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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 dithiadiazolylum / dithiadiazolyl compounds show that their solid state properties are particularly influenced by the substituent group¹. 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 dithiadiazolylum 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 dithiadiazolylum hexafluoroarsenate salts. The electrochemical technique known as cyclic voltammetry was used to measure $E_{1/2}$ reduction potentials² 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 $\Delta G^0 - \Delta G^0_o = -2.303RT\sigma\rho$. When $E_{1/2}$ reduction potentials were plotted against Hammett value σ_x , (where $x = \textit{ortho}, \textit{meta}$ and *para*) similar linear free energy relationships were found to exist. This indicates 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 - NO₂) is larger than for the *meta* analogue.

CONCLUSION

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

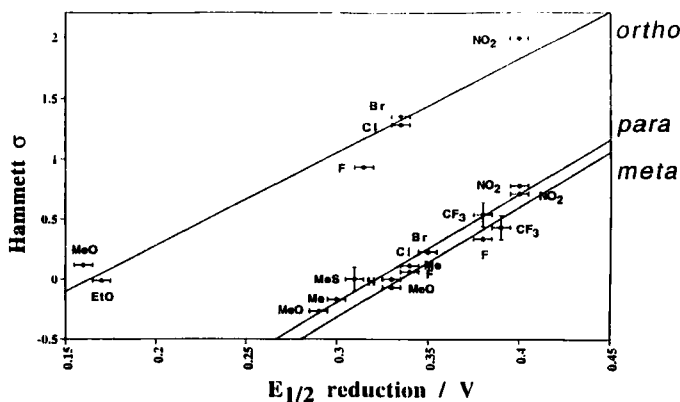


Fig 1. Plot of $E_{1/2}$ reduction potentials against Hammett σ values for substituted aryl 1,3,2,4 dithiadiazolylum cations, as hexafluoroarsenate salts.

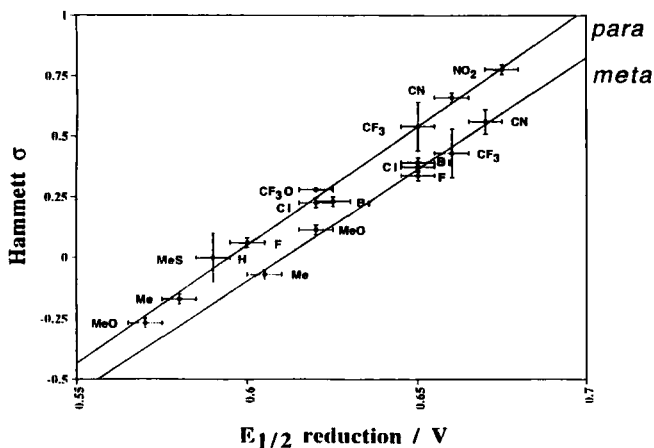


Fig 2. Plot of $E_{1/2}$ reduction potentials against Hammett σ values for substituted aryl 1,2,3,5 dithiadiazolylum cations, as hexafluoroarsenate salts.

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