

Product Detection and Kinetic Studies of Combustion Intermediates: The Case of the Substituted-Phenyl's Oxidation.

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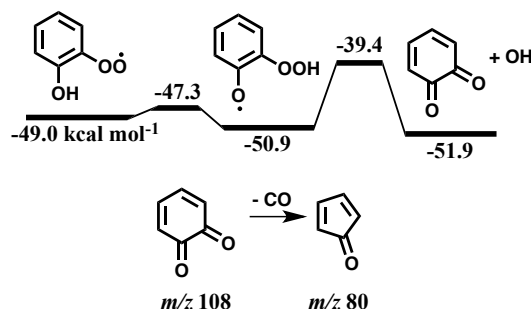
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For aromatic fuel additives (toluene, xylenes *etc.*), a general molecular understanding of their combustion properties is incomplete. This is despite aromatics composing one of the largest fractions of conventional gasoline (up to 40-45%). Since benzene is essentially out-lawed as a gasoline additive, many of the key aromatic species in combustion will be functionalized – the same applies to reaction products and radical intermediates. Lignin, a major portion of biomass and a prospective fuel stock, is made up of aromatic units, often bearing methoxy (CH₃O) and hydroxy (OH) groups, and the reactivity/decomposition pathways of these units are under intense study [1]. Our group is investigating the reactivity of substituted phenyl radicals to provide a useful framework for understanding aromatic oxidation in combustion environments. So far, our results show that *ortho*-substituted phenyl radicals have access to unique chemical pathways, compared to the *meta* and *para* counterparts, due to the proximity of nearby functional groups [2].

Our experimental approach utilizes two strategies: (i) ion-trap mass spectrometry with the distonic ion approach at the University of Wollongong [3], and (ii) VUV synchrotron photoionisation spectroscopy conducted at the Advanced Light Source, LBNL. Quantum chemical calculations and RRKM/Master Equation modeling are also performed to rationalise the experimental results and pin down the key mechanisms.

In the example of 2-hydroxyphenyl + O₂, the proximity of the OH group to the peroxy radical allows for rapid isomerization followed by OH elimination to form 1,2-benzoquinone (*o*BQ, *m/z* 108) (shown in the scheme). Cyclopentadienone (CPO, *m/z* 80) is also detected however its formation in this case is difficult to reconcile as a primary product. Utilising ion trap mass spectrometry, and charge-tagged analogues



(distonic radical ions), it is revealed that *o*BQ yields CPO by CO elimination. This important result, along with calculated reaction energies, supports the notion that neutral CPO is a secondary reaction product, formed via decomposition of the nascent *o*BQ primary product. Quantum chemical calculations are in accord with this mechanism. This system and several other substituted phenyl radical systems will be described in this presentation.

References

- [1] Robichaud *et al.* *J. Chem. Phys.* **140**, 234302 (2014) and Refs therein.
- [2] (i) Prendergast, *et al.*, *Phys. Chem. Chem. Phys.*, **15**, 20577–20584 (2013).
(ii) Prendergast, *et al.*, *Phys. Chem. Chem. Phys.*, **18**, 4320–4332 (2016).
- [3] Kirk, *et al.*, *Phys. Chem. Chem. Phys.*, **14**, 16719–16730 (2012).