

Structural consequences of electron transfer reactions. 8. Elucidation of isomerization mechanism of the radical anion of (η^4 -cyclooctatetraene)cyclopentadienylcobalt with FFT-Faradaic admittance measurements.

Autorzy

Maria Grzeszczuk

Donald E. Smith

William E. Geiger

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The reduction of (4-1,5-cyclooctatetraene)cyclopentadienylcobalt, (1,5-COT)CoCp, proceeds in an apparently irreversible one-electron step to an isomerized anion, (1,3-COT)CoCp⁻. The present study addressed the mechanistic question of whether the isomerization occurs concomitant with or subsequent to the electron-transfer step. Since the isomerization step was too fast to be studied by normal cyclic voltammetric or moderate frequency ac polarographic techniques, studies using Fast Fourier Transform Faradaic Admittance measurements were undertaken. Using ac frequencies up to 24 kHz, the reduction was characterized as an EC process (isomerization reaction following the electron-transfer step) with a rate constant for the isomerization step (at 298 K) of $(2 \pm 1) \times 10^3 \text{ s}^{-1}$ in dimethylformamide containing 0.1 M Bu₄NBF₄ as supporting electrolyte. The heterogeneous electron-transfer rates of the reductions of both isomers were evaluated as $k_{\text{app}} = 0.28 \text{ cm/s}$ for the 1,3-isomer and 0.06 cm/s for the 1,5-isomer.

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