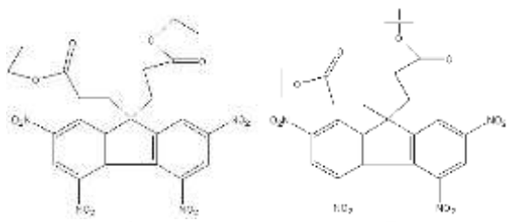
Electro-Reduction of Dialkyl-2,4,5,7-Tetranitrofluorene-9,9-Dipropionates: Simulation

Inam-ul-Haque* and Rabia Azam

Department of Chemistry University of Engineering and Technology Lahore-54890 Pakistan

*Present address: J-263 Defence Housing Authority Lahore-54792 Pakistan

Simulation of cyclic voltammograms of dialkyl-2,4,5,7-tetranitrofluorene-9,9-dipropionates in N,N-dimethyl formamide, using 0.1 M tetrabutylammonium perchlorate as supporting electrolyte at a mercury-bead cathode from literature [1] was carried out. Both cathodic and anodic peaks were analyzed using two shareware programs CVSIM [2] and ESP 2.4 [3]. CVSIM program written in Turbo Pascal was run using Turbo Pascal free downloaded from web. The ESP 2.4 written in DOS was run using DOS. All the simulations were executed on a PC Pentium IV. Structural formulas of diethyl-2,4,5,7-tetranitrofluorene-9,9-dipropionate and dibutyl-2,4,5,7-tetranitrofluorene-9,9-dipropionate are shown as A and B respectively. Our simulations are consistent with an Electrochemical-Electrochemical (EE) type pathway for compound A (Fig. 1) and Electrochemical-Electrochemical-Chemical (EEC) mechanism for compound B (Fig. 2).



A B

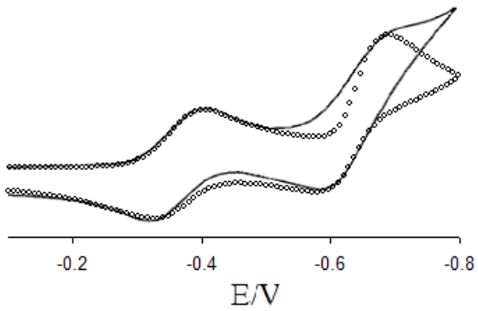


Fig 1:Cyclic voltammogram of diethyl-2,4,5,7-tetranitrofluorene-9,9-dipropionate, scan rate 0.2 V/s. Potential in volts vs. Ag/AgCl,Cl^{-1}. Experimental [1] continuous line; simulated, circles. Simulation carried out using EE mechanism using parameters: k_{h1} 0.05 cm.s^{-1}, k_{h2} 0.0015 cm.s^{-1}, α_1 0.18, α_2 0.28

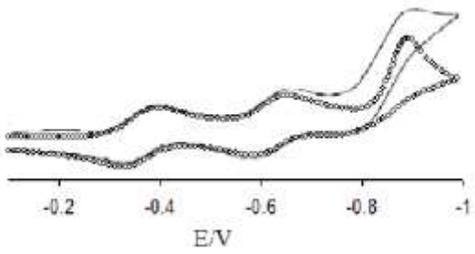


Fig 2:Cyclic voltammogram of dibutyl-2,4,5,7-tetranitrofluorene-9,9-dipropionate, scan rate 0.2 V/s. Potential in volts vs. Ag/AgCl,Cl^{-1}. Experimental [1] continuous line; simulated, circles. Simulation carried out assuming EEEC mechanism using parameters: k_{h1} 0.1cm.s^{-1}, k_{h2} 0.18 cm.s^{-1}, α_1 0.5, α_2 0.5 and large k, s^{-1}

Reaction Scheme for Compound A

$$A + e \underset{}{\overset{k_{h1},\ \alpha_1}{\rightleftharpoons}} A^{\cdot -}$$

$$A^{\cdot -} + e \overset{k_{h2},\ \alpha_2}{\rightleftharpoons} A^{2-}$$

Reaction Scheme for Compound B

$$B + e \overset{k_{h1},\ \alpha_1}{\rightleftharpoons} B^{\cdot -}$$

$$B^{\cdot -} + e \overset{k_{h2},\ \alpha_2}{\rightleftharpoons} B^{2-}$$

$$B^{2-} \xrightarrow{k} \text{Product(s)}$$

References

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