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Reaction of Bis[1-(2-pyridylazo)-2-naphtholato]cobalt(III) Chloride, $[Co^{III}(pan)_2]Cl$, with Hyperoxide in Dimethyl Sulfoxide†

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Synopsis. The complex $[Co^{III}(pan)_2]^+$ was found to react in DMSO with hyperoxide, O_2^-, to give a bivalent cobalt complex $[Co^{II}(pan)_2]^0$. The oxidation of $[Co^{II}(pan)_2]^0$ to $[Co^{III}(pan)_2]^+$ by oxygen did not proceed in DMSO in the absence of water and/or H^+. The standardization of O_2^- in DMSO were also described.

In aqueous solution the cobalt(II) complex $[Co^{II}(pan)_2]^0$ formed by the reaction of Co^{2+} and 1-(2-pyridylazo)-2-naphthol, PAN, was found to be successively oxidized to the cobalt(III) complex by dissolved oxygen.[1,2] In the present report the reaction of $[Co^{III}(pan)_2]^+$ and O_2^- in DMSO was investigated, where hyperoxide acts as a reducing agent.

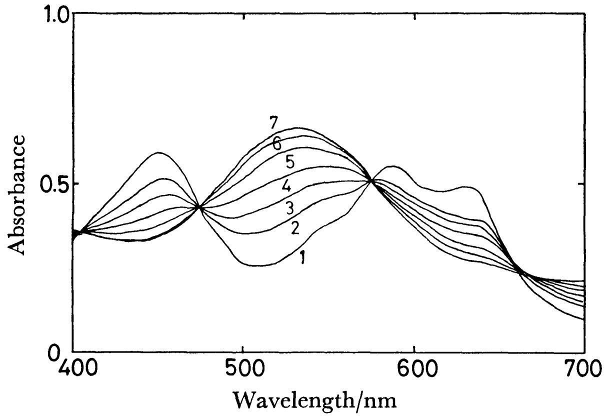

Fig. 1. The spectral change in the reaction of $[Co^{III}(pan)_2]Cl$ with O_2^- in DMSO. Initial concentrations of the complex and O_2^- are 2.18×10^{-5} and 2.99×10^{-4} mol dm^{-3}, respectively. The solution contains 1.42×10^{-3} mol dm^{-3} dicyclohexyl-18-crown-6 as a solubilizing agent. The spectrum was recorded at 0 (1), 0.5 (2), 4 (3), 11 (4), 30 (5), 60 (6), and 125 min (7).

Reaction of $[Co^{III}(pan)_2]Cl$ *with* O_2^-. Figure 1 shows a typical example of the spectral change for the reaction of $[Co^{III}(pan)_2]^+$ and O_2^- in DMSO. Each spectrum was recorded at appropriate time intervals. The spectra changed with isosbestic points at 475, 575, and *ca.* 650 nm.[3] The absorptions around 450 and 600 nm due to $[Co^{III}(pan)_2]^+$ decreased with the increase of a new absorption around 530 nm. The spectrum due to the free ligand PAN was not observed in the course of the reaction. The final spectrum of the reaction was essentially the same as the spectrum of (1) $[Co^{II}(pan)_2]^0$ observed as an intermediate in the course of the reaction between Co^{2+} and PAN,[2] (2) $[Co^{II}(pan)_2]^0$ observed in the deoxygenated system,[2] and (3) the final product obtained by the electrolytic reduction of $[Co^{III}(pan)_2]Cl$.[4] These results suggest the formation of $[Co^{II}(pan)_2]^0$ ($\lambda_{max}=530$ nm, $\varepsilon=28000$ mol^{-1} dm^{-3} cm^{-1} in DMSO) by the reaction of $[Co^{III}(pan)]^+$ with O_2^-.

The changes in the absorbance *vs.* time for the reaction of $[Co^{III}(pan)_2]^+$ with O_2^- in deoxygenated media and in undegassed solution were compared with each other. For the deoxygenated system the solutions of the two reactants were separately degassed beforehand by freezing several times. No difference in the rates of the reduction was observed between these two systems. This result suggests that the oxygen dissolved in the solution does not affect the rate of the reduction of $[Co^{III}(pan)_2]^+$ by O_2^-.

Kinetic measurements were carried out using a stopped-flow method under the conditions of O_2^- in large excess over the ligand. The pseudo-first-order rate constant, k_{obsd}, showed a first-order dependence on the total concentrations of $[O_2^-]_0$ (1.3×10^{-4}—6.3×10^{-4} mol dm^{-3}). From the slope and the intercept of the linear plots of k_{obsd} against $[O_2^-]$ the forward and the backward rate constants, k_f and k_d, were evaluated to be 5.2×10^2 mol^{-1} dm^3 s^{-1} and $<10^{-2}$ s^{-1}, respectively.

Stability of $[Co^{II}(pan)_2]^0$ *in DMSO.* When dry oxygen was passed for 1—2 h through a dry DMSO solution of $[Co^{II}(pan)_2]^0$ obtained by electrolytic reduction, no oxidation was observed, the spectrum remaining unchanged at least for 1 h. However the addition of a small amount of water (0.5 cm^3 H_2O to 3.5 cm^3 DMSO) changed the spectrum gradually to that of $[Co^{III}(pan)_2]^+$. Marked acceleration of the oxidation to $[Co^{III}(pan)_2]^+$ was observed by the addition of a slight excess of perchloric acid over $[Co^{II}(pan)_2]^0$; a large excess of perchloric acid dissociated the ligand PAN from cobalt(II) complex. These results suggest that the oxidation of $[Co^{II}(pan)_2]^0$ by oxygen does proceed in the presence of H_2O and/or H^+. The considerable stability of $[Co^{II}(pan)_2]^0$ in dry non-protonic solvent as DMSO and also the small value of k_d in dry DMSO support the following mechanism:

$$Co^{2+} + 2PAN \overset{H^+}{\rightleftharpoons} [Co^{II}(pan)_2]^0$$
$$\xrightleftharpoons[O_2^- \text{ in DMSO}]{O_2,\ H_2O \text{ and/or } H^+} [Co^{III}(pan)_2]^+,\ k_d,\ k_f.$$

This mechanism is the same as that postulated for the reaction of copper phenanthroline complex with oxygen and hyperoxide.[5]

Experimental

Materials. The complex $[Co^{III}(pan)_2]Cl$ was pre-

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pared from cobalt(II) chloride and PAN (Dojindo, Kumamoto). Stoichiometric amount of cobalt(II) chloride in water and PAN in dioxane were slowly mixed with stirring. The solution was diluted with a large amount of water. Precipitates formed were filtered, washed successively with dioxane–water (1: 20) and water, and dried *in vacuo*. Found: C, 58.66; H, 3.70; N, 13.57; Cl, 5.92%. Calcd for $C_{30}H_{20}N_6O_2CoCl \cdot H_2O$: C, 59.17; H, 3.64; N, 13.80; Cl, 5.82%.

Dicyclohexyl-18-crown-6 (perhydrodibenzo-18-crown-6) (Nippon Soda) and KO_2 (ICN Pharmaceuticals) were used without further purification. Dimethyl sulfoxide was dried with calcium hydride, distilled under reduced pressure, and stored under argon atmosphere. The solution of O_2^- was prepared by dissolving KO_2 in DMSO by adding dicyclohexyl-18-crown-6 in DMSO.⁵⁾

Standardization of O_2^- in DMSO with Iodine. The concentration of O_2^- in DMSO solution was determined titrimetrically. To three cubic centimeters of a *ca.* 1×10^{-3} mol dm^{-3} solution of O_2^- in a capped optical cell a freshly-prepared standard DMSO solution of iodine (2.0×10^{-2} mol dm^{-3}) was added using a microsyringe, and the absorbance at 400 nm was measured after 15 min. The final absorbance was plotted against the amounts of I_2 solution added, showing the gradual decrease until it began to increase at the end point **A** in proportion to the concentration of an excess of iodine (see the inset of Fig. 2). The concentration of O_2^- was determined from the amount of iodine consumed at **A** based on the following reaction.

$$2O_2^- + I_2 \longrightarrow 2O_2 + 2I^-$$

Stability of O_2^- in DMSO. Figure 2 shows the change in the concentration of O_2^- in DMSO with the lapse of time stored at room temperature in a tightly-sealed flask in the dark as described in the literature.⁵⁾ Seventy percent of O_2^- based on the weighed amount of KO_2 was found to remain unchanged even a day after preparation. After 2 weeks the concentration of O_2^- decreased to 60%.

Measurements. Absorption spectra were measured at 25±0.2 °C with a Hitachi recording spectrophotometer Model EPS-3T. Platinum electrodes were used for the electrolytic reduction of the complex. Kinetic measurements were carried out with a Union Giken stopped-flow spectrophotometer Model 1300.

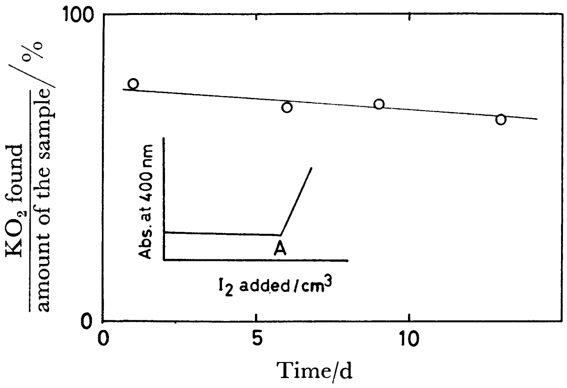

Fig. 2. The change in the concentration of O_2^- in DMSO solution with the lapse of time. The initial concentration of O_2^- was *ca.* 1×10^{-3} mol dm^{-3}. The inset shows a typical pattern for the change in absorbance at 400 nm against the volume of standard I_2 added (see the text).

References

1) K. L. Cheng and R. H. Bray, *Anal. Chem.*, **27**, 782 (1955).

2) K. Mochizuki, T. Imamura, T. Ito, and M. Fujimoto, *Bull. Chem. Soc. Jpn.*, **51**, 1743 (1978).

3) New absorption bands appeared around 600—700 nm after standing for long time may be ascribed to the decomposition of the ligand by excess of O_2^-.

4) The electrolytic reduction was carried out at 1.5 V for 12 h in DMSO under anaerobic conditions in the presence of 0.1 mol dm^{-3} Et_4NClO_4 as a supporting electrolyte.

5) J. S. Valentine and A. B. Curtis, *J. Am. Chem. Soc.*, **97**, 224 (1975).