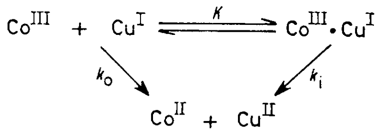
Mercaptide-bridged Intramolecular Electron Transfer from Copper(I) to Cobalt(III)

By James K. Farr and Robert H. Lane*
(*Department of Chemistry, University of Georgia, Athens, Georgia* 30602)

Summary Aqueous Cu^I binds tightly to the sulphur atom of *O,S*-mercaptoacetatobis(ethylenediamine) cobalt(III) to yield a binuclear ion which undergoes intramolecular electron transfer decay with $k = 2{\cdot}0 \times 10^{-3}$ s^{-1} (25 °C, 0·10 M $HClO_4$), $\Delta H^* = 21{\cdot}4 \pm 0{\cdot}4$ kcal mol^{-1} and $\Delta S^* = +1{\cdot}0 \pm 2{\cdot}5$ cal K^{-1} mol^{-1}.

Activation parameters for intramolecular electron transfer between transition metal ions, although of considerable theoretical interest,[1] have been reported only for the Ru^{II} reduction of Co^{III} which was mediated by several structurally related extended ligand bridges.[2]

When aqueous Cu^I[3] is injected into a nitrogen purged solution of $[Co(en)_2(SCH_2CO_2)]^+$,[4] the sulphur-to-cobalt charge transfer absorption at 282 nm (ε 11,700) disappears, and a new band appears at 365 nm (Δε 3300 ± 150) within the 8—10 s that elapse during mixing and the start of data collection on a Cary 15 spectrophotometer. Decay of the new band, with concomitant production of Co^{II}, follows first-order kinetics (k_{obs} $2{\cdot}0 \times 10^{-3}$ s^{-1}, 25 °C) over a range of concentration of the starting ions from $1{\cdot}0 \times 10^{-4}$ to $1{\cdot}0 \times 10^{-3}$ M $\{[Co^{III}]_0 \geqslant [Cu^I]_0$, 0·10 M $HClO_4\}$. The cobalt(II) produced, determined as $[CoCl_4]^{2-}$,[5] agreed well with the value for $[Cu^I]_0$. The species producing the new absorption was found by the method of continuous variations[6] to be equimolar in cobalt(III) complex and Cu^I. A plot of difference absorbance *vs.* $[Cu^I]_0$ $\{[Co^{III}] \geqslant [Cu^I]\}$ exhibits little deviation from linearity at the lowest concentrations used $\{[Cu^I] = [Co^{III}] = 10^{-4}$ M$\}$, suggesting *ca.* 10^6 l mol^{-1} as a lower limit for the formation constant of the binuclear ion.



(1)

That Cu^I is bound to sulphur in the binuclear ion is indicated by the observed spectral change which can be reasonably ascribed to a bathochromic shift of the sulphur-to-cobalt charge transfer absorption upon co-ordination of electron-rich Cu^I. A similar spectral perturbation and stoicheiometry are observed upon addition of Cu^I to $[Co(en)_2(SCH_2CH_2NH_2)]^{2+}$, where the only potential bridging ligand is sulphur. Vigorous aeration of a solution of the latter binuclear ion (which undergoes thermal electron transfer extremely slowly†) results in restoration of the spectrum of the starting cobalt(III)

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† Preliminary experiments indicate that production of Co^{II} in this system is accelerated by irradiation of the difference absorption band. This effect is under investigation.

complex. Further support for sulphur co-ordination derives from the known high binding affinity of Cu^I for thiolate[7] and its decided lack of affinity for carboxylate.[8]

Although first-order kinetic behaviour demonstrates that Co^{III}–Cu^I complexation takes place prior to electron transfer, it does not follow that electron transfer occurs in the resulting binuclear ion. A mechanism requiring prior dissociation of the dimer will exhibit similar kinetic behaviour (equation 1). Under rate saturation conditions the observed constant, k_{obs}, will equal the sum of the intramolecular constant, k_1 plus that for any pathway requiring prior dissociation, k_0, the latter divided by the formation constant of the binuclear ion, K, *i.e.*, $k_{obs} = k_1 + (k_0/K)$.

In order for a pathway involving prior dissociation of the sulphur-bound Cu^I to account for the observed rate constant, a value $> 2 \times 10^3$ l mol^{-1} s^{-1} for k_0 $(= k_{obs}K)$ is required. Two such pathways can be envisaged, (i) outer-sphere electron transfer or (ii) inner-sphere electron transfer *via* a carboxylate bridge. An outer-sphere mechanism requires a rate enhancement of more than four orders of magnitude over previously studied outer-sphere reductions of cobalt(III)-mercaptide complexes[4b] and an even greater enhancement over known rates of outer-sphere oxidation of Cu^I.[10] The required value for k_0 is likewise more than four orders of magnitude greater than rate constants previously determined for reductions of alkylcarboxylatocobalt(III) ions by Cu^I.[11] Since there is no readily apparent source for such a rate enhancement in the present system, we conclude that electron transfer is intramolecular within the mercaptide-bridged binuclear species.

Activation parameters, determined from a standard Eyring plot, were $\Delta H^* = 21{\cdot}4 \pm 0{\cdot}4$ kcal mol^{-1}; $\Delta S^* = 1{\cdot}0 \pm 2{\cdot}5$ cal K^{-1} mol^{-1}. The entropy of activation is zero within experimental error, which is expected for an intramolecular, adiabatic process,[1] but which is in marked contrast to the large negative values observed for intermolecular electron transfer between like-charged species. The major barrier to reaction is thus the requirement for reorganization of the inner and outer co-ordination spheres of the metals in the binuclear ion as directly reflected in the activation enthalpy. Work currently in progress on a series of sulphur donor complexes in which ligand substituents are systematically varied should thus lead to a clarification of the effects of non-bridging ligands on the energetics of electron transfer reactions.

Added in proof. A referee commented on the possibility of measurement of the forward rate constant for the equilibrium, K. We have investigated the reaction of $[(Co(en)_2(SCH_2CH_2O)]^+$ with Cu^I on a stopped flow instrument with a 5 ms dead time and have found that the formation of the binuclear ion is too fast to be observed, as expected for substitution reactions of Cu^I.

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