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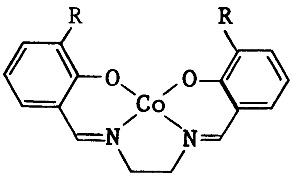
OXYGENATION OF COBALT(II) SCHIFF BASE COMPLEXES IN ALCOHOLS

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

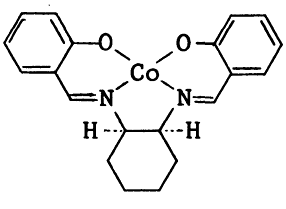
The oxygenation of cobalt(II) Schiff base complexes in alcohols resulted in irreversible oxidation to give the corresponding alcoholatocobalt(III) complexes, which were converted to hydroxocobalt(III) species by treatment with water. Kinetic studies on the oxidation suggest a mechanism involving rate determining proton transfer from alcohols to cobalt-dioxygen adducts.

Much attention has been focused on cobalt(II) complexes coordinating organic base ligands including Schiff bases in connection with biological oxygenations, because they interact reversibly with molecular oxygen to form dioxygen adducts,1) and promote dioxygen incorporation into organic compounds related to the substrates for dioxygenase reactions.2) These findings have, however, been observed in aprotic solvents. Little has been known about the behavior of these cobalt(II) complexes towards molecular oxygen in protic solvents.3) We now find that N,N'-ethylenebis(salicylideneiminato)cobalt(II), [Co(L^1)], and its related cobalt(II) Schiff base complexes are irreversibly oxidized by molecular oxygen in alcohols giving rise to the corresponding alcoholatocobalt(III) complexes, which are readily converted to hydroxocobalt(III) species by treatment with water. A mechanism involving rate determining proton transfer from alcohols to dioxygen-cobalt adducts is suggested for the oxidation of the cobalt Schiff base complexes on the basis of kinetic results.

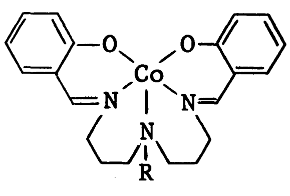
When oxygen was bubbled through a stirred suspension of [Co(L^1)] (3 g) in methanol (300 cm^3) at room temperature for 3 h, a clear yellow-brown solution was obtained. About 150 cm^3 of the solvent was evaporated and water (300 cm^3) was added to the resulting concentrated solution to give [Co(L^1)(OH)]4) as fine crys-



[Co(L^1)]; R = H
[Co(L^2)]; R = OMe
[Co(L^3)]; R = t-Bu
[Co(L^4)]; R = Cl



[Co(L^5)]



[Co(L^6)]; R = H
[Co(L^7)]; R = Me

$$[Co^{II}(L)] \xrightarrow[ROH]{O_2} [Co^{III}(L)(OR)]$$

tals (yield, 85%). Similar results were obtained with other cobalt(II) Schiff base complexes, $[Co(L)]$.5) The oxygenation of $[Co(L^1)]$ in absolute methanol followed by evaporation of the solvent, however, gave $[Co(L^1)(OMe)]$ contaminated by a comparable amount of $[Co(L^1)(OH)]$.6) In the oxygenation of $[Co(L^1)]$ in 2,2,2-trifluoroethanol, $[Co(L^1)(OCH_2CF_3)]$7) was deposited as crystals directly from the reaction mixture in nearly quantitative yield. $[Co(L^1)(OCH_2CCl_3)]$ was similarly obtained as crystals when $[Co(L^1)]$ was oxygenated in 2,2,2-trichloroethanol followed by dilution with hexane.7) All these alcoholatocobalt(III) complexes were converted quantitatively to $[Co(L^1)(OH)]$ when they were treated with water. When $[Co(L^1)(OH)]$ was dissolved in 2,2,2-trifluoroethanol, on the other hand, $[Co(L^1)(OCH_2CF_3)]$ was deposited as crystals nearly quantitatively. Further, in the oxygenation of $[Co(L^1)]$ in 2,2,2-trifluoroethanol as well as methanol, 0.25 equivalents of oxygen were taken up without oxidation of the alcohol. Similar results were obtained with other complexes, $[Co(L^2)]$ - $[Co(L^7)]$. These observations suggest the following stoichiometry for the present oxygenation;

$$[Co(L)] + (1/4)\,O_2 + ROH \longrightarrow [Co(L)(OR)] + (1/2)\,H_2O$$

$$[Co(L)(OR)] + H_2O \rightleftharpoons [Co(L)(OH)] + ROH.$$

The time course of the oxygenation of $[Co(L)]$ in alcohols could readily be observed by electronic spectroscopy. Figure 1 shows the electronic spectral change for the oxygenation of $[Co(L^1)]$ in methanol at room temperature, which follows the first order kinetics with respect to $[Co(L^1)]$. Interestingly, the kinetic order with respect to the cobalt(II) complexes in the oxygenation was found to depend on the nature of the alcohol employed and on the steric and electronic natures of the Schiff base ligand. Thus, with all the four coordinate complexes, $[Co(L^1)]$ - $[Co(L^5)]$, the oxygenation in methanol followed the first order kinetics irrespective of the nature of the ligand (Fig. 2), where an electron-releasing group in the Schiff base ligand accelerates the reaction and electron-withdrawing and bulky groups retarded the oxygenation. On the other hand, the kinetic order for the oxygenation of $[Co(L^1)]$ was 2.0 in 2,2,2-trifluoro-ethanol and 1.6 in 2,2,2-trichloro-ethanol, whereas a kinetic order of 1.0 was obtained in the oxygenation of $[Co(L^5)]$ in 2,2,2-trifluoroethanol.8)

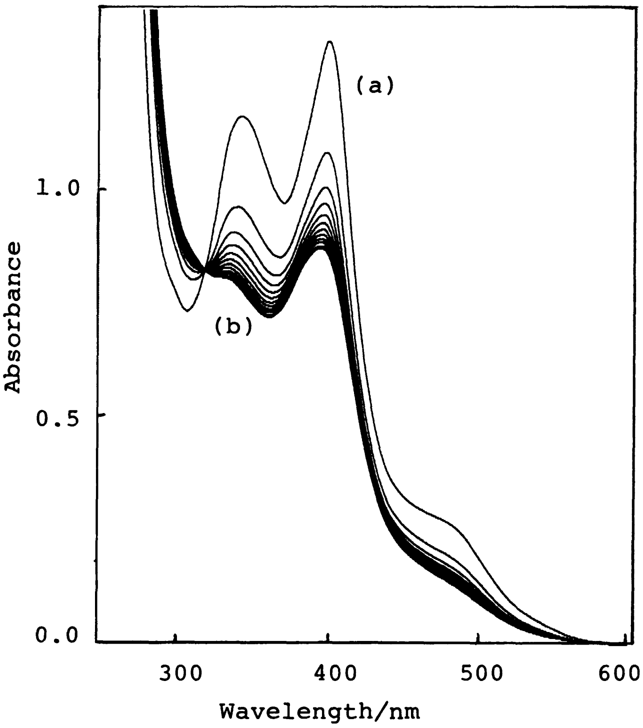


Fig. 1. Spectral change in the oxygenation of $[Co(L^1)]$ in methanol at 25 °C under air.
(a); $[Co(L^1)]$: (b); $[Co(L^1)(OH)]$.

It has been known that in the reversible interaction of cobalt(II) Schiff base complexes with molecular oxygen, superoxo and μ-peroxocobalt(III)

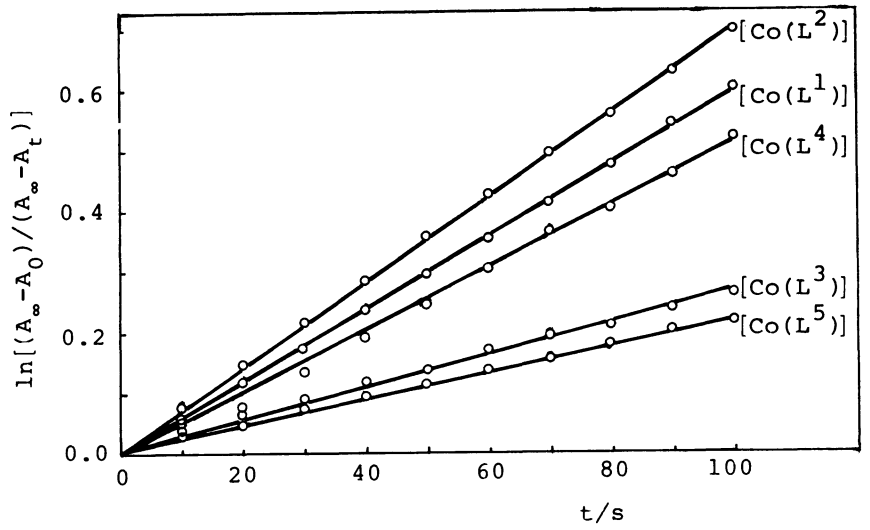
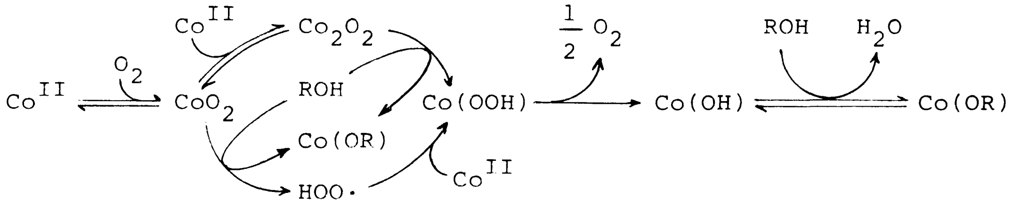


Fig. 2. First order kinetics for the oxygenation of [Co(L)] in MeOH determined by the spectral change shown in Fig. 1; [Co] = 1 x 10^{-4}mol/dm^3 at 25 °C under air. A_0, A_∞, and A_t refer to the absorbances at 400 nm for the Co^{II}, Co^{III}, and the reaction mixture at the time t, respectively.

species are formed, where the oxygenation ability and the ratio of the oxygen adducts depend on the nature of the Schiff base ligand: an electron-releasing ligand increases the affinity towards molecular oxygen as well as the concentration of the superoxo species, whereas electron-withdrawing and bulky ligand function conversely.[1)] Accordingly, the kinetic results mentioned above may be rationalized by assuming that methanol traps the superoxo species irrespective of the nature of the ligand, whereas in 2,2,2-trifluoroethanol, the μ-peroxo species is responsible for the irreversible oxygenation of [Co(L^1)] and the superoxo species for [Co(L^5)] which has a bulky ligand, and the both species reacted in 2,2,2-trichloroethanol. Therefore, the mechanism of the present oxygenation of cobalt(II) Schiff base complexes can be understood to involve the rate determining proton transfer from the alcohol to the dioxygen adducts, as illustrated in Scheme 1. The mechanism may be supported by the isotope effect of methanol on the



Scheme 1.

reaction rate in the oxidation of [Co(L^1)]: first order rate constants in CH_3OH and CH_3OD were 6.0 X 10^{-3} and 2.2 X 10^{-3} s^{-1}(25 °C), respectively (k_H/k_D = 2.7), and also by the fact that when [(DMF)Co(L^1)-(O_2)-Co(L^1)(DMF)], obtained by the oxygenation of [Co(L^1)] in N,N-dimethylformamide (DMF),[9)] was dissolved in methanol or 2,2,2-trifluoroethanol, a half equivalent of oxygen was evolved and [Co(L^1)(OH)] or [Co(L^1)(OCH_2CF_3)] was isolated quantitatively from the each reaction mixture, and that superoxo complex, [(py)Co(L^2)(O_2)],9) obtained in the oxygenation of [Co(L^2)] in pyridine also reacted with these alcohols to form the Co^{III} compounds with liberation of molecular oxygen.

Although [Co(L^1)] was unsusceptible to the oxygenation in CH_2Cl_2, the irreversible oxidation of [Co(L^1)] also took place even in CH_2Cl_2, when a proton donating compound was dissolved in it to give, e.g. [Co(L^1)(OAc)] with acetic acid. [Co(L^1(acac)]10) with acetylacetone, [Co(L^1)(OH)] with 2,4,6-tri-t-butylphenol. These Co^{III} complexes were also obtained readily by the reaction of [Co(L^1)(OH)] with the acidic substances, providing a convenient method for the preparation of cobalt(III) Schiff base complexes.10) Thus, the present findings provide fundamental informations for the preparation of cobalt(II) Schiff base complexes and their conversion to cobalt(III) species as well as for understanding of the reactive species in the [Co(L^1)] catalyzed oxygenation of protic substances: it may not be the cobalt-dioxygen adducts, but [Co(L^1)(OH)] or [Co(L^1)(OR)].

References

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2) A. Nishinaga and H. Tomita, J. Mol. Cat., 7, 179 (1980); T. Matsuura, Tetrahedron, 33, 2869 (1977).

3) The formation of [Co(L^1)(OH)] in the oxygenation of [Co(L^1)] in methanol has been reported without detail: G. Costa, G. Mestroni, and G. Pellizer, J. Organomet. Chem., 15, 187 (1965).

4) Anal. Found: C, 55.00; H, 4.60; N, 8.06%. Calcd for $C_{16}H_{15}N_2O_3Co\cdot 0.5\ H_2O$: C, 54.71; H, 4.59; N, 7.98%. Mol wt. Found: 402 (vapor pressure osmometry in a CH_2Cl_2 solution in the presence of an equimolar 1-methylimidazole). Calcd for [Co(L^1)(OH)(NMeIm)]: 424.6. The results indicate that this complex is monomeric.

5) Complexes [Co(L^2)] - [Co(L^7)] gave the corresponding [Co(L)(OH)] as crystals in excellent yields. Elemental analyses of all these hydroxocobalt(III) complexes gave satisfactory results.

6) Elemental analysis of a product obtained in the oxygenation of [Co(L^1)] in absolute methanol gave the results that can be analyzed as about 1 : 1 mixture of [Co(L^1)(OH)]and [Co(L^1)(OMe)].

7) [Co(L^1)(OCH_2CF_3)]: ^1H NMR (DMSO-d_6); δ 2.3 (q, 2H, J = 10.2 Hz), 3.9 (s, 4H), 6.2 - 7.4 (m, 8H), 8.0 (s, 2H). Found: C, 50.71; H, 3.81; N, 6.54%. Calcd for $C_{18}H_{16}F_3N_2O_3Co$: C, 50.96; H, 3.90; N, 6.60%. This complex was deposited quantitatively because of its insolubility in CF_3CH_2OH, whereas [Co(L^1)(OH)]was soluble in it. [Co(L^1)(OCH_2CCl_3)]: ^1H NMR (DMSO-d_6); δ 1.7 (s, 2H), 4.0 (s, 4H), 6.7 - 7.4 (m, 8H), 8.0 (s, 2H). Found: C; 45.92; H, 3.63; N, 5.94%. Calcd for $C_{18}H_{16}Cl_3N_2O_3Co$: C, 45.65; H, 3.40; N, 5.91%. This complex was soluble in CCl_3CH_2OH and obtained as crystals when hexane was added to the solution.

8) Oxidation rate constants (25 °C): [Co(L^1)] in CF_3CH_2OH, $1.27 \times 10^{-2} dm^3 mol^{-1} s^{-1}$; [Co($L^1$)] in CCl_3CH_2OH, $5.83 \times 10^{-3} dm^{1.8} mol^{-0.6} s^{-1}$; [Co($L^5$)] in CF_3CH_2OH, $1.38 \times 10^{-4} s^{-1}$.

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10) [Co(L^1)(acac)] was prepared by rather tedious procedures: S. N. Poddar and D. K. Biswas, J. Inorg. Nucl. Chem., 31, 565 (1969); R. J. Cozens and K. S. Murray, Aust. J. Chem., 25, 911 (1972); K. Dey and R. L. De, Z. Anorg. Allg. Chem., 402, 120 (1973).

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