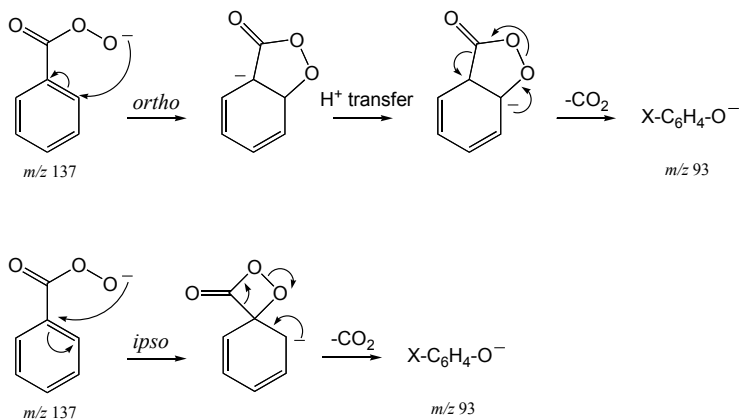


1.1

JUST HOW DO DEPROTONATED AROMATIC PERACIDS LOSE CO₂? AN EXPLORATION OF MECHANISM BY TANDEM MS AND COMPUTATIONAL METHODS.

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The mass spectrometer is an ideal tool with which to probe the intrinsic chemical reactivity of molecules and ions in the absence of complicating factors such as solvent and counter ions. Recently, as a part of a broad ranging study aimed at using electrospray mass spectrometry to identify and characterize organic peroxides, the $[M-H]^-$ anion from perbenzoic acid ($C_6H_5-CO_3H$) was observed at m/z 137. The collisional activation tandem mass spectrum of the perbenzoate anion in a triple quadrupole mass spectrometer (QuattroMicro, Waters) showed an unexpected fragment at m/z 93 (-44 Da) corresponding to decomposition via loss of carbon dioxide. The observation of this fragment, in preference to simple homolytic cleavage of the normally labile peroxide bond, was found to be common to a range of substituted perbenzoate anions (*e.g.*, $X-C_6H_4-CO_3^-$, where $X = H, Cl, NO_2$ and CH_3O). These data suggests unimolecular rearrangement of the precursor ion prior to fragmentation and we are unaware of any previous reports of such a process either in the gas phase or in solution. We have proposed 2 mechanisms to explain these results and both are illustrated in Scheme 1 below. The first involves a nucleophilic aromatic substitution at the *ortho* position yielding a five-centred intermediate, while the second proposal is an *ipso* substitution via a more highly strained four-centred intermediate. These proposals have been tested by the comparison of the MS/MS spectra from *meta* substituted aromatic peracids ($X-C_6H_4-CO_3H$) with their *para* substituted isomers, as well as, the comparison of effects of electron withdrawing verses electron donating substituents. We will present the results from these experiments and provide a detailed computational investigation of possible rearrangement mechanisms using hybrid density functional theory.



Scheme 1. Proposed mechanisms for CO₂ loss from deprotonated perbenzoic acid.