

PW4 Investigating the reactivity of strained carbon-centred radicals using distonic radical ions

Benjamin B. Kirk¹, David G. Harman¹ and Stephen J. Blanksby¹

1. School of Chemistry, University of Wollongong, Australia

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The intrinsic reactivity of carbon-centred radicals is significantly perturbed by bridgehead strain

Bridgehead radicals are unusual due to the enforced pyramidal geometry about the carbon-centred radical. This is a significant perturbation of the geometry in the archetypal *n*-alkyl radical which has a trigonal planar geometry [1]. Previous solution phase and computational studies have suggested that the reactivity of bridgehead radicals is enhanced due to their unique structure [1,2,3]. This research invokes ion-molecule reactions of distonic radical anions – radicals with a spatially and electronically separate charge and radical moiety [4] - with simple reagents including dioxygen, nitric oxide and dimethyl disulfide to model the reactivity of neutral bridgehead analogues. These experiments aim to further expand our understanding of the intrinsic structure reactivity relationship of these exceptional molecules in the gas phase.

A number of bridgehead radicals with varying strain about their radical centre were investigated including adamantyl, bicyclo[2.2.2]octyl, bisnoradamantyl, bicyclo[1.1.1]pentyl and cubyl radicals. Dioxygen, nitric oxide and dimethyl disulfide were used to probe distonic character and gauge varying reactivity trends between the bridgehead molecules. Dioxygen and nitric oxide were found to act predominately by radical addition whereas dimethyl disulfide reacted by substitution. Increasing the strain about the bridgehead was observed to alter the reactivity and reaction rate of these radicals with neutral reagents, and in general, greater strain led to an increased reaction rate.

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