

# Combined molecular beam and theoretical studies on the oxidation of unsaturated aliphatic and aromatic hydrocarbons: Primary products and branching ratios

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The elementary reactions of ground state oxygen atoms, O(<sup>3</sup>P), with unsaturated hydrocarbons (alkynes, alkenes, and dienes) play a central role in our understanding of the oxidation mechanisms of hydrocarbons relevant in combustion processes. These reactions exhibit a variety of product channels, some of which can only occur via intersystem crossing (ISC) from the triplet to the singlet potential energy surface (PES).<sup>1,2</sup> Despite extensive studies of their kinetics, little is known about the identity of the primary products and branching ratios (BRs), which are crucially needed to improve combustion models. The most suitable technique to determine unambiguously primary products, BRs and dynamics of these reactions is the crossed molecular beams (CMB) scattering method with “universal” mass-spectrometric detection and time of flight (TOF) analysis, empowered with soft ionization by tunable low energy electrons<sup>1,2</sup> or VUV synchrotron radiation<sup>3</sup>. The capabilities of this approach, which permits to investigate bimolecular reactions under single-collision conditions, have been illustrated in recent, combined experimental/theoretical studies of the O(<sup>3</sup>P) reactions with ethyne<sup>4</sup>, ethene<sup>4</sup>, propene<sup>5</sup>, allene<sup>5a</sup>, and propyne<sup>5b-7</sup>, for which product BRs and extent of ISC were quantified.

In this contribution, CMB studies were extended to O(<sup>3</sup>P) reactions with a higher alkene (**1-butene**), a higher diene (**1,2-butadiene**), and also a conjugated diene (**1,3-butadiene**) for which little information exists, in order to explore how product distributions, BRs and role of ISC vary with increasing molecular complexity, thus paving the way to an understanding of also more complex oxidation reactions of unsaturated aliphatic hydrocarbons. In addition, we have extended our studies to also the investigation of O(<sup>3</sup>P) reactions with the prototype of aromatics, namely **benzene**, and of its simplest alkyl substituted species, namely **toluene**. Reactions of O(<sup>3</sup>P) with benzene and toluene are of great interest for modeling aromatic oxidation. In general, to improve current kinetic models of combustion, detailed knowledge of primary products and branching ratios (BRs) is needed.

In the following we summarize our main findings.

## O(<sup>3</sup>P) + 1-butene

From product angular and velocity distributions at different mass-to-charge ( $m/z$ ) ratios we have identified primary products attributable to the **main (seven) channels** leading to H<sub>2</sub>CO+C<sub>3</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>5</sub>CHCO+H<sub>2</sub>, C<sub>3</sub>H<sub>7</sub>+HCO, CH<sub>3</sub>+CH<sub>3</sub>CHCHO, C<sub>2</sub>H<sub>5</sub>+CH<sub>2</sub>CHO, C<sub>2</sub>H<sub>5</sub>+CH<sub>3</sub>CO, C<sub>2</sub>H<sub>5</sub>CHCHO+H and have determined the BRs. The reaction dynamics are elucidated in the light of synergistic electronic structure calculations of the triplet/singlet PESs and related nonadiabatic statistical (RRKM/Master Equation) calculations [8, 9].

## O(<sup>3</sup>P) + 1,2-butadiene

From product angular and velocity distributions at different  $m/z$  ratios we have identified primary products attributable to **nine competing channels** leading to H displacement, H<sub>2</sub>

elimination, and C-C bond breaking pathways forming CO+C<sub>3</sub>H<sub>6</sub>, HCO+C<sub>3</sub>H<sub>5</sub>, CH<sub>3</sub>CO+C<sub>2</sub>H<sub>3</sub>, CH<sub>2</sub>CHO+C<sub>2</sub>H<sub>3</sub>, CH<sub>2</sub>CO+C<sub>2</sub>H<sub>4</sub>, H<sub>2</sub>CO+C<sub>3</sub>H<sub>4</sub>, and C<sub>3</sub>H<sub>3</sub>O+CH<sub>3</sub>, and have determined their BRs and characterized the reaction mechanism. Experimental product BRs and extent of ISC are supported by synergistic RRKM/Master equation non-adiabatic calculations on high-level *ab initio* triplet/singlet PESs, currently under way [10].

### O(<sup>3</sup>P) + 1,3-butadiene

From product angular and velocity distributions at different *m/z* ratios we have identified primary products attributable to **height competing channels** leading to H displacement (two isomers), H<sub>2</sub> elimination, and C-C bond breaking pathways forming CO+C<sub>3</sub>H<sub>6</sub>, HCO+C<sub>3</sub>H<sub>5</sub>, CH<sub>2</sub>CHO+C<sub>2</sub>H<sub>3</sub>, CH<sub>2</sub>CO+C<sub>2</sub>H<sub>4</sub>, and H<sub>2</sub>CO+C<sub>3</sub>H<sub>4</sub>. Data analysis is currently under way to determine the BRs. Synergistic high-level *ab initio* calculations of the triplet/singlet PESs are being performed by Cavallotti and will be used in RRKM/Master equation non-adiabatic calculations of BRs. The results are expected to lead to improved modelling of 1,3-butadiene oxidation (see ref. 11).

### O(<sup>3</sup>P, <sup>1</sup>D) + benzene and toluene

For O(<sup>3</sup>P)+benzene we find phenoxy+H to be the main products while CO+cyclopentadiene (via ISC) is minor [12]. This is in contrast to what found in recent kinetics studies with mass spectrometric detection using soft photoionization by synchrotron radiation [13], where phenol, phenoxy+H and CO+C<sub>5</sub>H<sub>6</sub> were found to be comparable at 4 torr and 900 K. For O(<sup>1</sup>D)+benzene we find as dominant products CO+H+C<sub>5</sub>H<sub>5</sub> (cyclopentadienyl), with CO+C<sub>5</sub>H<sub>6</sub> and H+C<sub>6</sub>H<sub>5</sub>O (phenoxy) being smaller, thus confirming previous CMB results.

For O(<sup>3</sup>P)+toluene the main channel is found to be phenoxy+CH<sub>3</sub> followed by methylphenoxy+H and negligible CO+methylcyclopentadiene. For O(<sup>1</sup>D)+toluene dominant channel is phenoxy+CH<sub>3</sub>, with methylphenoxy+H and CO+methylcyclopentadiene being also formed. Synergistic theoretical calculations are currently underway on O(<sup>3</sup>P)+toluene by Cavallotti (POLIMI) and this should bring to an accurate and detailed characterization of the O(<sup>3</sup>P) + toluene reaction mechanism and branching ratios which will ultimately be very useful for improving current combustion models of aromatics oxidation.

The relevance of these results for combustion modeling will be discussed.

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