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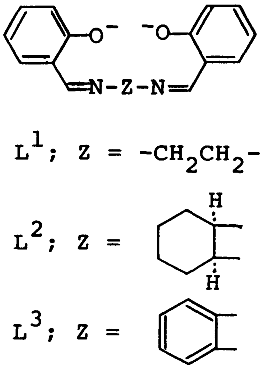
REDUCTION OF HYDROXOCOBALT(III) SCHIFF BASE COMPLEXES WITH ALCOHOLS

Akira NISHINAGA,* Toshiyuki KONDO, and Teruo MATSUURA
Department of Synthetic Chemistry, Faculty of Engineering,
Kyoto University, Yoshida, Kyoto 606

Hydroxocobalt(III) Schiff base complexes were reduced with alcohols to the corresponding cobalt(II) species quantitatively. Kinetic studies on the reduction suggest a mechanism involving rate determining β-elimination of an alcoholatocobalt(III) complex intermediate.

Cobalt(II) Schiff base complexes capable of binding dioxygen have been investigated intensively in connection with biological oxygenations.[1,2] We have recently reported that these cobalt(II) complexes are oxidized irreversibly by molecular oxygen in protic media to give alcoholatocobalt(III) species, which are readily converted to hydroxocobalt(III) complexes by treatment with water.[3] Much attention has been focused on transition metal complexes coordinating oxygen species as important intermediates in oxidations of organic compounds.[4] Little has, however, been known about the chemistry of hydroxocobalt(III) complexes.[5] Hydroxocobalt(III) Schiff base complexes have been shown to react with acids to give the corresponding cobalt(III) species coordinating the conjugate base of the acid, providing a convenient method for the preparation of a variety of cobalt(III) Schiff base complexes.[3,6] We now find that hydroxocobalt(III) Schiff base complexes are unexpectedly reduced with alcohols to give the corresponding cobalt(II) complexes quantitatively. A plausible mechanism proposed involves an alcoholatocobalt(III) complex intermediate which undergoes β-elimination to give a carbonyl compound and a hydridocobalt species, which then reacts with the hydroxocobalt(III) complex affording the cobalt(II) species.

When a solution of N,N'-ethylenebis(salicylideneiminato)hydroxo cobalt(III), $[Co^{III}(L^1)(OH)]$, in methanol was heated under nitrogen, the complex was reduced quantitatively to N,N'-ethylenebis(salicylideneiminato)cobalt(II), $[Co^{II}(L^1)]$, as determind by electronic spectroscopy. In a preparative experiment, $[Co^{II}(L^1)]$ was isolated as crystals in excellent yield. The reduction of $[Co^{III}(L^1)(OH)]$ also took place in ethanol and 2-propanol. The rate of the reduction decreases in the order: 2-propanol >> ethanol > methanol. With 2-propanol, the reduction took place at room temperature even in the air. The time course of the reaction of $[Co^{III}(L^1)(OH)]$ in 2-propanol observed by electronic spectroscopy (Fig. 1) showed that the reaction followed first order kinetics with respect to the cobalt complex ($k = 3.7 \times 10^{-4} s^{-1}$ at 25 °C). The determination of temperature dependent rate constants for the reduction of $[Co^{III}(L^1)(OH)]$ in 2-propanol based on the spectral change at 400 nm gave an activation energy of 130 kJ/mol. Since the



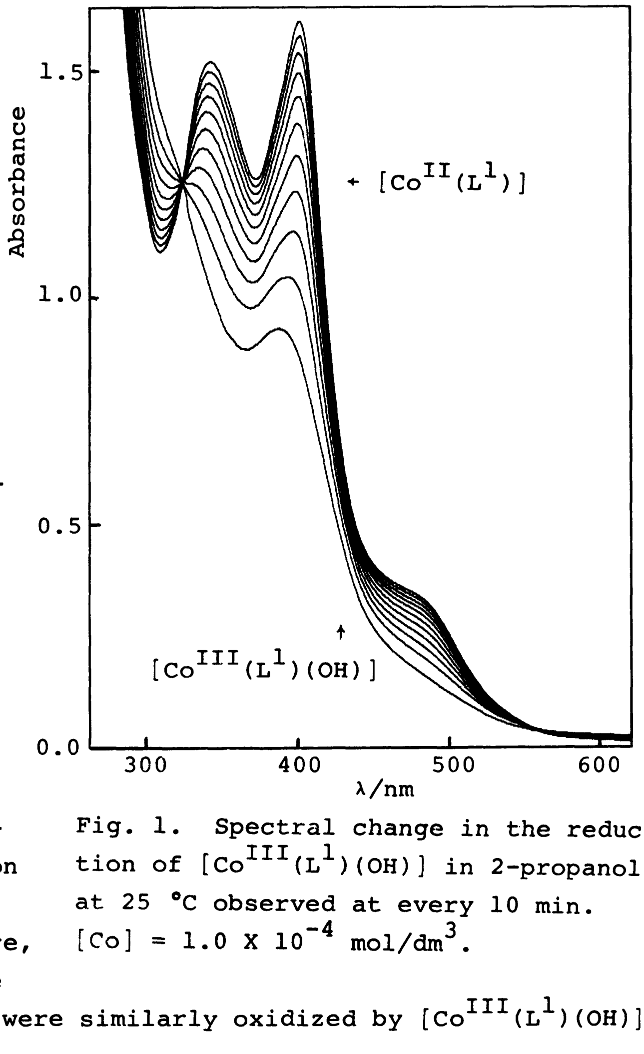


Fig. 1. Spectral change in the reduction of $[Co^{III}(L^1)(OH)]$ in 2-propanol at 25 °C observed at every 10 min. $[Co] = 1.0 \times 10^{-4}$ mol/dm^3.

hydroxo complex was not reduced with diisopropyl ether, the alcoholic hydroxyl group is evidently required for the reduction of the hydroxo complex. The stoichiometry of the reduction could be conveniently determined by the reaction of $[Co^{III}(L^1)(OH)]$ with benzyl alcohol. Thus, when a solution of $[Co^{III}(L^1)(OH)]$ (0.5 mmol) and benzyl alcohol (1 mmol) in 1,2-dichloroethane (20 cm^3) was warmed at 50 °C under nitrogen, the reduction of the complex was completed in 24 h to give benzaldehyde (0.25 mmol). Therefore, the following 2 : 1 stoichiometry can be derived. p-Substituted benzyl alcohols were similarly oxidized by $[Co^{III}(L^1)(OH)]$

$$2\ [Co^{III}(L^1)(OH)] + RCH_2OH \longrightarrow 2\ [Co^{II}(L^1)] + RCHO + 2\ H_2O$$

to the corresponding p-substituted benzaldehydes, where the reduction was accelerated by an electron-releasing group and retarded by an electron-withdrawing group.[7)]

Four hypothetically possible mechanisms are considered for the present reduction of $[Co^{III}(L^1)(OH)]$: (1) homolysis of the Co-O bond in the complex giving rise to $[Co^{II}(L^1)]$ and hydroxyl radical, which abstracts hydrogen from the alcohol finally to give the carbonyl product; (2) disproportionation of the complex under the coordination of the alcohol, R^1R^2CHOH, giving rise to $[Co^{II}(L^1)]$ and $[Co^{IV}(L^1)(OCHR^1R^2)]$, whose β-elimination gives $[Co^{II}(L^1)]$ and the carbonyl product, $R^1R^2C{=}O$;[8)] (3) homolysis of the Co-O bond in $[Co^{III}(L^1)(OCHR^1R^2)]$ produced by an acid-base reaction in the given alcohol to give $[Co^{II}(L^1)]$ and alkoxyl radical, $R^1R^2CHO\bullet$, which is converted to the carbonyl product, $R^1R^2C{=}O$; and (4) β-elimination of $[Co^{III}(L^1)(OCHR^1R^2)]$ giving rise to the carbonyl product, $R^1R^2C{=}O$, and $[Co(L^1)(H)]$, which reacts with $[Co^{III}(L^1)(OH)]$ to give $[Co^{II}(L^1)]$. Among these possibilities, hypotheses (1)-(3) may be ruled out by the following reasons. The hydroxo complex could not be reduced with ethers and the oxidation of substituted benzyl alcohols with the Fenton's reagent gave a complex reaction mixture, whereas the hydroxo complex gave only benzaldehydes, eliminating the mechanism (1). The mechanism (2) is not consistent with the first order kinetics observed for the reduction of the hydroxo complex in 2-propanol. Further, no reduction of $[Co^{III}(L^1)(OH)]$ took place at all with tertiary alcohols, excluding the mechanism (3). The unusually fast reduction of $[Co^{III}(L^1)(OH)]$ in 2-propanol compared to other alcohols may not be rationalized by the mechanisms (2) and (3).

Figure 2 shows the effects of the natures of the axial anionic and sixth ligands as well as the structure of the Schiff base ligand on the reaction rate for the reduction of cobalt(III) complexes with 2-propanol. The reduction of $[Co^{III}(L^1)(OAc)]$ was much slower than that of $[Co^{III}(L^1)(OH)]$ and almost no reaction took place with $[Co^{III}(L^1)(Cl)]$ (Fig. 2A), suggesting that the reduction involves the preformation of $[Co^{III}(L^1)(OPr^i)]$ under the reaction conditions, which depends on the basicity of the axial ligand. The results shown in Fig. 2B indicate that the coordinately unsaturated hydroxo complex is responsible for the reduction and the coordinately saturated species are unsusceptible to the reduction, since the coordination ability increases in the order: DMF < py < 1-methylimidazole. In Fig. 2C, the slightly slower reaction of $[Co^{III}(L^2)(OH)]$ than $[Co^{III}(L^1)(OH)]$ can be readily rationalized by comparison of the bulkiness of the Schiff base ligand with each other. The remarkable retardation in the reduction of $[Co^{III}(L^3)(OH)]$, on the other hand, may be attributable to the nonflexibility of the Schiff base ligand.[9)] It is therefore noted that the reduction of

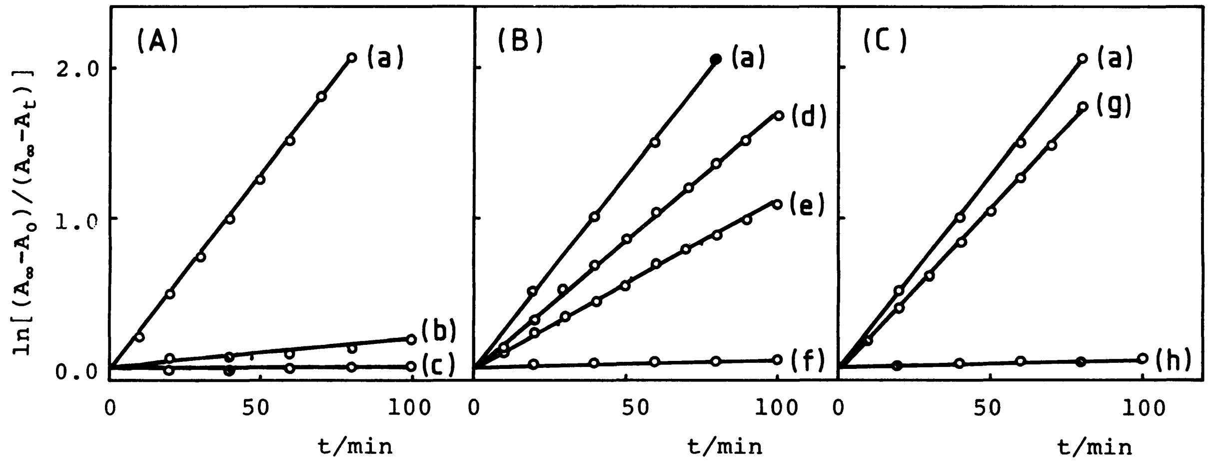
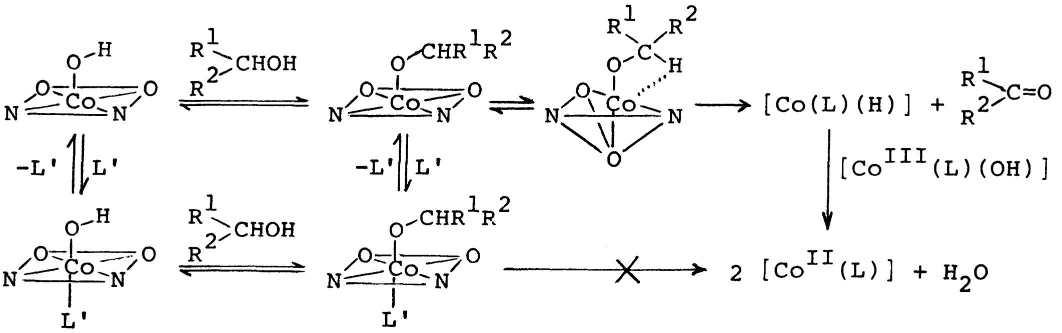


Fig. 2. Effects of the natures of the axial anionic ligand (X^-) in $[Co^{III}(L^1)(X^-)]$ (A), the sixth axial ligand (B), and the structure of the Schiff base ligand (C) on the rate in the reduction of the cobalt(III) species in 2-propanol determined by the spectral change. $[Co] = 1.0 \times 10^{-4}$ mol/dm^3, 25 °C (under N_2). A_∞, A_0, and A_t refer to the absorbances at 400 nm for the Co^{II}, Co^{III}, and the reaction mixture at the time t, respectively. (a); $[Co^{III}(L^1)(OH)]$: (b); $[Co^{III}(L^1)(OAc)]$: (c); $[Co^{III}(L^1)(Cl)]$: (d); $[Co^{III}(L^1)(OH)]$ with 20 equivalents of DMF: (e); $[Co^{III}(L^1)(OH)]$ with 20 equivalents of 2,6-lutidine: (f); $[Co^{III}(L^1)(OH)]$ with 20 equivalents of 1-methylimidazole: (g); $[Co^{III}(L^2)(OH)]$: (h); $[Co^{III}(L^3)(OH)]$.

the hydroxocobalt(III) Schiff base complexes by alcohols seems to involve a conformational change of the ligand. This is in accord with the unsusceptibility of the coordinately saturated hydroxocobalt(III) species. The conformational change of the Schiff base ligand affording a bent form has been reported for $[Co^{III}(L^1)(acac)]$.$^{10)}$ The following mechanistic diagram is therefore reasonably considered for the reduction of the hydroxocobalt(III) complexes with alcohols, supporting the hypothesis (4). The reduction of $[Co^{III}(L^1)(OH)]$ with 1-phenylethanol was much slower than that with 2-propanol. This may be due to steric hindrance of the phenyl group in the former, which inhibits the formation of the alcoholato complex. The fast reaction in 2-propanol compared to methanol and ethanol may result from the acceleration of the conformational change of the Schiff base ligand due to the electronic repulsion between the ligand and the two methyl groups in 2-propanol. The substituent effect of the p-substituted benzyl alcohols on the reduction rate should result from the β-elimination step.



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