SAND2012-1588C

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 (C_2H_2), 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 (C_2H_4), 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 (C_3H_6) 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 $O(^3P)$ + C_3H_6 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 C_3H_6O PESs[8,9] our results indicate that, like the case of $O(^3P)$ + C_2H_4, 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 $O(^3P)$ + C_3H_6 reaction.

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