Electrochemical Electron Transfer Reactions of $M(ttcn)_2^{3+/2+}$ (M = Co, Pd, Pt, Au; ttcn = 1,4,7-trithiacyclononane): the Relation of Reaction Volumes and Electron Transfer Rate Constants

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The reaction volumes (ΔV_M^0), corresponding to the volume change for the half-cell reactions for a series of $M(ttcn)_2^{3+/2+}$ couples were measured by using cyclic voltammetry at elevated pressures. The ΔV_M^0 values reflect the changes in the bond length between M and ligands accompanying the changes in the oxidation state of M from 3+ to 2+. The values of the estimated ΔV_M^0 are in the order of Co < Au < Pd < Pt. The reaction volume is larger for the slower ET reactions, indicating that the reaction volumes reflect the inner-sphere contribution to the activation free energies. The heterogeneous electron exchange rate constants for the $M(ttcn)_2^{3+/2+}$ couples, k_{el}, were measured by AC voltammetry, and by cyclic voltammetry. The latter method on the basis of the Kochi-Nicholson's method was carried out to examine the reliability of this rather simple method by setting the scan rate very fast to make the redox system irreversible. The results obtained by these two methods are in fair agreement with each other, especially when a glassy carbon working electrode was used for the measurements. The relation between the activation free energies for the heterogeneous electron exchange rate constants, ΔG_{el}^{*}, and those for the homogeneous reactions, ΔG_{ex}^{*}, is linear, which indicates that the homogeneous electron transfer reactions of a series of $M(ttcn)_2^{3+/2+}$ is also governed by the intrinsic structural change. However, the slope of log k_{el} *vs.* log k_{ex} plot is far smaller than 0.5 as predicted by the Marcus theory.