Synthesis and Properties of Alkylperoxocobalt(III) Porphyrin and Porphycene

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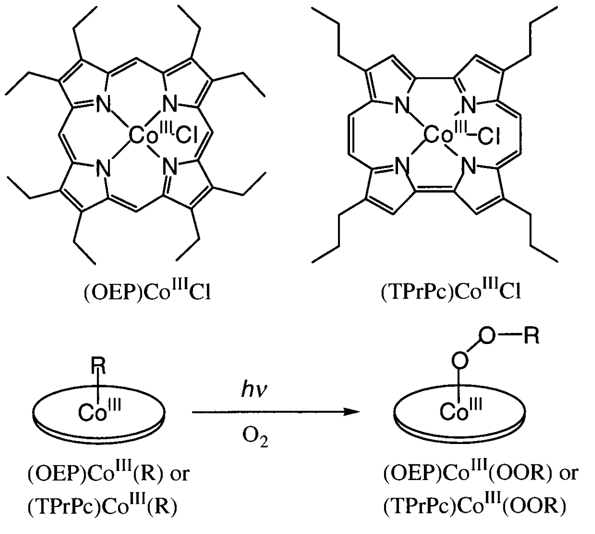
Alkylcobalt(III) and alkylperoxocobalt(III) species of porphyrin and porphycene have been prepared and characterized by UV-vis and ^{1}H NMR spectroscopic measurements. Thermal decomposition of the alkylperoxocobalt species proceeds via Co–O or O–O bond cleavage, which depends on the coordination of an axial ligand.

Alkylperoxo metalloporphyrins have been of particular interests for chemists and biochemists, since alkylperoxo species is a unique intermediate in various oxidations catalyzed by metalloporphyrins. In the last two decades, preparation and characterization of alkylperoxoiron(III) complexes have attracted much attention as a challenging target to elucidate the reaction mechanism of cytochrome P450 and peroxidase.[1] In contrast, there are few papers describing the properties of alkylperoxocobalt(III) porphyrins.[2-4] Although it is difficult to prepare the alkylperoxocobalt complex by addition of an alkylhydroperoxide to a cobalt(III) porphyrin,[5] one can obtain the alkylperoxocobalt porphyrin via dioxygen insertion into the alkylcobalt complex upon irradiation with visible light as shown in Scheme 1. Here, we wish to report the properties of alkylperoxocobalt(III) porphyrin, (OEP)$\mathrm{Co^{III}}$(OOR), and porphycene, (TPrPc)$\mathrm{Co^{III}}$(OOR); OEP = octaethylporphyrinato, TPrPc = 2,7,12,17-tetra-*n*-propylporphycenato, R = methyl or *n*-butyl.

Scheme 1.



Alkylcobalt(III) porphyrin, (OEP)$\mathrm{Co^{III}}$(R), and porphycene, (TPrPc)$\mathrm{Co^{III}}$(R), as a precursor of alkylperoxo species were prepared by the reaction of Grignard reagent and (OEP)$\mathrm{Co^{III}}$Cl or (TPrPc)$\mathrm{Co^{III}}$Cl, respectively, at room temperature in complete darkness.[6–8] The isolated alkylcobalt complex was then solved in dry CH_2Cl_2 under aerobic atmosphere. After the irradiation with 500-W tungsten lamp at –40 °C, a red-shifted Soret and/or Q-band absorption was observed, suggesting that the alkylperoxo complex was formed via dioxygen insertion into cobalt–carbon bond.[2] In the case of (TPrPc)$\mathrm{Co^{III}}$($OOCH_3$), the λ_{max} value of Soret band (385 nm) was almost same as that of (TPrPc)$\mathrm{Co^{III}}$(CH_3), whereas Q band was clearly shifted from 592 nm to 613 nm in CH_2Cl_2 as shown in Figure 1. ESI-Mass analysis also indicated the correct molecular weight number of alkylperoxo species.[9]

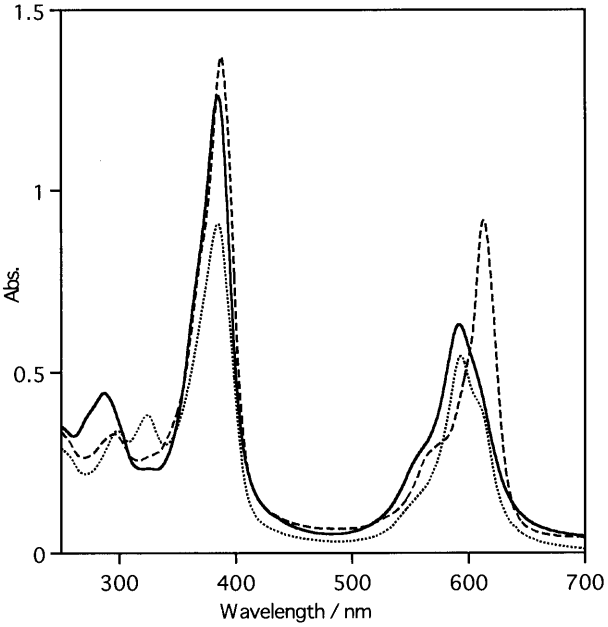


Figure 1. Formation and thermolysis of (TPrPc)$\mathrm{Co^{III}}$($OOCH_3$) in CH_2Cl_2. Solid line (——) represents (TPrPc)$\mathrm{Co^{III}}$(CH_3) at –40 °C. (TPrPc)$\mathrm{Co^{III}}$($OOCH_3$) (dashed line; -----) was prepared by 500-W tungsten lamp irradiation for 5 min under aerobic condition. Thermolysis of the alkylperoxo species gave (TPrPc)$\mathrm{Co^{II}}$ (dotted line; ·····) at 20 °C over 12 h.

^{1}H NMR spectra directly show the formation of alkylperoxo species from alkylmetalloporphyrin or alkylperoxometalloporphycene. Figure 2 is a representative spectra of (TPrPc)$\mathrm{Co^{III}}$(*n*-Bu) and (TPrPc)$\mathrm{Co^{III}}$(OO*n*-Bu) in CD_2Cl_2 at –40 °C. *n*-Butyl protons were shifted to below 0 ppm due to the diamagnetic ring current of the porphycene. Particularly, Co-CH_2 protons appeared at –4.47 ppm. After the irradiation with visible light to NMR sample tube over 10 min at –40 °C, the methylene protons were shifted to –2.06 ppm because of (TPrPc)$\mathrm{Co^{III}}$(OO*n*-Bu) formation under aerobic condition.[10] In contrast, there was no (TPrPc)$\mathrm{Co^{II}}$ species via homolysis of

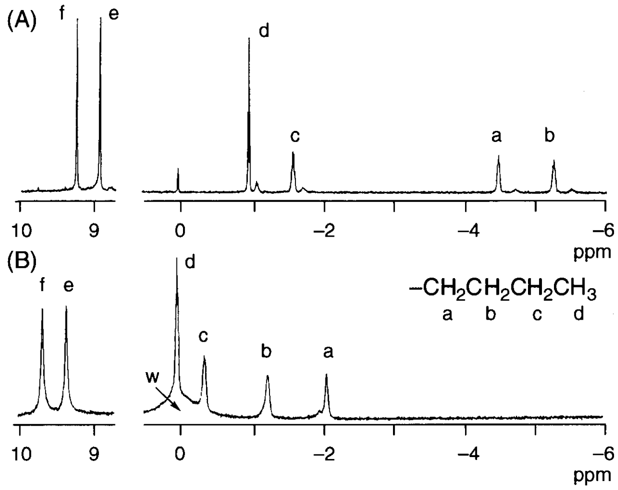


Figure 2. ^{1}H NMR spectra (500 MHz, –40 °C, in CD_2Cl_2) of (TPrPc)Co^{III}(*n*-Bu) (spectrum A) and (TPrPc)Co^{III}(OO*n*-Bu) (spectrum B) after irradiation for 10 min. Protons a–d are assigned to the coordinated *n*-butyl groups. Protons e and f are β-pyrrole-H and meso-H. Broad peak w could be H_2O in CD_2Cl_2. Each proton was assigned by 2D NMR measurement.

Co–C bond without insertion of dioxygen. These fashions in the present NMR spectra are comparable with those seen in (OEP)Co^{III} species. To our knowledge, the present work is the first example of the synthesis of alkylperoxocobalt porphycene which gives similar manner as alkylperoxocobalt porphyrins.

Thermal decomposition of alkylperoxo species of cobalt porphyrin or porphycene was monitored by UV-vis and ^{1}H NMR spectroscopic methods at ambient temperature. (OEP)Co^{III}(OOCH$_3$) and (TPrPc)Co^{III}(OOCH$_3$) decomposed to give the paramagnetic Co^{II} species with rate constants of (2.3 ± 0.2) x 10^{-3} s^{-1} and (1.3 ± 0.1) x 10^{-3} s^{-1} at 20 °C in CD_2Cl_2, respectively. It is clear that the alkylperoxocobalt porphycene is more stable than that of porphyrin. The formation of the Co^{II} species suggests that the thermal decomposition occurs via homolytic Co–O bond cleavage.[11] Furthermore, in the case of (TPrPc)Co^{III}(*n*-Bu) and (TPrPc)Co^{III}(OO*n*-Bu), *n*-butylaldehyde and *n*-butanol as thermolysis products were determined by gas chromatography. In the presence of an axial ligand such as piperidine, however, the thermolysis gave diamagnetic Co^{III} species monitored by ^{1}H NMR measurement. This result indicates that the ligation of piperidine to the cobalt atom accelerates the O–O bond cleavage.[12] It has been known that the coordination of the base ligand to the O_2 complex of cobalt porphyrin weakens the O–O bond and strengthens the Co–O_2 bond. Thus, our results concerning the effect of axial ligand in the decomposition of alkylperoxocobalt complex could be supported by the previous literature describing the O_2 adduct of cobalt porphyrins in the presence and absence of the ligand.[13]

Finally, the mechanism of generation and thermal decomposition of alkylperoxocobalt porphyrin and porphycene should be important to understand catalytic oxidation toward the aliphatic compounds. Characterization and reaction of the alkylperoxo species are in progress in our laboratory.

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References and Notes

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9 Parent peaks were assigned by the measurement of deuterated alkylperoxocobalt complex and the simulation of isotope distribution pattern. (OEP)Co^{III}(CH$_3$), 606.3 (M$^+$); (OEP)Co^{III}(OOCH$_3$), 638.3 (M$^+$). In the case of the porphycene, the signals were too weak to completely assign as the parent peaks.

10 ^{1}H NMR data for chemical shifts of coordinated methyl ligand in CD_2Cl_2 at -40 °C, ppm: (TPrPc)Co^{III}(CH$_3$), –5.60; (TPrPc)Co^{III}(OOCH$_3$), –1.47, (OEP)Co^{III}(CH$_3$), –5.32; (OEP)Co^{III}(OOCH$_3$), –1.76.

11 ^{1}H NMR data for chemical shifts of Co^{II} species in CD_2Cl_2 at 23 °C, ppm: (TPrPc)Co^{II}, –15.26, 3.51, 6.01, 7.55, 43.01; (OEP)Co^{II}, 5.98, 8.67, 28.99.

12 Coordinated piperidine protons (11 protons) appeared in the upfield region (–5.3 ppm – 0 ppm) due to the ring current of the porphyrin and porphycene. [piperidine]/[cobalt complex] = 10.

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