Temperature Dependence of Chiral Recognition in the Oxidation of Tris(ethylenediamine)cobalt(II) Complex by Optically Active Anionic Cobalt(III) Complexes

Akira Tatehata* and Akira Muraida
Department of Chemistry, Faculty of Science, Shizuoka University, Ohya, Shizuoka 422

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The temperature dependence of the stereoselectivity in the oxidation of tris(ethylenediamine)cobalt(II) complex by some chiral anionic cobalt(III) complexes has been studied over the temperature range of 5-45°C in aqueous solution. The activation enthalpy difference, $\Delta\Delta H^{\ddagger}$, and the entropy difference, $\Delta\Delta S^{\ddagger}$, between Δ-Λ and Δ-Δ pairs show two kinds of $\Delta\Delta H^{\ddagger}/\Delta\Delta S^{\ddagger}$ compensation behavior, indicating that the electron-transfer proceeds by two different types of reaction mechanisms. The relative importance of $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ is interpreted in terms of the difference in the stereoselective interactions upon formation of the precursor complex.

The investigation of stereoselectivity in outer-sphere electron-transfer reactions between metal complexes has been of considerable interest for the understanding of chiral induction mechanism.[1,2] It has been revealed that the magnitude and the sense of stereoselectivity are affected by many factors such as the structure and nature of reactants, particularly the spatial arrangement of coordinated atoms[3] and the chelate ring conformation of reactants,[4] and the reaction medium.[5,6] Further, our recent studies of the stereoselective electron-transfer reactions of tris(ethylenediamine)cobalt(II) have shown that the hydrogen bonding interaction between reactants plays an important role in determining the stereoselectivity.[7] However, temperature effects on the stereoselectivity have not been investigated, and therefore little is known about the nature of transition state. It should be helpful for understanding the reaction mechanism to get information about specific interactions in the precursor complex inferred from the activation parameter differences ($\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$) between diastereomeric pairs.[8] We report here the temperature dependence of stereoselectivity in the outer-sphere electron-transfer reactions of $[Co(en)_3]^{2+}$ with chiral anionic cobalt(III) complexes.

The complexes used as the oxidant were prepared by the literature method, and their purities were ascertained by absorption and circular dichroism (CD) spectra.

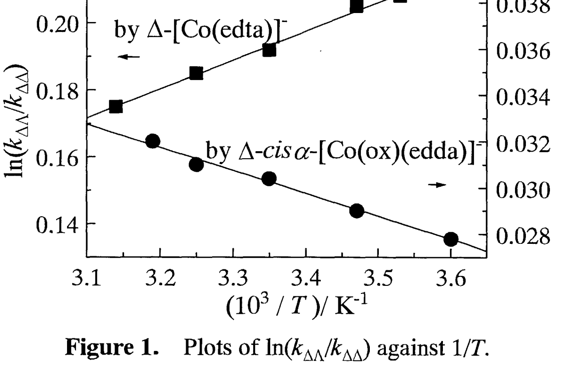

Figure 1. Plots of $\ln(k_{\Delta\Lambda}/k_{\Delta\Delta})$ against $1/T$.

Table 1. Differences in activation parameters between Δ-Λ and Δ-Δ pairs

Oxidant	$\Delta\Delta H^{\ddagger}$ kJmol^{-1}	$\Delta\Delta S^{\ddagger}$ JK^{-1}mol^{-1}	$\Delta\Delta G^{\ddagger\,a}$ kJmol^{-1}
$[Co(ox)_3]^{3-}$	-0.60 ± 0.06	-0.43 ± 0.19	-0.47 ± 0.08
$[Co(ox)_2(gly)]^{2-}$	-0.66 ± 0.03	-0.74 ± 0.10	-0.44 ± 0.04
$[Co(edta)]^-$	-0.71 ± 0.03	-0.76 ± 0.09	-0.48 ± 0.04
cisβ-$[Co(ox)(edda)]^-$	-0.69 ± 0.05	-0.80 ± 0.17	-0.45 ± 0.07
C_1-*cis*(N)-$[Co(ox)(gly)_2]^-$	-0.44 ± 0.03	0.04 ± 0.11	-0.45 ± 0.04
C_2-*cis*(N)-$[Co(ox)(gly)_2]^-$	0.11 ± 0.01	0.60 ± 0.05	-0.06 ± 0.01
trans(N)-$[Co(ox)(gly)_2]^-$	-0.20 ± 0.05	-0.61 ± 0.18	-0.02 ± 0.07
cisα-$[Co(ox)(edda)]^-$	0.08 ± 0.01	0.53 ± 0.02	-0.08 ± 0.01
$[Co(ox)_2(en)]^-$	-0.32 ± 0.04	-0.51 ± 0.13	-0.17 ± 0.06

[a] at T = 298 K

Stereoselectivity experiments were carried out as described previously[3] except for variations in temperature. All solutions were purged with N_2 gas for 10 min prior to use. In a typical experiment 10 cm^3 of 0.75 mol dm^{-3} ethylenediamine, 2 cm^3 of 0.375 mol dm^{-3} $Co(NO_3)_2$, and 10 cm^3 of 0.3 mol dm^{-3} KCl were mixed under a nitrogen atmosphere. An 8 cm^3 of 9.38x10^{-3} mol dm^{-3} oxidant was added to the mixture. After complete disappearance of the color of the oxidant (5-70 min), the reactions were quenched with 6 cm^3 of 3 mol dm^{-3} HCl. The temperature was kept constant in the range of 5 to 45°C till this procedure. The solution was then diluted with water to 1.5 dm^3 and passed through a 7x2.9 cm diameter SP-Sephadex C-25 cation exchange column. The column was washed with 0.075 mol dm^{-3} HCl, and the product, $[Co(en)_3]^{3+}$, was eluted with 1.5 mol dm^{-3} HCl and made up to 50 cm^3 in a volumetric flask. The absorption and CD spectra of the solution were recorded on a Shimadzu UV-3100 spectrophotometer and a Jasco J-500 spectropolarimeter, respectively. The optical purities of the products were calculated, and the stereoselectivities were expressed in terms of percent enantiomeric excess (%ee) and rate ratio ($k_{\Delta\Lambda}/k_{\Delta\Delta}$),[9] where $k_{\Delta\Lambda}$ and $k_{\Delta\Delta}$ denote the rate constants for the reactions of Λ- and Δ-reductant, respectively, with Δ-oxidant. The values used to obtain the activation parameter differences are the average of 2-4 runs at each temperature.

The plots of $\ln(k_{\Delta\Lambda}/k_{\Delta\Delta})$ against $1/T$ for the oxidants, Δ-$[Co(edta)]^-$ and Δ-*cisα*-$[Co(ox)(edda)]^-$, are given in Figure 1. The activation enthalpy and entropy differences, $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$, between Δ-Λ and Δ-Δ pairs were obtained from the slope and the intercept of each straight line when the plots were fitted to equation (1) using the least-squares method.

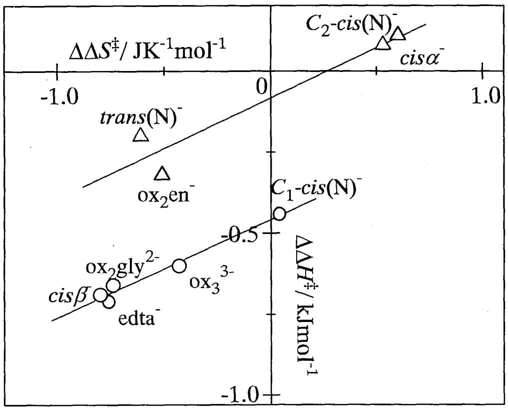

Figure 2. Correlations of $\Delta\Delta H^\ddagger$ and $\Delta\Delta S^\ddagger$.

$$\ln\frac{k_{\Delta\Lambda}}{k_{\Delta\Delta}} = \frac{\Delta\Delta S^\ddagger}{R} - \frac{\Delta\Delta H^\ddagger}{R}\frac{1}{T} \qquad (1)$$

where $\Delta\Delta H^\ddagger=\Delta H^\ddagger_{\Delta\Lambda}-\Delta H^\ddagger_{\Delta\Delta}$ and $\Delta\Delta S^\ddagger=\Delta S^\ddagger_{\Delta\Lambda}-\Delta S^\ddagger_{\Delta\Delta}$.

The results for all the oxidants examined are summarized in Table 1. Small but significant activation enthalpy and entropy differences are observed. The existence of two kinds of linear relationships between $\Delta\Delta H^\ddagger$ and $\Delta\Delta S^\ddagger$ is shown in Figure 2, indicating that the $\Delta\Delta H^\ddagger/\Delta\Delta S^\ddagger$ compensation behavior holds also for the present electron-transfer reactions depending upon the nature of oxidants. It should be noted that the $\Delta\Delta H^\ddagger/\Delta\Delta S^\ddagger$ compensation behavior and the relative magnitude of $\Delta\Delta H^\ddagger$ and $-T\Delta\Delta S^\ddagger$ in $\Delta\Delta G^\ddagger$ show clearly the presence of two groups of oxidants; that is, one are the oxidants in which $\Delta\Delta H^\ddagger$ makes a predominant contribution to the stereoselectivity ($|\Delta\Delta H^\ddagger| > |-T\Delta\Delta S^\ddagger|$), and the other are those in which $\Delta\Delta H^\ddagger$ and $-T\Delta\Delta S^\ddagger$ make a comparable contribution to the stereoselectivity ($|\Delta\Delta H^\ddagger| \approx |-T\Delta\Delta S^\ddagger|$). As shown in Figure 3, the former consists exclusively of the complexes which possess sterically unhindered pseudo-C_3 carboxylate face available for hydrogen bonding,[7] such as C_1-*cis*(N)-$[Co(ox)(gly)_2]^-$ and $[Co(edta)]^-$, whereas the latter consists of the complexes which do not possess such a carboxylate face, such as C_2-*cis*(N)-$[Co(ox)(gly)_2]^-$ and $[Co(ox)_2(en)]^-$. The ion pair formed between $[Co(edta)]^-$, one of the former oxidants, and $[Co(en)_3]^{3+}$ has been revealed by NMR study to adopt a structure involving strong hydrogen bondings between the unhindered pseudo-C_3 carboxylate oxygens of the anion and N-H protons on the cation.[10] A similar structure for the precursor ion pair between $[C(edta)]^-$ and $[Co(en)_3]^{2+}$ can be expected to bring about the larger $|\Delta\Delta H^\ddagger|$ due to the increased stabilization of the favorable ion pair, ΔΛ, through a strong hydrogen bonding interaction, but a weak interaction will lead to the smaller $|\Delta\Delta H^\ddagger|$.

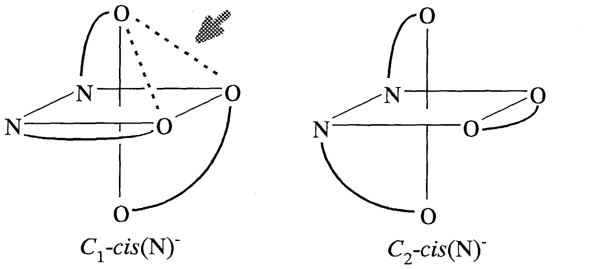

Figure 3. C_1-*cis*(N)-$[Co(ox)(gly)_2]^-$ possessing an unhindered pseudo-C_3 carboxylate face, and C_2-*cis*(N)-$[Co(ox)(gly)_2]^-$.

Thus, as a result of hydrogen bonding between $[Co(en)_3]^{2+}$ and the oxidants with the unhindered pseudo-C_3 carboxylate face in the precursor complex formation process, chiral recognition is primarily controlled by the activation enthalpy difference, $\Delta\Delta H^\ddagger$, to result in enhanced stereoselectivity. On the other hand, in the oxidants incapable of forming such a hydrogen bonding along the pseudo-C_3 axis, the small activation enthalpy difference is compensated by the entropy term with opposite in sign to result in reduced stereoselectivity. In addition, exactly the same classification of the oxidants was also found in the reaction rates studied previously.[7] These results indicate that the present electron-transfer reactions proceed through the two different types of intermediates depending upon hydrogen bonding mode between reactants.

References and Notes

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