

EVIDENCE FOR THE ELECTRON TRANSFER FROM $[\text{Co(II)(en)}_2\text{Cl}]^+$
TO $[\text{Co(III)(en)}_2\text{Cl}_2]^+$ IN METHANOL

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The addition of $[\text{Co(II)(en)}_2\text{Cl}]^+$ accelerated the isomerization of $\text{cis-}[\text{Co(III)(en)}_2\text{Cl}_2]^+$ to its trans-isomer in methanol. The reaction by use of $[\text{Co(II)(en)}_2\text{Br}]^+$ or $[\text{Co(II)}(\ell\text{-chxn})_2\text{Cl}]^+$ instead of $[\text{Co(II)(en)}_2\text{Cl}]^+$ produced $\text{trans-}[\text{Co(III)(en)}_2\text{BrCl}]^+$ or $\text{trans-}[\text{Co(III)}(\ell\text{-chxn})_2\text{Cl}_2]^+$, respectively. These evidences demonstrated the inner-sphere electron transfer from Co(II) to Co(III) in the acceleration mechanism of the title isomerization reaction.

It was reported by Kawaguchi and Fujioka¹⁾ that the addition of CoCl_2 and ethylenediamine (en) considerably accelerated the isomerization of $\text{cis-}[\text{Co(III)(en)}_2\text{Cl}_2]^+$ to its trans-isomer in methanol solution. The report stimulated the authors' interest on the supposition that the electron transfer had taken place from chlorobis(ethylenediamine)cobalt(II) ion ($[\text{Co(II)(en)}_2\text{Cl}]^+$) to $[\text{Co(III)(en)}_2\text{Cl}_2]^+$ in the acceleration mechanism of cis to trans isomerization of the latter. The present study offers the evidence for the quoted electron transfer mechanism in the above reaction through the kinetic as well as spectrophotometric analyses of several concerned reactions.

$\text{cis-}[\text{Co(III)(en)}_2\text{Cl}_2]$ tetraphenylborate was prepared from sodium tetraphenylborate and $\text{cis-}[\text{Co(III)(en)}_2\text{Cl}_2]\text{Cl}$, the latter being synthesized according to the method in the literature²⁾. $\text{trans-}[\text{Co(III)(en)}_2\text{Cl}_2]\text{Cl}$ and $\text{trans-dichlorobis}(\ell\text{-cyclohexdiamine})\text{cobalt(III) chloride}$ ($\text{trans-}[\text{Co(III)}(\ell\text{-chxn})_2\text{Cl}_2]\text{Cl}$) were also prepared similarly²⁾. Obtained salts dissolved easily in methanol flushed with deoxygenated nitrogen. The initial concentration of Co(III) complex was set at 2.0×10^{-3} M in the reaction mixture. Co(II) complexes were prepared by dissolving CoCl_2 (CoBr_2) and en ($\ell\text{-chxn}$) in the methanol. Concentration of the Co(II)Cl_2 was varied between $1.0 \sim 10.0 \times 10^{-3}$ M. To obtain the stable reaction kinetics, LiCl was added into the Co(II) complex solution to keep a constant Cl^- concentration of 60×10^{-3} M in the reaction mixture. A rapid scan spectrophotometer RA-1300 and a stopped flow spectrophotometer RA-1100 of UNION GIKEN CO. were employed for the kinetic and spectrophotometric analyses of the reaction at 25°C.

The isomerization was followed spectrophotometrically by measuring the

change in optical density at 540 nm wave-length, where the $\text{cis-}[\text{Co(III)}(\text{en})_2\text{Cl}_2]^+$ has a strong absorption, while the trans- isomer and $\text{Co(II)}(\text{en})_2\text{Cl}_2$ have negligible weak absorption. The first-order kinetics ruled over the reaction as shown in Figure 1, giving a rate constant, $k_{\text{obs}} = 4.3 \text{ sec}^{-1}$ at the indicated conditions, where D_t and D_∞ are the optical densities of the reaction mixture at time t and after ten half-lives, respectively.

The molar ratio of Co(II)Cl_2 to en affected the rate of reaction considerably as had already been pointed out by Kawaguchi and Fujioka. The result of reexamination revealed that at the constant Co(II)Cl_2 concentration k_{obs} comes to its highest value at the $\text{Co(II)Cl}_2/\text{en}$ molar ratio of 0.5. The fact confirms the existence of $1\text{Co(II)}:2\text{en}$ complex, presumably $[\text{Co(II)}(\text{en})_2\text{Cl}]^+$, as an active species in the reaction mixture.

Figure 2 gives the relation $k_{\text{obs}} = k[\text{Co(II)}(\text{en})_2\text{Cl}]^+$, when the concentration of Co(II)Cl_2 was varied. So that the overall reaction kinetics can be written as

$$-d(\text{cis-}[\text{Co(III)}(\text{en})_2\text{Cl}_2]^+)/dt = k[\text{Co(II)}(\text{en})_2\text{Cl}]^+(\text{cis-}[\text{Co(III)}(\text{en})_2\text{Cl}_2]^+).$$

$$k = 2.1 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}, \text{ at } 25^\circ\text{C}.$$

To obtain the evidence for the electron transfer from $[\text{Co(II)}(\text{en})_2\text{Cl}]^+$ to $[\text{Co(III)}(\text{en})_2\text{Cl}_2]^+$, Co(II)Cl_2 was replaced by Co(II)Br_2 in the equimolar reaction of $\text{cis-}[\text{Co(III)}(\text{en})_2\text{Cl}_2]^+$ and $[\text{Co(II)}(\text{en})_2\text{Cl}]^+$ complexes. The results by a rapid scan spectrophotometries are given in Figure 3 for the reaction with Co(II)Cl_2 in the upper and Co(II)Br_2 in the bottom part, setting the transmittance (%) of the solution in the coordinate. The obtained two groups of spectra have intrinsic differences at the wave-length longer than 620 nm. The result comes from

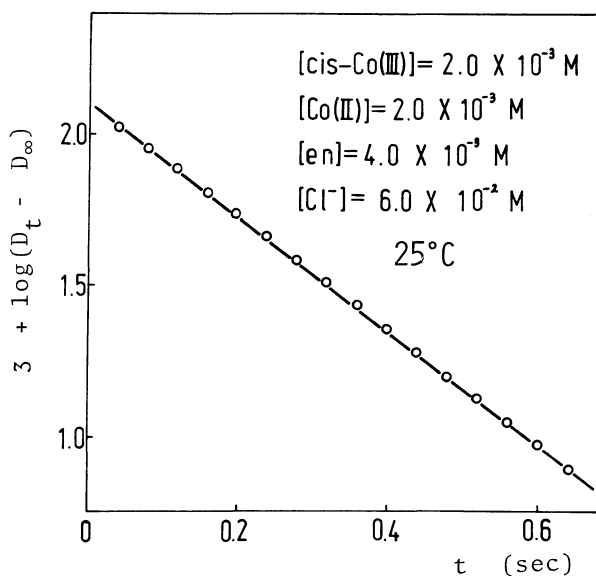


Figure 1. First-order kinetics at constant $[\text{Co(II)Cl}_2]$.

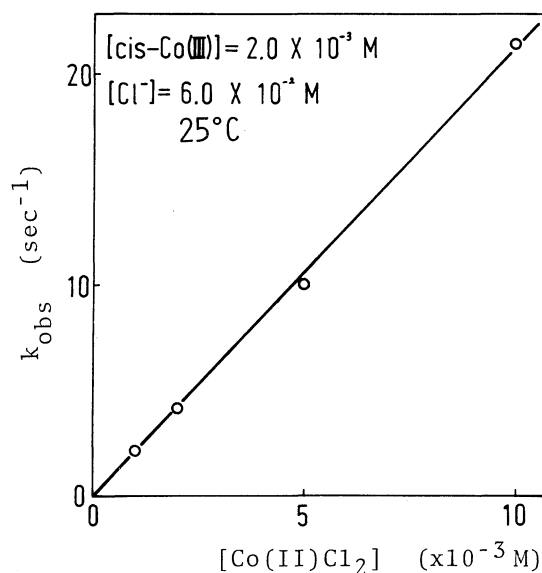
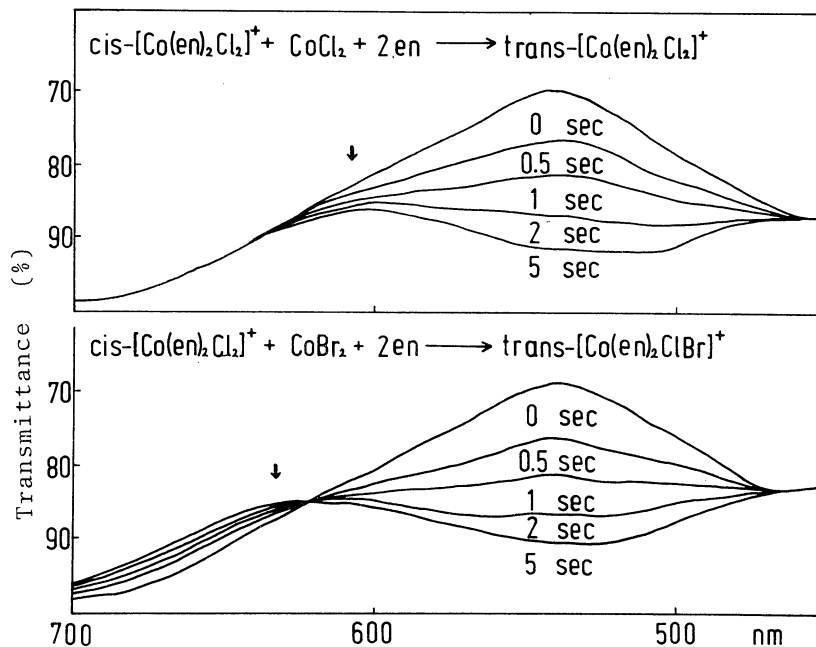


Figure 2. k_{obs} vs. $[\text{Co(II)Cl}_2]$.

Figure 3.

Spectral change in reactions induced with Co(II)Cl_2 (upper) and Co(II)Br_2 (bottom).



different products, that is, $\text{trans-[Co(III)(en)}_2\text{Cl}_2\text{]}^+$ in the case of Co(II)Cl_2 and mainly $\text{trans-[Co(III)(en)}_2\text{BrCl]}^+$ in the case of Co(II)Br_2 . Two arrows, upper and bottom, in the figure represent the wave-length of the maximum absorption for the authentic $\text{trans-[Co(III)(en)}_2\text{Cl}_2\text{]}^+$ and $\text{trans-[Co(III)(en)}_2\text{BrCl]}^+$ in methanol, respectively.

Moreover, when en in $[\text{Co(II)(en)}_2\text{Cl}]^+$ was replaced by ℓ -cyclohexdiamine (ℓ -chxn) in the isomerization of $\text{cis-[Co(III)(en)}_2\text{Cl}_2\text{]}^+$, the obtained compound was mainly $\text{trans-[Co(III)(}\ell\text{-chxn)}_2\text{Cl}_2\text{]}^+$. The evidence is shown in Figure 4 in two ORD spectra at the starting and the final points of the reaction course. The final ORD spectrum came near to that of the authentic $\text{trans-[Co(III)(}\ell\text{-chxn)}_2\text{Cl}_2\text{]}^+$ of the same concentration. The complete coincidence of the final spectrum and the authentic spectrum cannot be attained, because the early-stage reaction of $\text{cis-[Co(III)(en)}_2\text{Cl}_2\text{]}^+$ with $[\text{Co(II)(}\ell\text{-chxn)}_2\text{Cl}]^+$ produces $[\text{Co(II)(en)}_2\text{Cl}]^+$ which reacts with $\text{cis-[Co(III)(en)}_2\text{Cl}_2\text{]}^+$ to form $\text{trans-[Co(III)(en)}_2\text{Cl}_2\text{]}^+$.

The results obtained above allow us

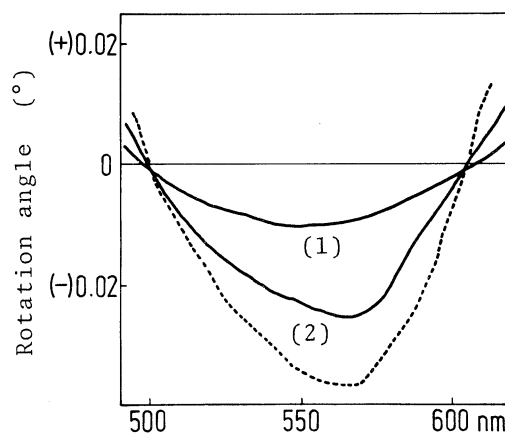
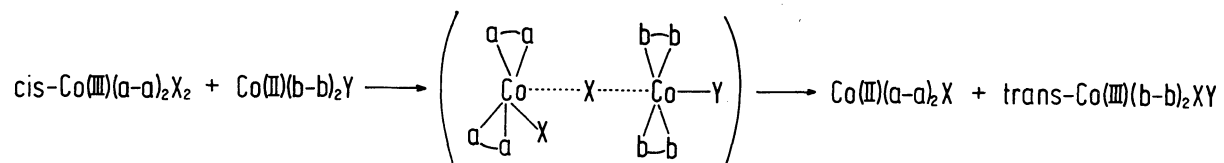


Figure 4. Change of ORD spectrum with reaction course.

- (1) at starting point.
- (2) at final point.
- authentic $\text{trans-[Co(III)(}\ell\text{-chxn)}_2\text{Cl}_2\text{]}^+$ solution.

to state that the acceleration mechanism of Co(II)Cl_2 in the cis to trans isomerization of $[\text{Co(III)(en)}_2\text{Cl}_2]^+$ is represented by the inner-sphere electron transfer from Co(II) to Co(III) through the following bimolecular reaction.



X=Cl, Y=Cl or Br, (a-a)=en, (b-b)=en or chxn.

Furthermore, the rate of reaction obtained in the present study implies the rate of electron transfer from Co(II) to Co(III) through the chlorine bridge.

Literature cited

- 1) S. Kawaguchi and H. Fujioka, Bull. Chem. Soc. Japan., 40, 802 (1967).
- 2) A. Werner, Ann., 386, 1 (1912).

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