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Experimental and computational studies of the unimolecular rearrangements of sulphonated azo dyes and phenoxide anions in the gas-phase

Aravind Ramachandran

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**Experimental and Computational Studies of
the Unimolecular Rearrangements of
Sulphonated Azo Dyes and Phenoxide
Anions in the Gas-Phase**

A thesis submitted in fulfilment of the requirements for the award of the degree

MASTER OF SCIENCE (RESEARCH)

from

UNIVERSITY OF WOLLONGONG

by

Aravind Ramachandran

School of Chemistry, Faculty of Science

2008

CERTIFICATION

I, Aravind Ramachandran, declare that this thesis, submitted in fulfilment of the requirements for the award of Master of Science (Research), in the Faculty of Science, University of Wollongong, is wholly my work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other academic institutions.

Aravind Ramachandran

April 14, 2008

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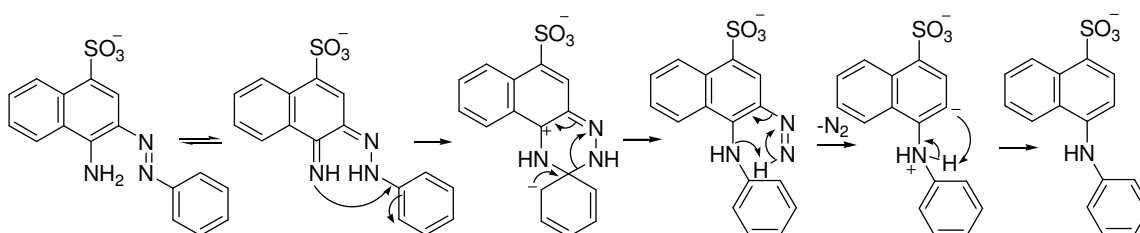
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ABSTRACT

The tandem mass spectrometer is an ideal tool to probe unimolecular reactions of ions. Of particular interest are reactions involving skeletal rearrangement of ions prior to dissociation. Given that such unimolecular reactions occur in the absence of complicating factors such as solvent and counter ions, within the vacuum environment of the mass spectrometer, computational methods employing molecular orbital and density functional theories are ideally suited to examine the reaction mechanisms.

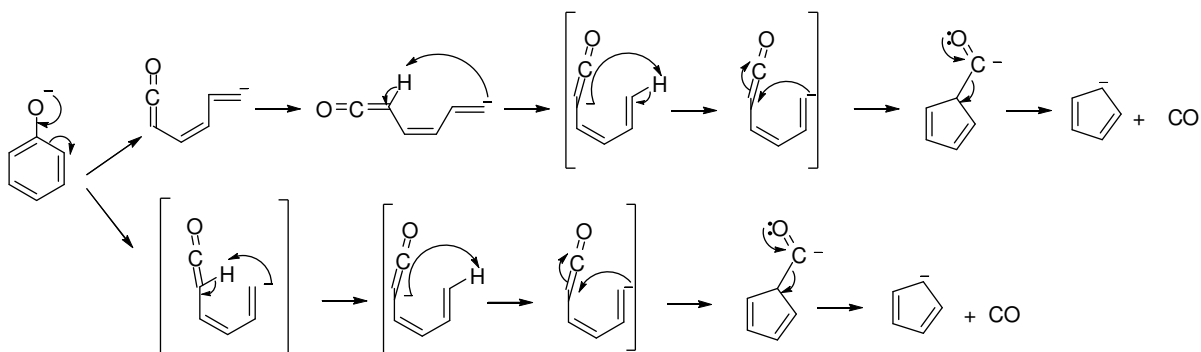
*A surprising rearrangement was identified by electrospray ionization tandem mass spectrometry of anions of azo dyes and the rearrangement was found to effect a loss of the azo moiety bridging aromatic rings as nitrogen. Even though the fragmentation reaction was previously reported, we are unaware of any conclusive mechanistic study. In the present thesis, by combination of tandem mass spectrometry and computational methods, we have identified that the rearrangement proceeds via an initial tautomerization, followed by nucleophilic aromatic substitution reaction (**Scheme-1**).*



Scheme-1

For the past two decades, phenoxide anions were reported to undergo unimolecular fragmentation resulting in the loss of CO. The present thesis presents an electronic structure calculation study on this unimolecular fragmentation, where in it was

identified that the loss of CO occurs via reaction pathways involving ketene like intermediates and transition states (**Scheme-2**).



Scheme-2

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