

# Crossed molecular beam studies of the $O(^3P) + 1$ -butene reaction: Primary products, branching ratios and role of intersystem crossing

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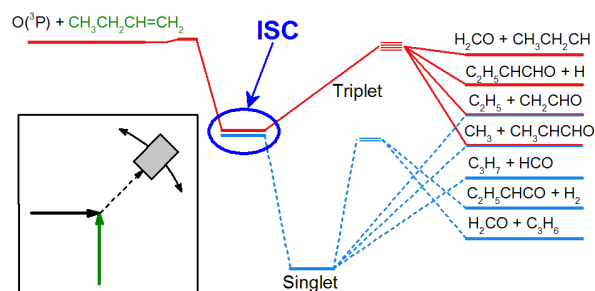
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The reactions of  $O(^3P)$  with unsaturated hydrocarbons (alkenes and alkynes) play a central role in our understanding of combustion processes and oxidation mechanisms of hydrocarbons. These reactions exhibit a variety of competing product channels, some of which can only take place via intersystem crossing (ISC) from the entrance triplet to the underlying singlet potential energy surface (PES)<sup>1</sup> (see Figure). While there have been extensive studies on the overall kinetics of many of these reactions, much less is known about the identity of the primary products and branching ratios (BRs), especially at combustion temperatures. Despite progress in kinetics studies with synchrotron radiation at 298 K,<sup>2a</sup> the most suitable technique to unravel unambiguously the primary products, the BRs and the detailed dynamics of this class of reactions is the "crossed molecular beams" (CMB) scattering technique with "universal" mass-spectrometric detection and time-of-flight analysis, empowered with "soft" ionization by tunable low energy electrons<sup>1</sup> (or VUV synchrotron radiation<sup>2b</sup>). The capabilities of the CMB technique have been well illustrated in recent studies of the reactions  $O + \text{ethyne}$ <sup>3a</sup>,  $O + \text{ethene}$ <sup>3b</sup>,  $O + \text{propene}$ <sup>4</sup>,  $O + \text{allene}$ <sup>5</sup> and, very recently, also  $O + \text{propyne}$ <sup>6</sup>, where the product BR and extent of ISC have been quantified. The experimental results were validated either by accurate quasiclassical trajectory surface-hopping calculations on ab initio coupled triplet/singlet PESs<sup>3b</sup> or by statistical (RRKM/Master equation) calculations on coupled PESs with ISC taken into account.<sup>4,6</sup>

In this contribution CMB studies were extended to a reaction with a higher alkene:  $O(^3P) + 1$ -butene, at a collision energy of 10.4 kcal/mol. From product angular and velocity distributions at different mass-to-charge ratios we have identified primary products attributable to seven competing channels (see schematic Figure) and determined the BRs. The reaction dynamics is elucidated in the light of the electronic structure calculations<sup>7</sup> of the triplet and singlet PESs.



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