DME) and methyl formate HCOOCH₃ (MF). Absolute reactive cross sections and product branching ratios have been measured as a function of the collision energy and the DME and MF radical cations are never detected, speaking for completely dissociative charge transfer processes. A semiclassical model based on an improved Landau-Zener approach [1], an analytical representation of the PES for the entrance and exit channels [2] and taking into accounts electron densities of the molecular orbitals from which electron is removed, has been developed to interpret experimental results and extract rate constant values as a function of temperature. Interestingly, our modelling shows that the large interaction anisotropy among colliding partners induces a pronounced orientation of the polar DME and MF, confining them, especially at low collision energies, into configurations ("pendular states") that are inefficient for charge-transfer due to poor orbital overlap. Hence the reaction is increasingly driven by the Coriolis coupling rather than by the orbital overlap. Our dynamical study casts light on some new and general guidelines to be properly taken into account for an appropriate evaluation of kinetics of ion-molecule reactions that goes beyond simple capture models, often adopted to estimate temperature dependent rate coefficients [3].

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