

Reaction Dynamics of O(³P) + Propyne: Primary Products, Branching Ratios and Role of Intersystem Crossing from Crossed Molecular Beam Experiments and *Ab Initio* Coupled Triplet/Singlet Potential Energy Surfaces and Statistical Calculations

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We have performed synergic experimental/theoretical studies on the mechanism of the O(³P) + CH₃CCH (propyne) reaction by combining crossed molecular beams experiments with mass spectrometric soft electron ionization detection and time-of-flight (TOF) analysis at 9.2 kcal/mol collision energy (*E_c*) with high-level *ab initio* electronic structure calculations of the relevant triplet and singlet potential energy surfaces (PESs) and statistical (RRKM/Master Equation) calculations of branching ratios (BRs) taking into account intersystem crossing (ISC).¹⁻³ From laboratory angular and TOF distributions at different *m/z* ratios, angular and translational energy distributions in the center-of-mass system have been obtained for the five most important product channels and their BRs. The reactive interaction of O(³P) with propyne under single collisions is mainly leading to the rupture of the three-carbon atom chain, with production of the radical products methylketenyl+atomic hydrogen (CH₃CCO+H) (BR=0.04), methyl+ketenyl (CH₃+HCCO) (BR=0.10), vinyl+formyl (C₂H₃+HCO) (BR=0.11), and molecular products ethylidene /ethylene+carbon monoxide (CH₃CH/C₂H₄+CO) (BR=0.74) and propandienal + molecular hydrogen (CH₂CCO+H₂) (BR=0.01). Because some of the products can only be formed via ISC from the entrance triplet to the low-lying singlet PES, from their BRs we infer an amount of ISC larger than 80%. This value is dramatically large when compared to the negligible ISC reported for the O(³P)+ethyne.⁴ At the same time, it is much larger than that (about 20%) recently found in the related O(³P)+propene reaction.⁵ This poses the question of how important it is to consider ISC and its dependence on molecular structure for this kind of combustion reactions.⁶ It is concluded that the main co-product of the CO forming channel is singlet ethylidene (¹CH₃CH) rather than ground state ethylene.¹ By comparing the derived BRs with those recently derived from kinetics studies at room temperature and 4 Torr using synchrotron radiation,⁷ we have obtained information on how BRs vary with *E_c*. The experimental results when compared with those from the statistical calculations on the *ab initio* coupled PESs lead to an in depth understanding of the complex reaction mechanism of O+propyne, and are expected to contribute to the development of more refined models of hydrocarbon combustion.

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References

- (1) Vanuzzo, G.; *et al. J. Phys. Chem. Letters* **2016**, *7*, 1010.
- (2) Vanuzzo, G.; *et al. J. Phys. Chem. A* **2016**, (DOI: 10.1021/acs.jpca.6b01563).
- (3) Gimondi, I.; *et al. J. Phys. Chem. A* **2016** (DOI: 10.1021/acs.jpca.6b01564).
- (4) (a) Leonori, F.; *et al. PCCP* **2014**, *16*, 10008.
- (5) Cavallotti, C.; *et al. J. Phys. Chem. Lett.* **2014**, *5*, 4213. Leonori, F.; *et al. J. Phys. Chem. C* **2015**, *119*, 14632.
- (6) Casavecchia, P.; Leonori, F.; Balucani, N. *Int. Rev. Phys. Chem.* **2015**, *34*, 161-204; and references therein.
- (7) Savee, J. D.; *et al. J. Phys. Chem. A* **2015**, *119*, 7388.