If α is considered to be about ½ as usual, the Tafel slope and pH dependance of current will be 120 mV and − 1 respectively. The observed values in Fig. 2. are in agreement with this prediction within the experimental error.

The cyclic voltammetry data of Figure 1 and Table 1 can be also interpreted by the reaction scheme (1) to (4). If the two reduction waves are corresponding to reaction (2) and (4), respectively, the height of the second wave presumably increases with increasing scan rate because dimerization of radical (reaction(3)) is fast enough. Furthermore, when the potential sweeping rate is very slow the second wave is to be probably disappeared.

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Studies of Induced Electron Transfer Reaction: Kinetics of the Oxidation of Cu(phen)$_2^+$ by Co(TrDTA)$^-$ Ion

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The unusal redox reactivity of Co(EDTA)$^-$ with reduced stellacyanin has been attributed to the formation of an oxidant protein precursor complex in which overlap between the donor redox orbital of the distorted tetrahedral type Cu(I) center and the e_g acceptor orbital of the oxidant is poor; it is reported that nonadiabacity is not a requisite feature of the outer sphere oxidation of Cu(I) by Co(EDTA)$^-$ complex ion.[1-5]

In order to determine the reactivity of the electron transfer from Cu (phen)$_2^+$ to Co(TrDTA)$^-$, we have investigated the oxidation of the bis(1,10-phenanthroline) copper(I) ions by trimethylenediaminetertraacetato Co(III) ions. The trimethylenediaminetetraacetato Co(III) complex and bis(1,10-phenanthroline) copper(I) complex ions were prepared by literature methods.[6-8] The kinetics of oxidation of Cu(phen)$_2^+$ by trimethylenediamine tetraacetato Co(III) complex ion was monitored by following the absorbance decrease at 435 nm. Pseudo-first order conditions were employed, maintaining the concentration of the cuprous complex at ca. 10-25 M and varying the oxidant concentration from 2.5×10^{-4} to 2.5×10^{-2}M.

Observed first order rate constants, k_{obs}, were derived from the slopes of linear ln(A_t−A_∞) vs. time plots for the oxidation of Cu(phen)$_2^+$ by Co (TrDTA)$^-$ as shown in Fig. 1 and 2. For all the redox reactions considered, plots of k_{obs} (25°C) vs. oxidant were found to be linear with small positive intercepts (0.04-0.23 s^{-1}) over 50-100 fold concentration ranges covered. it is clear that electron transfer from Cu(I) to Co(III) obeys that rate law: −d[Cu(I)]/dt = k[Cu(I)] [Co(III)].

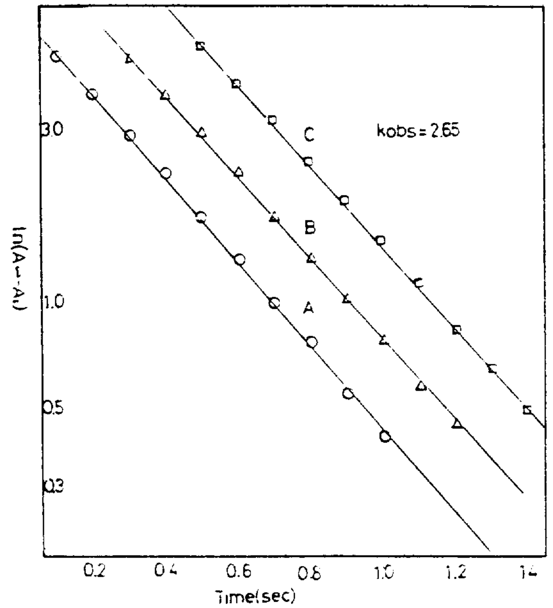

Figure 1. Plot of ln(A_∞ − A_t) vs time for the oxidation of Cu(phen)$_2^+$ by Co(TrDTA)$^-$. pH 6, μ 0.5, 25°C, 5×10^{-3}M

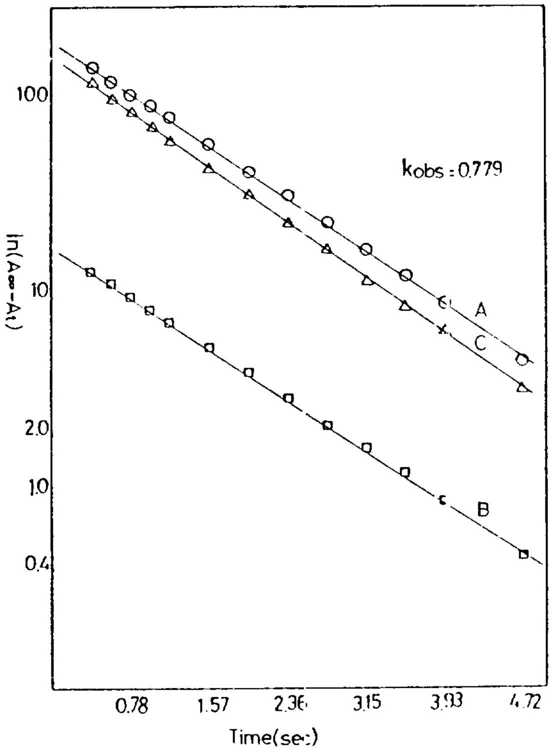

Figure 2. Plot of ln (A_∞ - A_t) vs time for the oxidation of $Cu(phen)_2^+$ by $Co(TrDTA)^-$. pH 6, μ 0.5, 5×10^{-3}M, 30°C

The small intercepts may be attributed to reactions of $Cu(phen)_2^+$ with traces of oxygen which can not be excluded from oxidant solutions contained in the drive syringe of the stopped flow apparatus (Fig. 3). The second order electron transfer rate constants ($k = 29.5 M^{-1}sec^{-1}$) were evaluated from the linear least square analyses of k_{obs} vs. $[Co(TrDTA)^-]$ plots. Activation parameters of $\Delta H^\neq$: 5.7 Kcal/mol and $\Delta S^\neq$:-25 cal/mol-deg were obtained from the linear Eyring plots of temperature. The remarkably low activation enthalpy and large negative activation entropy obtained for $Co(TrDTA)^-$ as the oxidant strongly suggest that overlap between the donor and acceptor redox orbitals is particulary poor and the electron transfer process has to be substantially nonadiabatic.

Considering the structure of $Co(TrDTA)^-$, it is clear that substitutions on the methylene groups of the $NCH_2CH_2CH_2N$ backbone of the ligand will have little effect on the accessibility of these carboxyl groups to inner or outer sphere of the reductants. The present results are consistent with relative Marcus theory[9] which predicts that rate constants for the outer sphere oxidation of $Cu(phen)_2^+$ by $Co(TrDTA)^-$ complex ion are similar.

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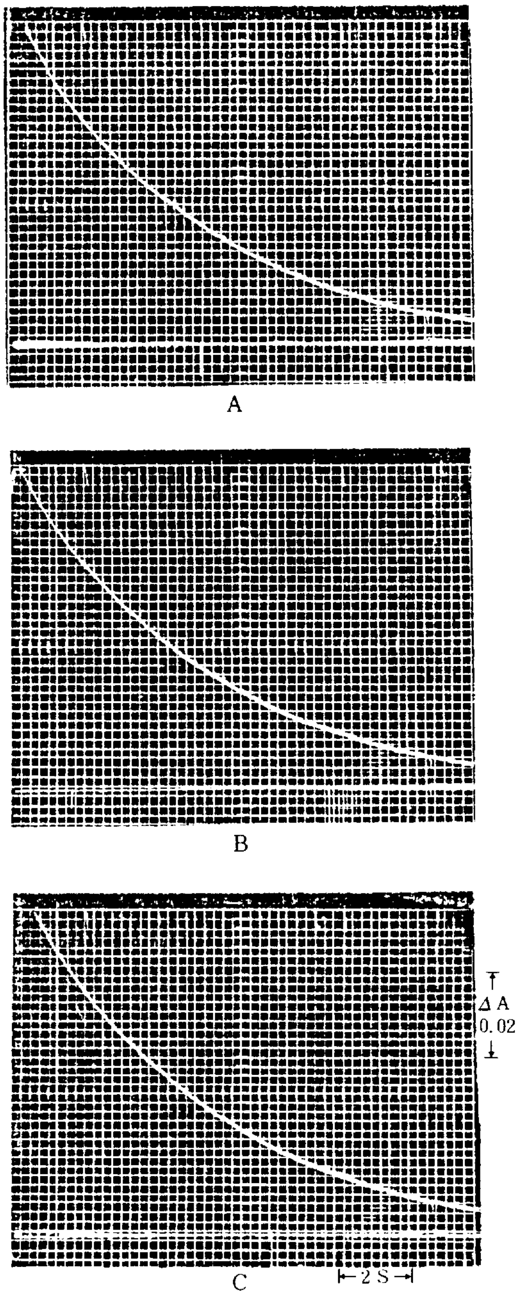

Figure 3. Oscilloscope tracing of absorbance changes upon rapid mixing of $Cu(phen)_2^+$ and $Co(TrDTA)^-$ at 25°C.

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