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REACTION OF SUPEROXO Co(III) COMPLEX WITH QUINONES
FORMATION OF A SEMIQUINONE Co(III) COMPLEX

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The superoxo complex $[Co(CN)_5O_2]^{3-}$ was found to act as a reducing agent towards quinones. One-electron reduction took place with o-quinones whereas two-electrons reduction with p-quinones. 3,5-Di-t-butyl-o-benzoquinone gave the corresponding semiquinone Co(III) complex quantitatively.

The reactions of dioxygen metal complexes have become of interest in recent years.[1] Previously, we have reported that superoxo Co(III) complexes display reactivities as a radical and a base towards 2,6-di-t-butylphenols depending on the nature of ligand in the superoxo complex used.[2] Superoxo Co(III) complexes have also been shown to act as a nucleophile towards benzoquinone methides.[3] We wish to report here that the superoxo complex $[Co(CN)_5O_2]^{3-}$ acts as a reducing agent towards quinones.

When equimolar amounts of 3,5-di-t-butyl-o-benzoquinone (1) and $[Co(CN)_5O_2][Ph_3P{=}\overset{+}{N}{=}PPh_3]_3$,[2] a superoxo complex were mixed in CH_2Cl_2 under nitrogen bubbling at room temperature or 0 °C, the mixture turned green immediately. The resulting solution showed ESR signals due to the corresponding semiquinone which is fully coordinated with the Co(III) species ($a_{Co} = 7.9$ G, $a_H = 2.9$ G)[4] (Figure 1). With the same reaction in DMF, on the other hand, ESR spectrum showed predominant formation of the o-semiquinone in its free state, indicating that the coordination depends on the nature of the solvent used. Acidification of the reaction mixtures obtained in both cases gave 1 (50%) and 3,5-di-t-butylcatechol (50%), which is indicative of quantitative formation of the semiquinone, quantitative one-electron reduction. The quantitative formation of the semiquinone was observed even if the superoxo complex was present in excess, indicating that neither further reduction nor radical coupling with the superoxo complex took place. Similar quantitative formation of semiquinones was observed in the reactions of 1,2-naphthoquinone and 9,10-phenanthra-

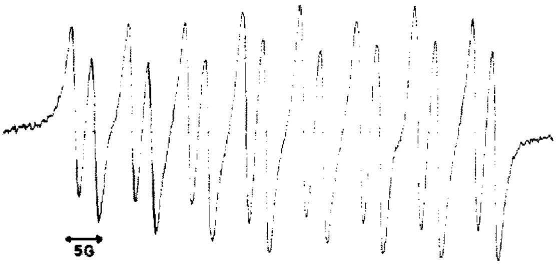

Figure 1. ESR spectrum of 3,5-di-t-butyl-o-semiquinone Co(III) complex obtained from 3,5-di-t-butyl-o-benzoquinone (0.1 mmol) and $[Co(CN)_5O_2][Ph_3P{=}\overset{+}{N}{=}PPh_3]_3$ (0.1 mmol) in CH_2Cl_2 (10 ml) at room temperature.

quinone with the superoxo Co(III) complex. By contrast, in the reaction of 2,6-di-t-butyl-p-benzoquinone with the superoxo Co(III) complex, it was found that the corresponding p-semiquinone was formed quantitatively in an equimolar reaction but further reduction took place by the use of an excess of the superoxo complex. From the reaction with two equivalents of the superoxo complex, 2,6-di-t-butylhydroquinone was isolated in 80% yield together with the starting quinone (20%). Similarly, the two-electrons reduction was observed with p-quinones such as 1,4-naphthoquinone, 9,10-anthraquinone, and 2,3-dimethyl-1,4-naphthoquinone. The diference between the reactions of the o-quinones and the p-quinones is remained obscure to be explained.[5]

Dioxygen bubbling through a solution obtained from the reaction of 9,10-phenanthraquinone (2) with two equivalent amounts of the superoxo Co(III) complex in DMF, where 9,10-phenanthrenesemiquinone (3) is formed quantitatively, gave 2,2'-dicarboxybiphenyl in quantitative yield. Therefore, the formation of the dicarboxylic acid results obviously from the reaction between O_2 and the semiquinone, which is contrary to the argument by Le Berre, et al[6] who proposed a nucleophilic attack by superoxide anion on the dione system in the reaction of 2 with NaO_2 giving rise to 2,2'-dicarboxybiphenyl.[7]

References and Notes

1) J. Mol. Cat., 7, 1-320 (1980); A Special Issue Devoted to "The First International Symposium on Activation of Molecular Oxygen and Selective Oxidations Catalysed by Transition Metal Complexes," Bendor (France), 1979.
2) A. Nishinaga, H. Tomita, and T. Matsuura, Tetrahedron Lett., 2893 (1979); 2833 (1980).
3) A. Nishinaga, H. Tomita, and T. Matsuura, Tetrahedron Lett., submitted.
4) The spectrum is similar to that observed in the reaction between 3,5-di-t-butyl-o-benzoquinone and a Co(I)-Schiff base complex: D. G. Brown and W. D. Hemphill, Inorg. Chem., 18, 2039 (1971).
5) Isolation of the semiquinone Co(III) complex, which should give significant informations for its structure, has not been successful.
6) A. Le Berre and Y. Berguer, Bull. Soc. Chim. Fr., 2368 (1976).
7) We actually observed ESR signals of 3 in the reaction of 2 with KO_2 under nitrogen bubbling.

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