

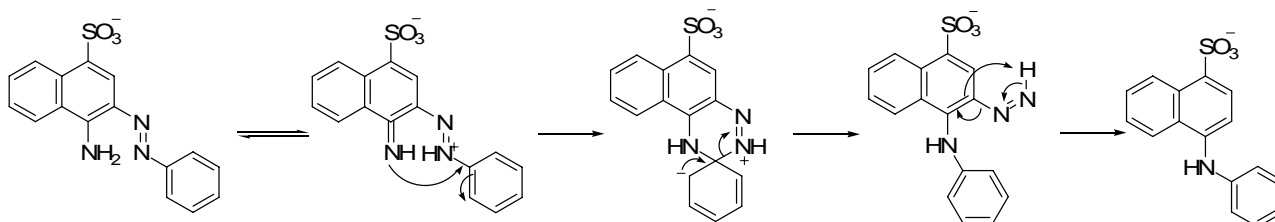
## THE UNUSUAL UNIMOLECULAR REACTIONS OF A DIANION: ARE REARRANGEMENTS DRIVEN OR RETARDED BY COULOMBIC REPULSION?

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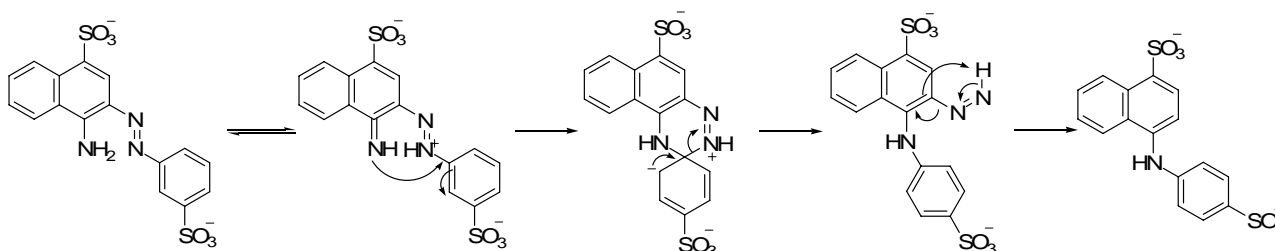
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### Abstract

The mass spectrometer is an ideal tool for providing insight into the reactivity of ions and molecules in the absence of complicating factors such as solvent, catalysis or counter ions. Recently, as a part of a broad ranging study aimed at using electrospray ionization tandem mass spectrometry (ESI-MS/MS) to elucidate the structure of sulphonated azodyes, a characteristic fragmentation *via* loss of molecular nitrogen was observed. Although such dissociations had previously been observed, no mechanism to account for this rearrangement had previously been proposed that could successfully account for the loss of the bridging diazo moiety.<sup>1-3</sup> We have proposed that the reaction proceeds *via* an intramolecular nucleophilic aromatic substitution reaction (**Scheme-1**). Evidence will be presented to support this mechanism, including isotopic labelling studies, fragmentation of authentic products, comparison of homologues and *ab initio* calculations. Interestingly, the analogous dinitrogen loss was also observed in the dissociation of the  $[M-2H]^{2-}$  dianion formed from some disulphonated azodyes suggesting that the analogous rearrangement can also occur in this multiply charged system (**Scheme-2**). Given that there are relatively few precedents of unimolecular reactions within multiply charged ions, we have investigated the additional energetic influence imposed by Coulombic repulsion on this rearrangement reaction.



Scheme-1: Proposed mechanism for the loss of dinitrogen from sulphonated azodyes.



Scheme-2: Proposed mechanism for the loss of dinitrogen from disulphonated azodyes.

### References:

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