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Analysis of the Induction Period and Proposal of Mechanism for the Catalysis of 3-Methylindole Oxygenation by Two Isomers of *N,N'*-(1,2-Cyclohexylene)bis(3-*tert*-butylsalicylideneaminato)cobalt(II)

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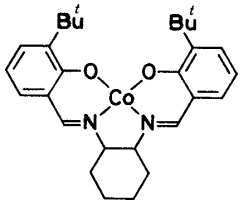
The factors which govern the induction period in the catalysis of 3-methylindole oxygenation by the title complexes were investigated. Electron spin resonance measurements showed that the superoxo-cobalt complex observed in the induction period disappeared at the start of the steady-state consumption and that the superoxo complex was preferentially converted to a cobalt(II)–substrate complex. During the induction period, the cobalt(II) complexes are converted to cobalt(III) species *via* their dioxygen adducts in the presence of dioxygen and the substrate, 3-methylindole. For the steady state, a mechanism is proposed which involves a cobalt(III)–anion complex as the catalytic species; facile oxygen introduction takes place at the coordinated deprotonated substrate.

Keywords——3-methylindole; oxygenation; catalysis; *N,N'*-(1,2-cyclohexylene)bis(3-*tert*-butylsalicylideneaminato)cobalt(II); reaction mechanism

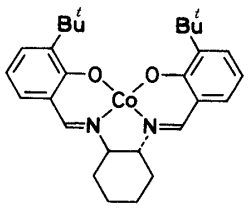
The oxygenation of 3-methylindole catalyzed by *N,N'*-ethylenebis(salicylideneaminato)cobalt(II), Co(salen), has been reported to yield 2-formylaminoacetophenone as a major product.[1] This reaction is considered to be a model of the oxygenation of tryptophan by tryptophan-2,3-dioxygenase.[2] Several analogous systems have been reported to serve as catalysts for this reaction.[3,4]

In the previous paper,[5] the oxygenation of 3-methylindole was studied in the presence of two series of Co(salen) derivatives. The consumption curves of 3-methylindole were characterized by induction periods followed by steady consumption of the substrate. There was a correlation between the steric crowdedness of the catalyst and the reaction pattern. Sterically crowded catalysts showed a long induction period and a rather fast consumption of the substrate (pattern 1), while simple catalysts showed an initial decrease in 3-methylindole by an amount equivalent to the catalyst, followed by slow consumption of the substrate (pattern 2).

In this report, the factors which govern the induction period were investigated by using *N,N'*-(*cis*-1,2-cyclohexylene)bis(3-*tert*-butylsalicylideneaminato)cobalt(II) and *N,N'*-[(1*R*,2*R*)-1,2-cyclohexylene]bis(3-*tert*-butylsalicylideneaminato)cobalt(II), which show typical pattern 1 and pattern 2 behavior, respectively; their structures are shown below.



Co(Busal-*cis*-chxn)



Co(Busal-*R*-chxn)

Experimental

Materials——Both catalysts used in this study were the same as those reported previously.[5] The abbreviations are as follows: Busal-*R*-chxn, *N,N'*-[(1*R*,2*R*)-1,2-cyclohexylene]bis(3-*tert*-butylsalicylideneaminato); Busal-*cis*-chxn, *N,N'*-(*cis*-1,2-cyclohexylene)bis(3-*tert*-butylsalicylideneaminato). *tert*-Butyl hydroperoxide was distilled twice under reduced pressure: bp 37 °C (17 mmHg), lit.[6] 37—38 °C (16 mmHg). Methanol was distilled over magnesium methoxide. Other reagents were used as received.

Preparation of Co^{III}(Busal-*R*-chxn)(OH^-)——Co^{II}(Busal-*R*-chxn) (0.70 g) was suspended in 100 cm^3 of methanol and oxygen was passed through the suspension (30 cm^3 min^{-1}) at 25 °C for 10 h. Undissolved complex was filtered off and the filtrate was concentrated to a volume of about 10 cm^3. Water (*ca.* 20 cm^3) was added to this solution and the resultant fine yellow-brown precipitates were collected. *Anal.* Calcd for $C_{28}H_{37}CoN_2O_3 \cdot 0.5H_2O$: C, 64.98; H, 7.40; N, 5.41. Found: C, 65.08; H, 7.02; N, 5.46. IR (Nujol): 3600 (νO–H) cm^{-1}.

Kinetic Measurements——The same procedure (at 25 °C) was used as reported previously.[5] The decrease in 3-methylindole was determined by gas liquid chromatography (GLC).[5]

Products Analysis——The reaction products were analyzed by high-performance liquid chromatography (HPLC) as described previously.[5] The amounts of substances were determined based on the absorption coefficients of authentic samples of 2-formylaminoacetophenone, 2-aminoacetophenone, and 3-methylindole.

Electron Spin Resonance (ESR) Measurements——ESR spectra were recorded on a Varian E-112 spectrometer at −195 °C (X-band, with 100 kHz modulation). Chloroform solutions of Co(Busal-*cis*-chxn) and Co(Busal-*R*-chxn) and a mixture of 3-methylindole and the cobalt(II) complex in chloroform were degassed by three freeze–pump–thaw cycles. The concentration of cobalt(II) complex was $2—3 \times 10^{-2}$ mol dm^{-3}. A chloroform solution of cobalt(II) complex (5×10^{-3} mol dm^{-3}) and pyridine was prepared in a molar ratio of about 1 : 80. The g values were measured relative to 2,2-diphenyl-1-picrylhydrazyl ($g = 2.004$).

Change in ESR Spectra during the Reaction——Oxygenation of 3-methylindole was carried out as described previously.[5] Periodically an aliquot of the mixture was withdrawn and taken into a quartz capillary. The sample was quenched by immersing it in liquid nitrogen. ESR spectra were recorded at −195 °C using the Varian E-112 spectrometer.

Change in Nuclear Magnetic Resonance (NMR) Spectra during the Reaction——Oxygenation of 3-methylindole by Co(Busal-*cis*-chxn) was carried out with CD_3OD as a solvent. Aliquots were periodically withdrawn and tetramethylsilane was added. The proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a JEOL MH-100 spectrometer.

Results

Consumption Curves Determined by GLC and HPLC

Figure 1A shows the time courses of the reaction catalyzed by Co(Busal-*cis*-chxn)

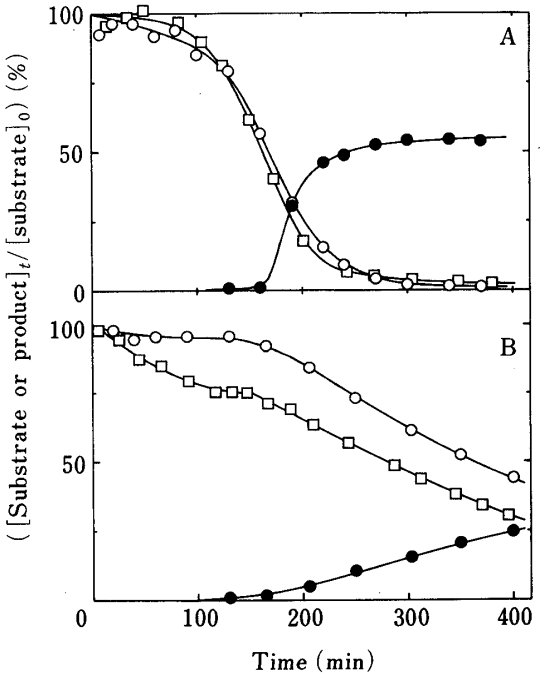


Fig. 1. Comparison of the Time Courses of Oxygenation of 3-Methylindole as Determined by GLC and HPLC

[Substrate]$_0$, 3.5×10^{-2} mol dm^{-3}; [Co complex], 8.7×10^{-3} mol dm^{-3}; solvent, methanol; temp., 25 °C. Substrate by GLC, □; substrate by HPLC, ○; 2-formylaminoacetophenone, ●. The catalysts employed for A and B were Co(Busal-*cis*-chxn) and Co(Busal-*R*-chxn), respectively.

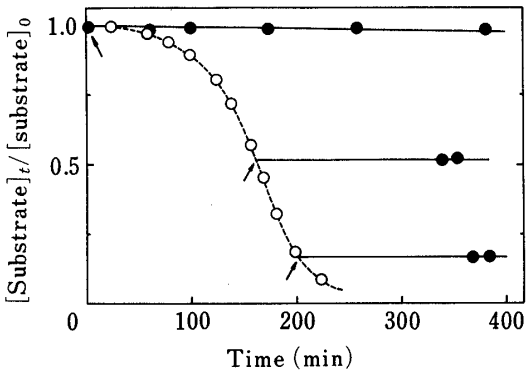


Fig. 2. Inhibition of the Oxygenation on Addition of Pyridine

[3-Methylindole]$_0$, 3.5×10^{-2} mol dm^{-3}; [Co(Busal-*cis*-chxn)], 8.7×10^{-3} mol dm^{-3}; solvent, methanol; temp., 25 °C. With pyridine, ●; without pyridine, ○. Pyridine was added at the time indicated by arrows so as to give [pyridine] = 2.6×10^{-2} mol dm^{-3}.

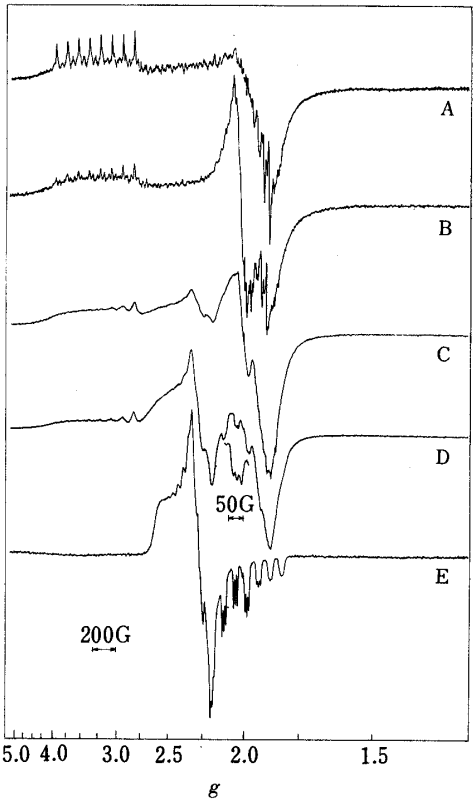


Fig. 3. ESR Spectra of Co(Busal-*cis*-chxn) in Chloroform Glasses under Various Conditions at Liquid Nitrogen Temperature

A, Co^{II} complex; B, Co^{II} complex + O_2; C, Co^{II} complex + 3-methylindole (1 : 10) + O_2; D, same as C after standing for 1 h at room temperature; E, Co^{II} complex + pyridine (1 : 80).

determined by both methods. Both methods gave almost identical consumption curves and the main product, 2-formylaminoacetophenone, appeared after the start of steady consumption of the substrate. Figure 1B shows the time courses of the reaction catalyzed by Co(Busal-*R*-chxn). Simultaneous analyses revealed that the consumption of the substrate measured by GLC was greater by the amount of the catalyst used than that measured by HPLC in the early stage of the reaction. 2-Formylaminoacetophenone began to form at the time corresponding to the bend in the consumption curve determined by GLC.

Inhibition by Pyridine

Addition of pyridine in an amount three times that of the catalyst inhibited the reaction. The additions were done at time 0 and at times corresponding to 50 and 85% consumption of the substrate, as shown in Fig. 2. The oxygenation was completely stopped on each addition of pyridine.

The use of 2,6-di-*tert*-butylpyridine instead of pyridine did not affect the oxygenation.

ESR Measurements

In order to obtain information on the interaction among the cobalt complex, dioxygen and the substrate, ESR measurements were carried out under various conditions. First, a chloroform solution of Co(Busal-*cis*-chxn) was measured at −195 °C. The observed spectrum is shown in Fig. 3A. As was found for *N,N'*-(*cis*-1,2-cyclohexylene)bis(salicylideneaminato)cobalt(II),[7] superposition of at least three species was evident in the region of $g_\perp$.

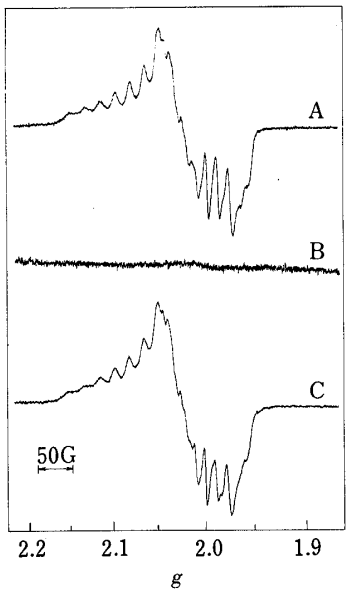


Fig. 4. ESR Spectral Change during the Oxygenation of 3-Methylindole Catalyzed by Co(Busal-*cis*-chxn)

[Substrate]$_0$, 3.5×10^{-2} mol dm^{-3}; [Co complex], 8.7×10^{-3} mol dm^{-3}; solvent, methanol; temp., 25 °C; observation temp., −195 °C. A, induction period (70 min); B, steady state (230 min); C, after completion of the reaction (1060 min).

This multiplicity has been ascribed to the interaction between chloroform and cobalt(II) complex.[7] The ESR parameters of the perpendicular region are $g_\perp=3.285$ and $a_\perp=9.67$ and 9.58 mT for Co(Busal-*cis*-chxn) and Co(Busal-*R*-chxn), respectively. The $g_\perp$ values of *tert*-butyl-bearing complexes are slightly larger than those of the complexes without *tert*-butyl groups ($g_\perp=3.24$—3.23).[7]

Addition of the substrate in ratios of 2 : 1 and 10 : 1 caused the above signal to be slightly broadened. Addition of pyridine to a chloroform solution of Co(Busal-*cis*-chxn) changed the spectrum to that of a typical pyridine adduct of cobalt(II) Schiff-base chelates,[8] the superhyperfine coupling constant with the nitrogen nucleus of coordinated pyridine being evident ($a_{\parallel,N}=1.6$ mT), as shown in Fig. 3E. The ESR parameters for the parallel region are $g_\parallel=2.01$ and $a_{\parallel,Co}=10.0$ mT (Co(Busal-*R*-chxn): $g_\parallel=2.01$, $a_{\parallel,Co}=9.9$ mT, and $a_{\parallel,N}=1.6$ mT). These values are slightly different from those of Co(salen): $g_\parallel=2.02$, $a_{\parallel,Co}=8.8$ mT, and $a_{\parallel,N}=1.4$ mT.[8b]

On the other hand, when oxygen was passed through a chloroform solution of the cobalt(II) complex, a new signal appeared around $g=2.0$ in addition to the signal of cobalt(II) species, as shown in Fig. 3B. The new signal was assigned to the superoxo-cobalt complex.[9]

Next, oxygen was passed through a mixture of 3-methylindole and Co(Busal-*cis*-chxn) in a molar ratio of 10 to 1. When the change in color from deep orange to brown was complete, the sample was sealed and frozen at −195 °C. The spectrum at this stage is shown in Fig. 3C. New signals appeared in the region between $g=2.0$ and 2.8. After standing at room temperature for 1 h, this sample was measured again. The spectrum (Fig. 3D) revealed that while the signals due to the superoxo complex decreased in intensity and the new signal increased its intensity ($g_\parallel=2.00$, $a_{\parallel,Co}=9.9\pm0.1$ mT), the signal due to the cobalt(II) species maintained its intensity. The new signal closely resembles that of cobalt(II)–pyridine adduct, and furthermore, the superhyperfine structure due to coordinated nitrogen ($a_{\parallel,N}=1.4\pm0.1$ mT) was observed.

The oxygenation of 3-methylindole in methanol was followed by quenching the reaction mixture at −195 °C. During the induction period, ESR spectra showed the presence of the superoxo complex ($g_\parallel=2.08$ and $a_{\parallel,Co}=2.5$ mT) as shown in Fig. 4A. The intensity of this signal decreased with time. During the steady-state phase, no signal was observed, as shown in Fig. 4B. After all the substrate had been consumed, the ESR spectrum reverted to that of the superoxo complex as shown in Fig. 4C.

Addition of *tert*-Butyl Hydroperoxide

Two minutes before the addition of Co(Busal-*cis*-chxn) to the methanolic substrate solution, various amounts of *tert*-butyl hydroperoxide (in molar ratios of 1/100, 1/10, 1/4, and 1/1 to the catalyst) were added. The reaction pattern changed from pattern 1 to one resembling pattern 2, and the initial loss of the substrate increased with the amount of *tert*-butyl hydroperoxide added. The molar ratio, time (min), and consumption of the substrate (%) at the bend in the consumption curves were as follows: 1/10, 40, 17; 1/4, 20, 28; 1/1, 20, 57. However, the reaction rate for the second stage did not alter significantly from that of the steady state without *tert*-butyl hydroperoxide. The consumption of the substrate and the formation of two main products as determined by HPLC are shown in Fig. 5 for the molar ratio of 1/10.

In the absence of the catalyst, *tert*-butyl hydroperoxide did not react with 3-methylindole in methanol. On the other hand, addition of *tert*-butyl hydroperoxide to a methanol suspension of Co(Busal-*cis*-chxn) resulted in a vigorous reaction to give a dark brown solution.

Oxygenation with Isolated Co(Busal-*R*-chxn)(OH^-)

As shown in Fig. 6, addition of the hydroxy-cobalt(III) complex to a methanol solution of the substrate under a nitrogen atmosphere caused a decrease in the substrate as determined by GLC, but no consumption of the substrate was observed by HPLC. When oxygen was introduced into this mixture, the consumption of the substrate began after 20 min (by HPLC).

^{1}H-NMR Spectral Change during the Oxygenation

In order to detect small amounts of by-products by NMR measurement, the oxygenation was carried out using CD_3OD instead of CH_3OH and with higher concentrations of Co(Busal-*cis*-chxn) and the substrate. The spectral change is illustrated in Fig. 7. In the induction period, two methyl signals appeared at 1.44 and 1.52 ppm and the intensities of these signals increased with time. After 163 min, the methyl signal of 2-formylaminoacetophenone appeared as a singlet but this signal exhibited multiplicity because of incorporation

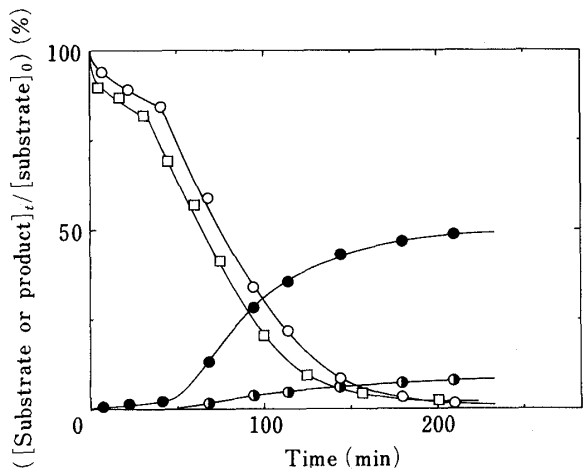


Fig. 5. Effect of the Addition of *tert*-Butyl Hydroperoxide on the Time Course of Oxygenation of 3-Methylindole Catalyzed by Co(Busal-*cis*-chxn)

[Substrate], 3.6×10^{-2} mol dm^{-3}; [Co complex], 8.9×10^{-3} mol dm^{-3}; [*tert*-BuOOH], 9.2×10^{-4} mol dm^{-3}; solvent, methanol; temp., 25 °C. Substrate by GLC, □; substrate by HPLC, ○; 2-formylaminoacetophenone, ●; 2-aminoacetophenone, ◑.

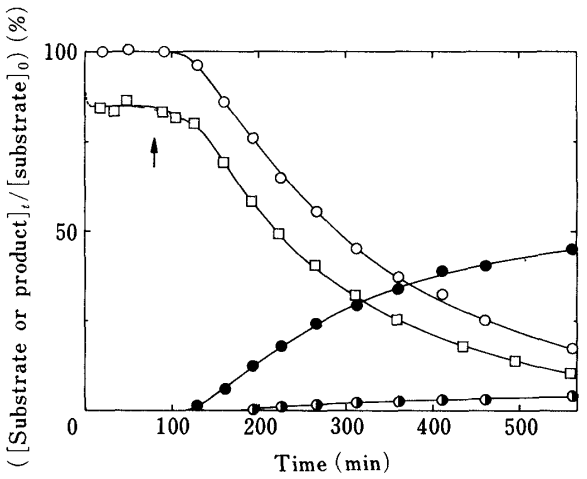


Fig. 6. The Oxygenation of 3-Methylindole Catalyzed by Co(Busal-*R*-chxn) (OH^-)

Reaction was initiated under nitrogen and oxygen was introduced at the time indicated by the arrow (80 min). [Substrate], 3.5×10^{-2} mol dm^{-3}; [Co complex], 9.1×10^{-3} mol dm^{-3}; solvent, methanol; temp., 25 °C. Substrate by GLC, □; substrate by HPLC, ○; 2-formylaminoacetophenone, ●; 2-aminoacetophenone, ◑.

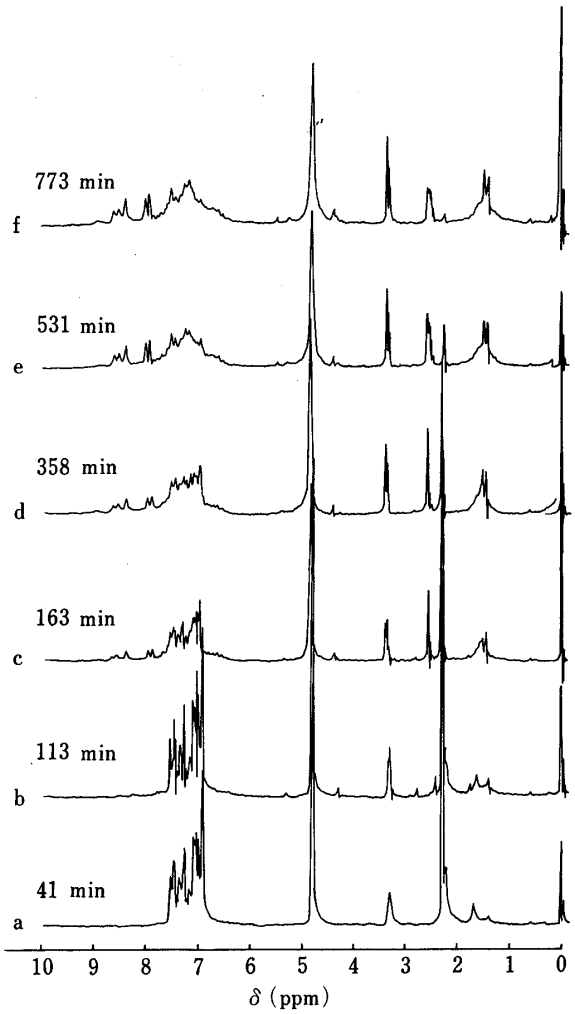


Fig. 7. NMR Spectral Changes during the Oxygenation of 3-Methylindole Catalyzed by Co(Busal-*cis*-chxn) in CD_3OD

[Substrate], 1.2 mol dm^{-3}; [Co complex], 2.1×10^{-2} mol dm^{-3}.

of deuterium in the later stage (after 531 min). The incorporation of hydrogen into the CD_3 group of methanol was also observed.

Discussion

The formation of dioxygen complexes with cobalt(II) chelates of porphyrins and Schiff bases has been studied extensively.[10] Both a peroxo complex (CoLB-O_2-CoLB) and a superoxo complex (CoLB-O_2) are formed, where L and B stand for the quadridentate ligands and bases which serve to stabilize coordinated dioxygen as electron donors. The sequences of formation of these dioxygen–cobalt complexes are as follows,

$$\text{Co(II)} + O_2 \rightleftharpoons \text{Co(III)-}O_2^- \quad (1)$$

$$\text{Co(III)-}O_2^- + \text{Co(II)} \rightleftharpoons \text{Co(III)-}O_2^{2-}\text{-Co(III)} \quad (2)$$

$$\text{Co(III)-}O_2^{2-}\text{-Co(III)} + O_2 \rightleftharpoons 2\ \text{Co(III)-}O_2^- \quad (3)$$

The difference in substrate consumption curves between the two pattern reactions shown in Fig. 1 can be ascribed to a smooth production of the peroxo complex (Eqs. 1 and 2) for pattern 2 and to the stop at Eq. 1 for the pattern 1 reaction. Co(Busal-*R*-chxn) has a planar structure but Co(Busal-*cis*-chxn) has the cyclohexane ring moiety in the apical region at the sixth coordination site.[5] The presence of superoxo-cobalt complex was detected during the induction period but the cobalt complex was converted to an ESR-silent species (cobalt(III)

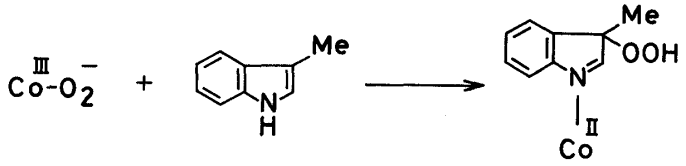
or peroxo complex) during the steady-state reaction as shown in Fig. 4. The reappearance of superoxo complex after completion of the reaction with Co(Busal-*cis*-chxn) indicates the participation of the substrate for making up ESR-insensitive species.

The amount of consumed substrate was dependent on the analysis method (HPLC and GLC) for the reaction catalyzed by Co(Busal-*R*-chxn) and the difference in the amounts determined by the two methods corresponded to the amount of the catalyst. This difference shows that the substrate interacts with the catalyst in such a way as to dissociate in a nonpolar solvent (hexane) and to be converted to an undefined compound at high temperature (as used in GLC analysis). The structural features of Co(Busal-*R*-chxn) are compatible with the formation of the peroxo complex in the pattern 2 reaction. The ratio of consumed amounts of substrate (by GLC) and dioxygen to the cobalt complex employed at the end of the first process was 2 : 1 : 2, but the formation of peroxo complex is improbable for the pattern 1 reaction which is characteristic of sterically crowded catalysts such as Co(Busal-*cis*-chxn).

However, these peroxo and superoxo complexes cannot be the active species because no consumption of the substrate was detected by HPLC until the end of the induction period, which was characterized by the disappearance of superoxo complex. Furthermore, the smaller rate of oxygenation at the steady state with Co(Busal-*R*-chxn) than with Co(Busal-*cis*-chxn) rules out the peroxo complex as the active species. Thus, further oxidation of these dioxygen–cobalt complexes is required to generate the active species, cobalt(III) complexes.

The ESR measurements have shown that there is little interaction between the cobalt(II) complexes and the substrate but that the superoxo complex is formed between cobalt(II) complex and dioxygen. These observations show that the formation of the active species for the oxygenation of the substrate requires the copresence of cobalt(II) complex, substrate, and dioxygen, so that formation of a ternary complex may be involved.

The ESR measurements shown in Fig. 3 revealed that the superoxo complex of Co(Busal-*cis*-chxn) changed to a species in which an sp^2 nitrogen is bonded to a cobalt(II) center based on the $g_{\parallel}$ value and the triplet superhyperfine coupling with ^{14}N, in preference to a cobalt(II) complex. This species may be the complex with 3-hydroperoxy-3-methyl-3*H*-indole or its



degradation product. The ^1H-NMR spectral change (Fig. 7) shows several methyl signals in the region between 1.2 and 1.8 ppm in the initial stage of the reaction, and by-products derived from the hydroperoxide are presumably responsible for these signals.

An addition of *tert*-BuOOH to a mixture of Co(Busal-*cis*-chxn) and the substrate in methanol caused a reduction in the induction period. Nishinaga *et al.* reported the isolation of Co(salen) (*tert*-BuOO$^-$) after the addition of *tert*-BuOOH to a dichloromethane solution of Co(salen) and also suggested that Co^{III}(salen) complexes with *tert*-BuOO$^-$ and *tert*-BuO$^-$ initiate the oxygenation of 3-methylindole.[11,12] This supports the view that a cobalt(III) species is responsible for the oxygenation of 3-methylindole. Furthermore, the fact that addition of a 1 : 10 ratio of *tert*-BuOOH to the cobalt(II) complex sufficed to reduce the induction period shows that the generated cobalt(III) complex acts as a catalyst for conversion of the cobalt(II) complex to the corresponding active species as well as the catalyst for oxygenation of 3-methylindole.

The inhibition of the reaction by pyridine can be ascribed to blocking of the substrate from coordination to the metal center and indicates the necessity for such coordination for the reaction to occur. However, the substrate, 3-methylindole, is not a good σ-donor ligand and

deprotonation of N–H is necessary for coordination to metal ions. A cobalt(III)–anion complex is expected to cause such deprotonation. Addition of isolated Co(Busal-*R*-chxn) (OH^-) to the substrate in methanol under oxygen-free conditions resulted in loss of the substrate as determined by GLC but no consumption of the substrate as found by HPLC. Introduction of oxygen into this mixture caused the steady reaction to start. This observation shows that the oxygenation requires non-coordinated oxygen to accomplish electron transfer from a coordinated anion of the substrate to the cobalt(III) center, if electron transfer is involved.

Nishinaga *et al.* reported the isolation of the cobalt(III) complex with an anion of the product, 2-formylaminoacetophenone, and showed that this complex acts as the catalyst; they also claimed that deprotonation of the substrate is the rate-determining-step.[12] Further, Nishinaga recently proposed that the function of the cobalt(III) center is to ease spin conversion of the triplet state to the singlet state of the coordinated anion of the substrate and dioxygen.[13] However, the fact that the rate of consumption of the substrate shows a linear dependency on the redox potential of $Co^{II/III}$ couples with various cobalt complexes indicates the involvement of intramolecular electron transfer from the coordinated anion of the substrate to the cobalt(III) center;[5] this process would increase the susceptibility of the substrate by developing radical character at the 3-position of 3-methylindole and dioxygen should then attack to yield the 3-hydroperoxide. This is another probable reaction path, and

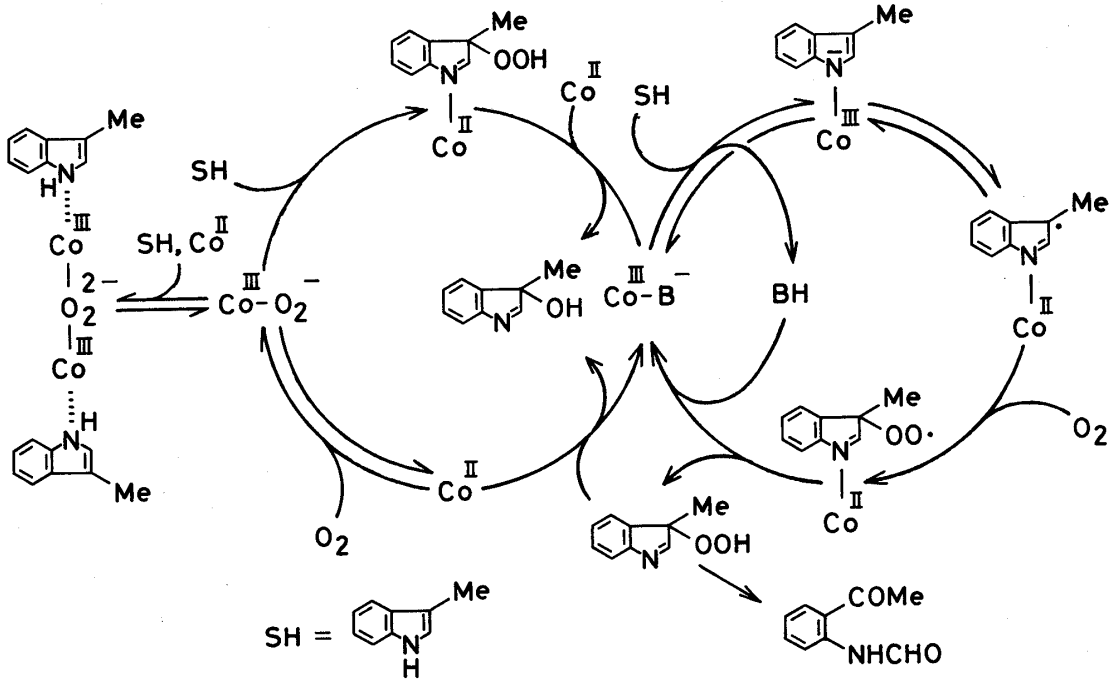


Chart 1

is outlined in Chart 1. The decomposition of the hydroperoxide yields 2-formylaminoacetophenone as discussed by Hamilton *et al.*[14] and Muto and Bruice.[15]

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