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Stereoselectivity in Electron-Transfer Reactions of Tris(ethylenediamine)cobalt(II) with Several Anionic Cobalt(III) Complexes

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The stereoselectivities in the electron-transfer reactions of $[Co(en)_3]^{2+}$ with eight Δ anionic Co(III) complexes in aqueous solution have been determined by observing the enantiomeric excesses of the $[Co(en)_3]^{3+}$ product. The results are compared with the ion-pairing stereoselectivity between $[Co(en)_3]^{3+}$ and the anionic complexes. Even the Δ anionic complexes which form favorable pairs with Δ-$[Co(en)_3]^{3+}$ yielded the excesses of Λ-$[Co(en)_3]^{3+}$ product.

Much attention have been paid to the existence of stereoselectivity in outer-sphere electron-transfer reactions between chiral metal complexes.[1-3] Since Geselowitz and Taube reported in 1980 the first cases of stereoselective electron-transfer reactions,[4] a fair number of examples have been published.[5-10] Recently, Lappin et al. have reported the stereoselectivity in the oxidation of $[Co(en)_3]^{2+}$ (en = ethylenediamine) and related complexes by $[Co(edta)]^-$ (edta = ethylenediaminetetraacetate),[11] and Geselowitz et al. have reported the results of the solvent dependence of the stereoselectivity in the reaction and the effects of the oxidation by $[Co(pdta)]^-$ (pdta = propanediaminetetraacetate) and $[Co(cdta)]^-$ (cdta = 1,2-cyclohexanediaminetetraacetate).[12] However, the oxidants used for the reaction have been limited to $[Co(edta)]^-$ and its derivatives. If a wide variety of anionic complexes are used as the oxidant, it can be expected that more extensive information on the electron-transfer stereoselectivity are obtained. The formal redox potentials for some Co(III)/Co(II) couples are shown in Table 1. The data in Table 1 indicate that $[Co(ox)_3]^{3-}$ (ox = oxalate) and $[Co(mal)_3]^{3-}$ (mal = malonate), as well as $[Co(edta)]^-$, can readily oxidize $[Co(en)_3]^{2+}$, following the equation $[Co(en)_3]^{2+} + [Co(ox)_3]^{3-} \longrightarrow [Co(en)_3]^{3+} + [Co(ox)_n]^{2-2n} + (3-n)ox^{2-}$. Thus, attempts were made to use various other anionic Co(III) complexes as the oxidant for $[Co(en)_3]^{2+}$.

Table 1. Formal Redox Potentials for Co(III)/Co(II) Couples at 25 °C

Oxidized form	$E°'$ /V	Medium/mol·dm^{-3}	Ref.
$[Co(en)_3]^{3+}$	-0.18	0.1-0.2 ($NaClO_4$)	7
$[Co(edta)]^-$	0.38	0.05 (acetate)+0.2 (KNO_3)	13
$[Co(ox)_3]^{3-}$	0.57	1.0 (KCl)	14
$[Co(mal)_3]^{3-}$	0.741	1.0 (KCl)	15

In a typical run, 10 cm^3 of 7.5×10^{-1} M (M = $mol \cdot dm^{-3}$) ethylenediamine solution, 2 cm^3 of 3.75×10^{-1} M $Co(NO_3)_2 \cdot 6H_2O$ solution, and 10 cm^3 of 0.3 M KCl solution, which were purged with a N_2 gas prior to use, were mixed at 25±0.5 °C under a nitrogen atmosphere in a glass vessel (ϕ4.5x5.0 cm). To the mixture were added 8 cm^3 of 9.38×10^{-3} M oxidant solution. The reaction was rapid and virtually completed within 1 min in the case of oxidation by $[Co(ox)_3]^{3-}$. After completion of the reaction (usually 5-10 min), the reaction mixture was acidified with about 6 cm^3 of 3 M HCl below pH 1, and the solution was diluted with water to about 1 dm^3 and was passed through an SP-Sephadex C-25 column (ϕ2.9x7 cm). After the column was thoroughly washed with 0.075 M HCl, the adsorbed $[Co(en)_3]^{3+}$ was eluted with 1.5 M HCl. The eluate was collected and subsequently made up to 50 cm^3 with 1.5 M HCl in a volumetric flask. The absorbance and CD spectrum of the solution at the first absorption band of $[Co(en)_3]^{3+}$ were measured by a Jasco Uvidec-320 spectrophotometer and a Jasco J-500 spectropolarimeter, respectively, using a 2 cm cell. By comparison with an optically pure $[Co(en)_3]^{3+}$ complex, each stereoselectivity was expressed in terms of the percentage of enantiomeric excess in the $[Co(en)_3]^{3+}$ product for at least triplicate runs.

The results of stereoselectivity are summarized in Table 2, together with the stereoselectivities in ion pair formation (in the last column).16,17) For the oxidation products by all the Δ anionic complexes examined here, the Λ enantiomer preference of $[Co(en)_3]^{3+}$ was observed. A comparison of the stereoselectivities in electron-transfer reactions with those in ion-pairing reveals that Δ anionic complexes form favorable pairs with Λ-$[Co(en)_3]^{3+}$ give enantiomeric excesses of 9.0-10.2% Λ in 0.1-1.0 M KCl solution, whereas Δ anionic complexes which form favorable pairs with Δ-$[Co(en)_3]^{3+}$ give appreciably smaller enantiomeric excesses (0.5-3.6% Λ) than the former. Moreover, it should be noted that the stoichiometries of reactions by the latter are fairly smaller than unity. As a check for the latter systems, reactions were performed with both the Δ and Λ forms of $[Co(ox)_2(en)]^-$. The Δ-$[Co(ox)_2(en)]^-$ oxidant yielded an excess of the Λ-$[Co(en)_3]^{3+}$ product, and the Λ oxidant yielded the Δ product, with enantiomeric excesses of 3.6-3.0%. This confirms that the observed overall stereoselectivity in the electron-transfer reaction is different from the ion-pairing stereoselectivity. As proposed by Saito et al.5) to interpret the ionic strength dependence of stereoselectivity in an outer-sphere redox reaction, the results may be reasonably accounted for by assuming that the ion pair formation constant between the redox couple (K_{IP}) and the electron-transfer rate constant within the ion pair (k_e) have different stereoselectivities, though it needs to be proved experimentally by kinetic study. To examine the dependence of stereoselectivity on the extent of the precursor ion pair formation, the effect of the reactant concentrations was studied for the cases of Δ-$[Co(ox)_3]^{3-}$ and Δ-$[Co(ox)_2(en)]^-$ oxidants in 0.1 M KCl solution. No significant dependence on the reactant concentrations was observed in the overall stereoselectivity. Thus, as pointed out by Lappin et al.11) and Geselowitz et al.,12) the results in Table 2 suggest an importance of the precursor ion pair formation between reactants, but cannot be explained satisfactorily solely by the stabilization of the precursor due to hydrogen bonding.

Table 2. Stereoselectivities in Electron-Transfer Reactions of $[Co(en)_3]^{2+}$ with Anionic Co(III) Complexes at 25 °C

10^3[anion] $mol \cdot dm^{-3}$	$10^2[Co^{2+}]$ $mol \cdot dm^{-3}$	10[en] $mol \cdot dm^{-3}$	Medium $mol \cdot dm^{-3}$	Selectivity ee %[a]	Stoichiometry of reaction[b]	Selectivity of ion pair[c]
Δ-$[Co(ox)_3]^{3-}$						Λ
2.5	2.5	2.5	0.1(KCl)	10.0±0.1Λ	0.99±0.01	
2.5	2.5	2.5	1.0(KCl)	10.1±0.2Λ	1.01±0.01	
1.25	2.5	2.5	0.1(KCl)	10.2±0.2Λ	0.97±0.02	
5.0	1.0	1.0	0.1(KCl)	10.0±0.1Λ	0.95±0.01	
2.14	2.14	2.14	0.5(Na_2d-tart)	9.6±0.1Λ	1.04±0.01	
2.14	2.14	2.14	0.5(Na_2SO_4)	9.2±0.1Λ	0.99±0.01	
2.13	2.14	2.14	0.5(Na_3PO_4)	9.2±0.1Λ	1.02±0.01	
Δ-$[Co(ox)_2(gly)]^{2-}$						Λ
2.5	2.5	2.5	0.1(KCl)	9.0±0.1Λ	0.94±0.01	
2.15	2.14	2.14	0.5(Na_3PO_4)	7.4±0.2Λ	0.98±0.01	
Δ-$[Co(ox)_2(en)]^-$						Δ
2.5	2.5	2.5	0.1(KCl)	3.6±0.1Λ	0.71±0.07	
1.25	2.5	2.5	0.1(KCl)	3.4±0.1Λ	0.73±0.06	
5.0	1.0	1.0	0.1(KCl)	3.8±0.1Λ	0.55±0.02	
2.14	2.14	2.14	0.5(Na_3PO_4)	2.6±0.1Λ	0.85±0.07	
Λ-$[Co(ox)_2(en)]^-$						Λ
2.5	2.5	2.5	0.1(KCl)	3.0±0.1Δ	0.74±0.07	
Δ-$[Co(edta)]^-$						Λ
2.5	2.5	2.5	0.1(KCl)	9.7±0.1Λ	1.01±0.01	
2.15	2.14	2.14	0.5(Na_3PO_4)	9.2±0.2Λ	0.99±0.01	
0.47	0.82	0.96		10±2Λ[d]		
10	1.0	3.0		9.0Λ[e]		
1.84	1.8	1.8	1.0(Cl^-)	10.8±0.5Λ[f]		
1.84	1.8	1.8	1.0(ClO_4^-)	9.3±0.5Λ[f]		
1.84	1.8	1.8	1.0(PO_4^{3-})	0.6±0.1Λ[f]		
Δ-cis(N)-$[Co(ida)_2]^-$ [g]						Λ
2.08	2.5	2.5	0.1(KCl)	9.2±0.1Λ	1.00±0.01	
Δ-C_1-cis(N)-$[Co(ox)(gly)_2]^-$						Λ
2.5	2.5	2.5	0.1(KCl)	9.4±0.1Λ	0.98±0.01	
Δ-C_2-cis(N)-$[Co(ox)(gly)_2]^-$						Δ
2.5	2.5	2.5	0.1(KCl)	2.1±0.1Λ	0.71±0.01	
Δ-trans(N)-$[Co(ox)(gly)_2]^-$						Δ
2.5	2.5	2.5	0.1(KCl)	0.5±0.1Λ	0.77±0.04	

a) ee % stands for the percentage of enantiomeric excess in the $[Co(en)_3]^{3+}$ product. b) the ratio of the amount of $[Co(en)_3]^{3+}$ product to that of anionic complex used as the oxidant. c) the chirality of $[Co(en)_3]^{3+}$ favorable to the formation of ion pairs with the chiral anionic complexes used as the oxidant. d) Ref. 4. e) Ref. 12. f) Ref. 11, the values at 23±1 °C. g) ida = iminodiacetate.

The effects of anions, such as d-tartrate, SO_4^{2-}, and PO_4^{3-}, on stereoselectivity were examined using $[Co(ox)_3]^{3-}$ as the oxidant. Although Lappin et al. reported that PO_4^{3-} brought about a marked decrease in the stereoselectivity,11) only small effect of PO_4^{3-} was observed for the oxidation reactions by $[Co(ox)_3]^{3-}$, $[Co(ox)_2(gly)]^{2-}$ (gly = glycinate), $[Co(ox)_2(en)]^-$, and $[Co(edta)]^-$.

Preliminary study also revealed that Δ-$[Co(mal)_3]^{3-}$ oxidant yielded enantiomeric excess of about 1% Λ, and hence was the less stereoselective oxidant for $[Co(en)_3]^{2+}$ than Δ-$[Co(ox)_3]^{3-}$. However, for some conformational isomers of $[Co(\pm pn)_3]^{2+}$ (pn = 1,2-propanediamine), $[Co(mal)_3]^{3-}$ was found to be an effective stereoselective oxidant. Further studies on the stereoselectivity in electron-transfer reactions between a variety of cationic and anionic complexes are needed.

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