

***ortho*-Substituted Phenyl Radical Reactions Leading to PAH Precursors**

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Substituted aromatics comprise a large fraction of transportation fuels, including conventional and biologically derived fuels. Early stages of combustion will likely result in substituted phenyl radicals yet our understanding of their subsequent reactions and resulting products is incomplete. This presentation describes experimental and computational studies of gas-phase *ortho*-substituted phenyl radical reactions with allene, propyne, and propene that could lead to PAH formation in reactive environments.

Experiments utilise VUV synchrotron photoionisation mass spectrometry at the Advanced Light Source (ALS), USA, and distonic ion studies with ion-trap mass spectrometry at the University of Wollongong, Australia, to study the reactions of *o*-substituted phenyl radicals.^{1,2} Quantum chemical calculations and RRKM/Master Equation modelling are also used to rationalise observed results and to establish the salient reaction mechanisms.

Preliminary ALS data are shown in Figure 1 where the photoionisation product mass spectra for *o*-methylphenyl + propyne (i) and allene (ii) reactions are plotted (top). Photoionised products detected at *m/z* 116 and 130 are consistent with C₃H₄ addition followed by either CH₃ or H-atom elimination. Likely products include indene (*m/z* 116) and methylindene (*m/z* 130). As we will show, the proposed mechanistic pathways to these products share common stationary points except for the final transition state structures, which are similar in barrier heights (~37 kcal mol⁻¹). The *m/z* 116 photoionisation spectrum is compared to a reference spectrum for indene (Figure 1. bottom) and their agreement is unequivocal evidence that indene is the dominant isomer. The *m/z* 130 assignment reveals two isomers: 2-methylindene and 1,2-dihydronaphthalene. Inspection of *o*-hydroxyphenyl + C₃H₄ reactions suggest similar mechanisms are at play.

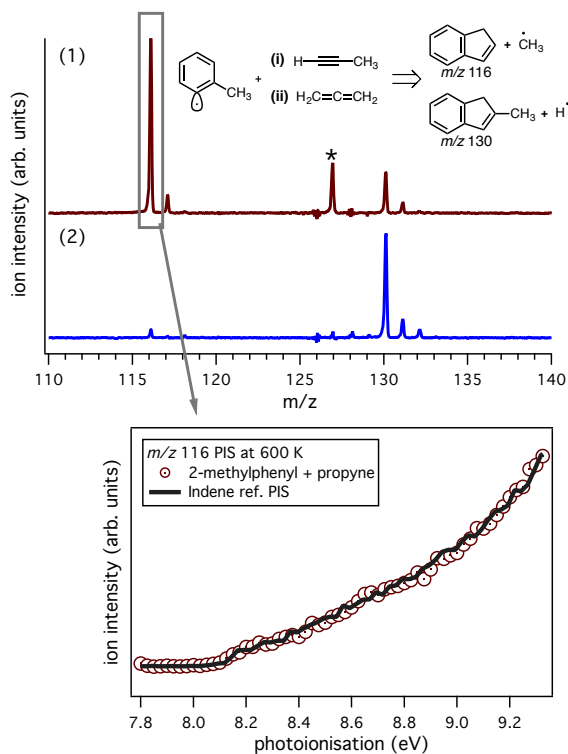


Figure 1. Top: Product mass spectra from *o*-methylphenyl + C₃H₄ reactions. Bottom: Photoionisation spectrum of *m/z* 116 compared to a reference spectrum for indene. (**m/z* 127 arises from dissociative ionisation of I₂ contaminant)

References

- (1) Prendergast, M. B.; *et al. Phys. Chem. Chem. Phys.* **2013**, 15, 20577-20584.
- (2) Prendergast, M. B.; *et al. Phys. Chem. Chem. Phys.* **2016**, 18, 4320-4332.