

New Mechanistic Insights to the O(³P) + Propene Reaction from Multiplexed Photoionization Mass Spectrometry

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The reaction of O(³P) with unsaturated hydrocarbons is a critical part of the rich oxidation chemistry that occurs in combustion. At low temperatures, the general mechanism for these types of reactions begins with electrophilic attack of O(³P) on a carbon atom from the unsaturated carbon-carbon bond to form a triplet biradical species that can then isomerize, dissociate, or undergo collisional stabilization.¹ In the case of O(³P) + acetylene (C₂H₂), observed products can be explained entirely by reaction on the initial triplet potential energy surface (PES).^{2,3} However, in the case of O(³P) + ethene (C₂H₄), recent experiments and calculations suggest that intersystem crossing (ISC) to the singlet PES is surprisingly facile.^{4,5} The role of ISC in larger alkenes is difficult to ascertain using existing theoretical approaches, thus making experimental measurements critical to our general understanding of these reactions.

The case of O(³P) + propene (C₃H₆) and the rich chemistry available to this prototypical larger alkene has received little attention. In the present experiments, multiplexed photoionization mass spectrometry is applied to the reaction of O(³P) + C₃H₆ to provide a global 'image' of this fundamental chemical reaction.^{6,7} Coupled with tunable vacuum ultraviolet radiation from the Advanced Light Source synchrotron, this time-resolved account of all photoionizable products allows quantitative isomer-resolved identification of primary and secondary products. In light of the few theoretical characterizations of relevant C₃H₆O PESs^{8,9} our results indicate that, like the case of O(³P) + C₂H₄, significant ISC must be invoked to explain the observed products. These results offer considerable mechanistic insight that can be used in future theoretical accounts of the O(³P) + C₃H₆ reaction.

References

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