

Product Detection and Kinetic Studies of Combustion Intermediates: Substituted-Phenyl Oxidation Reactions

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Using a combination of experimental and computational techniques, we are examining ortho-substituted phenyl + O₂ reactions to provide a useful framework for understanding aryl radical oxidation in combustion environments. 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. The links between the molecular details, such as this ortho effect, and the combustion properties of these molecules are not well understood despite aromatic molecules comprising a large fraction of conventional gasoline (40-45%).

Our experimental investigation utilizes two strategies: (i) ion trap mass spectrometry, with the distonic ion approach [1], and (ii) VUV synchrotron photoionisation spectroscopy conducted at the Advanced Light Source, LBNL, in collaboration with scientists at Sandia National Laboratories. Quantum chemical calculations and RRKM/Master Equation modelling are also performed to rationalise the experimental results.

In the example case of 2-hydroxyphenyl + O₂, after O₂ addition, proximity of the OH group to the peroxy radical allows for peroxy → phenoxy isomerization and subsequent OH elimination to produce 1,2-benzoquinone (oBQ, m/z 108). Cyclopentadienone (CPO, m/z 80) is also detected. Isomers are identified by examining VUV photoionization spectra. The CPO product has also been identified in the decomposition of biofuel surrogates [2], 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), allows for the isolation and collisional activation of the charge-tagged oBQ. Upon collisional activation, this oBQ is found to yield the corresponding CPO (by CO elimination). This important result, along with computational reaction energies, supports the notion that neutral CPO is a secondary reaction product, formed via decomposition of the nascent oBQ 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

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