

THE ELECTROCHEMICAL REDUCTION OF PENTAMMINECOBALT (III)  
COMPLEXES. THE QUESTION OF LIGAND  
BRIDGING AT ELECTRODES

William M. Schwarz

National Bureau of Standards  
Washington, D. C. 20234

The electrochemical reduction of a number of pentamminecobalt complexes was investigated using linear scan voltammetry at a slowly dropping mercury electrode. An attempt was made to obtain direct evidence for the existence of an electron conducting ligand bridge intermediate in an electrochemical reduction, chiefly by comparing the electrochemical reduction--the electrochemical rate parameters (particularly  $\alpha$ ) and activation effects--with the corresponding homogeneous reductions. The electron transfer coefficient,  $\alpha$ , was found to range from 0.64 to 0.84 for complexes containing succinic, fumaric, maleic and various isomeric pyridinium carboxylic acids as ligands. The values showed little correlation with the ability of the ligand to form electron conducting bridges in the homogeneous sense; they did correlate with the degree of saturation of the ligand. One type of activation effect was investigated--the isomerization of maleic to fumaric acid when maleic acid is functioning as an electron conducting bridging ligand. No isomerization was found to occur for the electrochemical reduction of the maleatopentamminecobalt complex. Similarly no isomerization was observed in the case of homogeneous reduction by vanadium (II) in acidic solutions. The latter results are in disagreement with previous reports of this "activation effect." These results show no evidence for a ligand bridging electroreduction mechanism in these systems.