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Reaction between Superoxide Ion and the Superoxide Coordinated in a Cobalt(III) Complex

Sir:

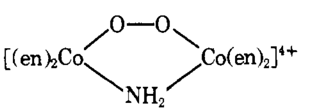
The importance of dioxygen species in biological redox reactions,[1] in photosynthesis and in combustion of materials,[2] is well recognized. One-electron reduction of oxygen produces the superoxide ion, $O_2^-\cdot$, and the redox potential observed for the process

$$O_2 + H^+ + e^- \rightarrow HO_2\cdot$$

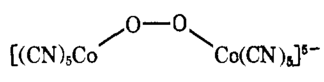
is −0.33 V which is independent of pH.[2] The reactions of $O_2^-\cdot$ are of considerable interest; the spontaneous dismutation reaction

$$2O_2^-\cdot + 2H^+ \rightarrow O_2 + H_2O_2$$

is known to be catalyzed by protons. In enzymatic systems, superoxide dismutases which contain transition metal ions such as copper, zinc and manganese bring about this reaction.[3] Several transition-metal complexes have been used to show model behavior of the superoxide dismutase reaction.[4,5] In the cobalt(III) dioxygen complexes the nature of the -O-O- bridge is known to be superoxo or peroxo as determined by ESR[6] and crystallographic studies.[7] One-electron reduction of the superoxo complexes produce the peroxo bridge complexes which are diamagnetic and the process does not reduce the metal center.[8-12] We have investigated the redox reactions between the $O_2^-\cdot$ ion and the coordinated $O_2^-\cdot$ in the transition-metal complexes, μ-amido-μ-superoxo-bis[bisethylenediamine cobalt(III)] (I) and μ-superoxo-bis(pentacyano)cobalt(III)] (II).



I



II

Superoxide ion was produced pulse radiolytically[13] in aqueous solutions, saturated with oxygen, containing 0.1 M sodium formate. The reaction of $O_2^-\cdot$ with the superoxo coordinated complex was followed by monitoring the formation of the peroxo complex using spectrophotometric pulse radiolysis technique.[14] Solutions of the superoxocobalt(III) complexes I or II in 0.1 M sodium formate saturated with oxygen were irradiated with a 10-MeV beam of electrons from Notre Dame linear accelerator. The rate of formation of the peroxo complex was followed at 380 nm and 310 nm for I and II respectively; absorbance increase at 380 nm corresponds to the formation of the μ-amido-μ-peroxo-bis[bisethylenediamine cobalt(III)] complex, whereas absorbance decrease for the cyanide complex at 310 nm is proportional to the formation of the corresponding peroxo complex.[15,16] The rate constants for the reaction of $O_2^-\cdot$ with the cobalt(III) superoxo complexes were determined varying the pH and by varying the concentration of the complex in the solution. The bimolecular rate constants which were found to be independent of the concentration of the superoxo complex present in the solution are shown in Figure 1 as a function of pH.

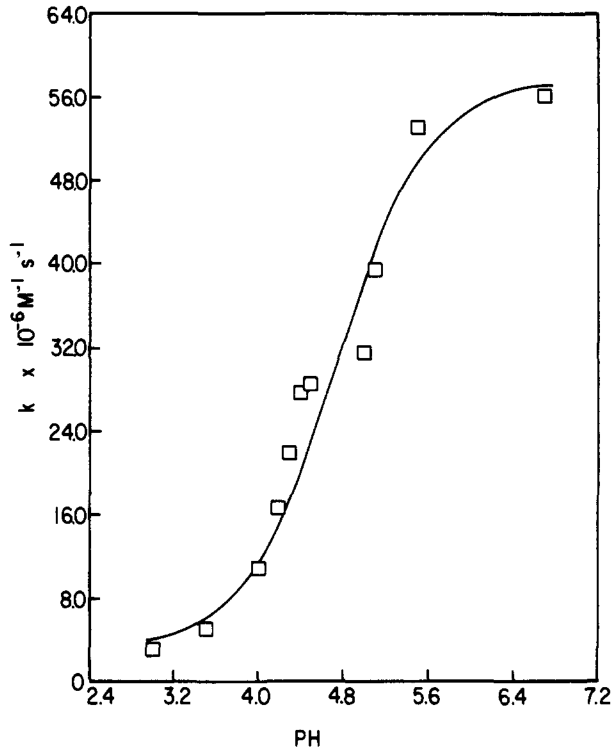


Figure 1. Bimolecular rate constants.

γ radiolysis of the complexes in oxygenated 0.1 M formate solutions produces the peroxo complex quantitatively. No cobalt(II) was detected in the γ-irradiated solution. γ radiolysis of II also shows spectral changes corresponding to the formation of the peroxo complex. However, in this case, the peroxo complex decomposes slowly in aqueous solutions.[15]

With the identification of the peroxo product the reduction of the coordinated superoxide by O_2^- may be formulated as shown in Scheme I. A generalized rate treatment including the hydroperoxy radical as the additional reducing species shows that the bimolecular rate constant k for the reduction process is a sum of the rate constants due to the fraction of $O_2^-\cdot, f_{O_2^-}$, and the fraction of $HO_2\cdot, f_{HO_2}$, present in the solution:

$$k = (k_{O_2^-} \times f_{O_2^-} + k_{HO_2} \times f_{HO_2})$$
$$= \frac{k_{O_2^-}}{1 + (K/[H^+])} + \frac{k_{HO_2}}{1 + ([H^+]/K)}$$

K is the acid dissociation constant for $HO_2\cdot$ and $k_{O_2^-}$ and k_{HO_2} are the rate constants for the reduction process by $O_2^-\cdot$ and $HO_2\cdot$, respectively. The best fit to the data shown in Figure 1 is obtained for $k_{O_2^-} = 5.8 \pm 0.3 \times 10^7$ and $k_{HO_2} = 3.0 \pm 0.5 \times 10^6\ M^{-1}\ s^{-1}$. The p$K_a$ for $HO_2\cdot$ is known[17] to be 4.75 and above pH 5.0 reduction by $O_2^-\cdot$ is the predominant pathway. The reaction between two $O_2^-\cdot$ ions is negligibly slow compared with that of $O_2^-\cdot$ and $HO_2\cdot$ for which a rate constant of

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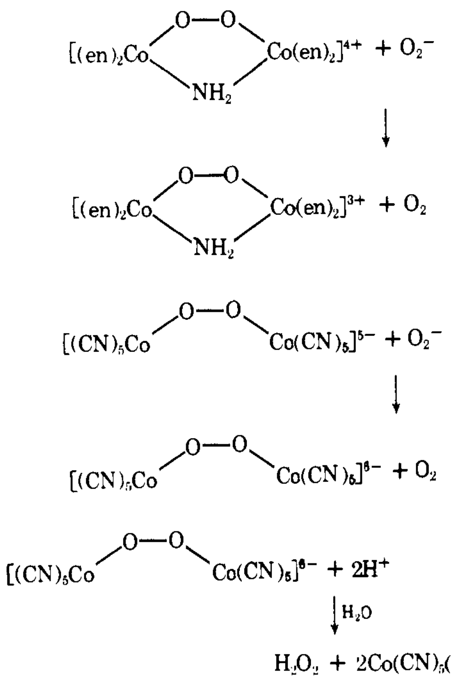
Scheme I



$8.86 \pm 0.43 \times 10^7\ M^{-1}\ s^{-1}$ is known.[18] It appears that the coordination of the superoxide with cobalt(III) has the same effect as the hydrogen ion in the superoxide dismutation reaction.

For the cyanide complex II we could not measure a rate constant with $O_2^{-}\cdot$ since the reaction is too slow to compete with the decay of $O_2^{-}\cdot$ by other processes. $HO_2\cdot$ reacts with the complex with a bimolecular rate constant of $4.7 \pm 0.3 \times 10^5\ M^{-1}\ s^{-1}$. It appears that the rate with a negatively charged species like $O_2^{-}\cdot$ is drastically reduced for the cyanide complex due to electrostatic effects. This behavior is clearly indicated for the reduction processes of these complexes with unstable metal ions and free radicals.[19]

Superoxide ion reduction of metal ions like Cu(II) and Mn(III) complexes are known.[3-5,20-22] This is the first report of a reaction of superoxide ion with the bound superoxide other than hydroperoxide ion. The present investigation shows the existence of a pathway catalyzed by a transition-metal complex. Although no known superoxide dismutase contains cobalt, the present study emphasizes that in enzymatic mechanisms superoxo coordinated metal ion centers could exist and oxidize the superoxide ion analogously to the proton-catalyzed dismutation reaction.

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Palladium(II)-Promoted Cyclizations of Olefinic Silyl Enol Ethers. Preparations of σ-(1-Substituted 3-oxocyclopentyl)methylpalladium(II) Complexes and Their Oxidative Rearrangements

Sir:

In a preceding paper,[1] we reported that cyclization of 2-trimethylsilyloxy-1,5-hexadiene (**1a**) was performed by a catalyst of $Pd^{II}(OAc)_2$ in acetonitrile to produce 3-methyl-2-cyclopentenone (**5**). The Pd(II)-promoted cyclization of **1a** was explained by assuming an intermediate of oxo-π-allylpalladium(II) complex (**2a**), which undergoes intramolecular olefin insertion followed by β elimination of palladium hydride from the resultant σ-(3-oxocyclopentyl)methylpalladium(II) complex (**4a**) as shown in Scheme I. Herein, we report preparations of air-stable σ-(1-substituted 3-oxocyclopentyl)methylpalladium(II) chloride (acetonitrile) complexes (**4**) by Pd(II)-promoted cyclizations of 2-trimethylsilyloxy(5-substituted)-1,5-hexadienes (**1**) (Scheme I), and their oxidations with cupric chloride causing novel ring-expansion reactions (Scheme I).

A sample procedure for the preparation of σ-(1-substituted 3-oxocyclopentyl)methylpalladium(II) chloride (acetonitrile) complexes (**4**) is illustrated as follows. To a solution of $Pd^{II}Cl_2(PhCN)_2$ (1 mmol) in benzene (12 mL), silyl enol ether (**1d**, 1 mmol) was added and stirred at 8–10 °C for 2 h. The reaction mixture was condensed in vacuo to ca. one fourth of the volume and triturated with hexane (30 mL) to precipitate σ-(4-phenyl-4-pentenoyl)methylpalladium(II) chloride complex (**3d**,[2] 92%). Next, a solution of the palladium(II) complex (**3d**, 1 mmol) in acetonitrile (10 mL) was heated at reflux for 2 h. After the mixture was filtered to remove a small amount of depositing palladium metal, it was evaporated in vacuo to leave crude σ-(1-phenyl-3-oxocyclopentyl)methylpalladium(II) chloride (acetonitrile) complex (**4d**) in an 87% yield, which was recrystallized from acetonitrile to prepare an analytically pure sample.[3] Spectral data of **4d** [IR (KBr disk) 2305, 1735 cm^{-1}; NMR ($CDCl_3$ with Me_4Si) δ 1.98 (s, 3 H), 2.2–2.8 (m, 8 H), 7.1–7.7 (m, 5 H)] are consistent with the assigned structure. In support of the structure, hydrogenation of **4d** in benzene (1 atm of H_2, 1 h) furnished 3-methyl-3-phenylcyclopentanone (**6d**) quantitatively. The preparation of **4** can be more conveniently performed in one flask starting with olefinic silyl enol ether without the isolation of **3** just by changing the solvents. Similarly, olefinic silyl enol ethers **1b**, **1c**, **1e**, **1f**, and **1g** were cyclized to the corresponding complexes **4**[4] [**4b** (88%), **4c** (91%), **4e** (68%), **4f** (82%), and **4g** (96%)