

Correlation Analysis of Reactivity in the Photo- and Electro-Reduction of Cobalt(III) Complexes in Binary Organic Solvent/Water Mixtures

Kumarasamy Sivaraj and Kuppanagounder P. Elango

Department of Chemistry, Gandhigram Rural University, Gandhigram 624 302, India

Reprint requests to Dr. K. P. E.; E-mail: drkpelango@rediffmail.com

Z. Naturforsch. **63a**, 482 – 492 (2008); received January 3, 2008

The photo- and electro-reduction of a series of cobalt(III) complexes of the type *cis*- β -[Co(trien)(RC₆H₄NH₂)Cl]Cl₂ with R = H, *p*-OMe, *p*-OEt, *p*-Me, *p*-Et, *p*-F, and *m*-Me has been studied in binary propan-2-ol/water mixtures. The redox potential ($E_{1/2}$) and photo-reduction quantum yield ($\Phi_{\text{Co(II)}}$) data were correlated with solvent and structural parameters with the aim to shed some light on the mechanism of these reactions. The correlation of $E_{1/2}$ and $\Phi_{\text{Co(II)}}$ with macroscopic solvent parameters, viz. relative permittivity, indicated that the reactivity is influenced by both specific and non-specific solute-solvent interactions. The Kamlet-Taft solvatochromic comparison method was used to separate and quantify these effects: An increase in the percentage of organic co-solvent in the medium enhances both reduction processes, and there exists a good linear correlation between $E_{1/2}$ and $\Phi_{\text{Co(II)}}$, suggesting a similar solvation of the participants in these redox processes.

Key words: Cobalt(III) Complexes; Photo-Reduction; Electrochemistry; Solvent Effect; Hammett Equation.