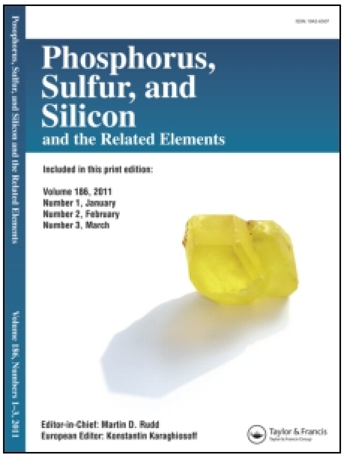

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Redox Chemistries of Substituted Aryl 1,2,3,5 Dithiadiazolyls and 1,3,2,4 Dithiadiazolylium Cations

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To cite this Article Aherne, Christine M. and Banister, Arthur J.(1994) 'Redox Chemistries of Substituted Aryl 1,2,3,5 Dithiadiazolyls and 1,3,2,4 Dithiadiazolylium Cations', Phosphorus, Sulfur, and Silicon and the Related Elements, 93: 1, 453 — 454

To link to this Article: DOI: 10.1080/10426509408021900

URL: http://dx.doi.org/10.1080/10426509408021900

Phosphorus, Sulfur, and Silicon, 1994, Vol. 93–94, pp. 453–454
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REDOX CHEMISTRIES OF SUBSTITUTED ARYL 1,2,3,5 DITHIADIAZOLYLS AND 1,3,2,4 DITHIADIAZOLYLIUM CATIONS

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Abstract A detailed study of the electrochemistry of substituted aryl dithiadiazolium species is presented.

INTRODUCTION

Recent studies on dithiadiazolylium / dithiadiazolyl compounds show that their solid state properties are particularly influenced by the substituent group[1]. Studying their redox potentials is a method of assessing substituent effects. We briefly report an investigation into how position and type of substituent relates to reduction potentials.

DISCUSSION

The synthesis of several *meta* and *para* substituted phenyl 1,2,3,5 dithiadiazolylium hexafluoroarsenates was undertaken so that their redox chemistry could be compared. A similar investigation was performed for *ortho*, *meta* and *para* substituted phenyl 1,3,2,4 dithiadiazolylium hexafluoroarsenate salts. The electrochemical technique known as cyclic voltammetry was used to measure $E_{1/2}$ reduction potentials[2] of all the cationic derivatives.

$E_{1/2}$ reduction potentials within a series were found to decrease as the substituent becomes more electron donating. This can be attributed to an increasing cation stabilisation; from the relationship $\Delta G^0=-nE_{1/2}F$, the larger the $E_{1/2}$, the easier the system is to reduce.

The free energy term can also be expressed as $\Delta G^0-\Delta G^0{}_0=-2.303RT\sigma\rho$. When $E_{1/2}$ reduction potentials were plotted against Hammett value σ_x, (where x=*ortho*, *meta* and *para*) similar linear free energy relationships were found to exist. This indicatives similar electrochemical mechanisms for all the reduction processes. These plots now enable us to predict $E_{1/2}$ reduction potentials of derivatives with known Hammett values and vice versa.

Para and especially *ortho* substituents impose the largest electronic effect on the ring as $\Delta E_{1/2}$ (MeO - NO_2) is larger than for the *meta* analogue.

CONCLUSION

These relationships enable us to rationalise dipole moments, bond lengths and relative reactivities to metals.

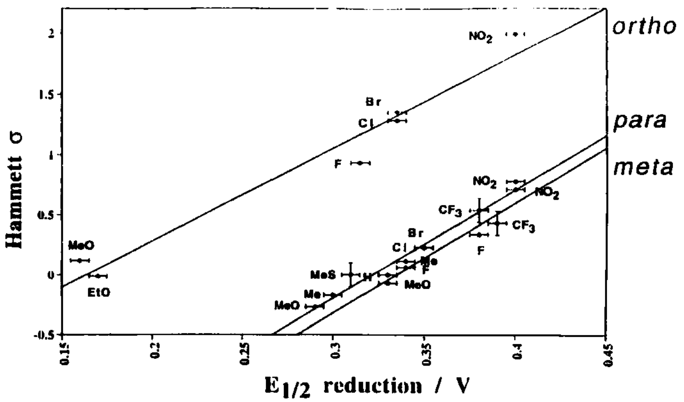

Fig 1. Plot of $E_{1/2}$ reduction potentials against Hammett σ values for substituted aryl **1,3,2,4** dithiadiazolylium cations, as hexafluoroarsenate salts.

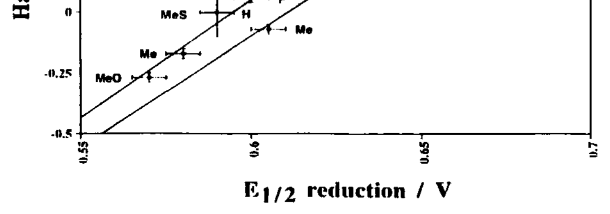

Fig 2. Plot of $E_{1/2}$ reduction potentials against Hammett σ values for substituted aryl **1,2,3,5** dithiadiazolylium cations, as hexafluoroarsenate salts.

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