

REACTION OF SUPEROXO Co(III) COMPLEX WITH STABLE PHENOXY RADICALS

A. Nishinaga,\* H. Tomita, and T. Matsuura

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan

A typical superoxo complex  $[\text{Co}(\text{CN})_5\text{O}_2][\text{Ph}_3\text{P}=\text{N}^+\text{PPh}_3]_3$  combines with stable phenoxy radicals in  $\text{CH}_2\text{Cl}_2$  leading to selective formation of peroxy-*p*-quinols except for 2,4,6-tri-*t*-butylphenoxy radical, representing radical reactivity of the complex.

Although superoxo metal complexes are considered to play an important role in biological oxygenations, only a little is known about the chemical reactivity of superoxo complexes towards organic molecules.<sup>1</sup> Superoxo Co(III)-Schiff base complexes have been shown to abstract hydrogen from 2,6-di-*t*-butylphenols giving rise to the corresponding phenoxy radicals<sup>2</sup> whereas the superoxo complex  $[\text{Co}(\text{CN})_5\text{O}_2]^{3-}$  acts as a base towards these phenols to give phenolato Co(III) complexes.<sup>3</sup>

In the present communication, we wish to report that the superoxo complex  $[\text{Co}(\text{CN})_5\text{O}_2]^{3-}$  displays radical reactivity towards stable 2,6-di-*t*-butylphenoxy radicals (1). When equimolar amounts of  $[\text{Co}(\text{CN})_5\text{O}_2][\text{Ph}_3\text{P}=\text{N}^+\text{PPh}_3]_3$  and 1 were mixed in  $\text{CH}_2\text{Cl}_2$  at  $-70^\circ\text{C}$  under efficient nitrogen bubbling, the color of the radical 1 disappeared. The reaction rate depended upon the nature of the group R in 1. Filtration of the resulting mixture through a short column of silica gel gave the parent phenols 4 and the peroxy-*p*-quinols 3 (Table 1).

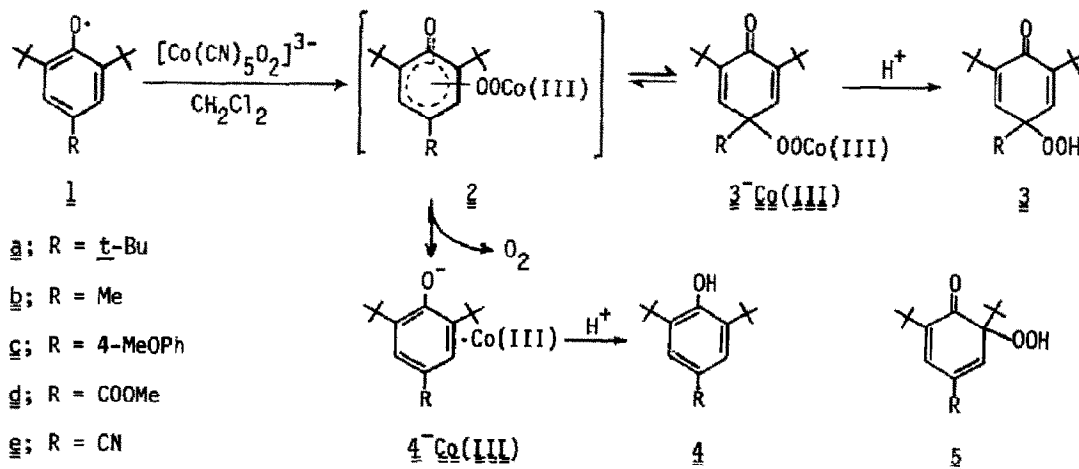


Table 1. Reaction of  $[\text{Co}(\text{CN})_5\text{O}_2]^{3-}$  with Stable Phenoxy Radicals in  $\text{CH}_2\text{Cl}_2$ .<sup>a</sup>

<u>1</u>	Reaction Temperature (°C)	Reaction Time (min)	Conversion (%)	Product Yield (%) <sup>b</sup>		
				<u>3</u>	<u>4</u>	<u>5</u>
<u>1a</u>	-70	60	94	20	13	67
<u>1a</u>	0	4	100	26	29	45
<u>1a</u>	20	1	100	15	59	26
<u>1b</u> <sup>c</sup>	-70	5	100	70	30	-
<u>1c</u>	-70	30	100	90	10	-
<u>1d</u> <sup>c</sup>	-70	10	100	58 <sup>d</sup>	42	-
<u>1e</u> <sup>c</sup>	-70	120	100	29 <sup>d</sup>	71	-

<sup>a</sup> A solution of 1 (0.2 mmol) in benzene (3 ml) prepared by alkaline  $\text{Fe}(\text{CN})_6^{3-}$  oxidation of the parent phenol 4 was added to a solution of  $[\text{Co}(\text{CN})_5\text{O}_2][\text{Ph}_3\text{P}=\text{N}^+\text{PPh}_3]_3$  (0.2 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 ml). <sup>b</sup> All products except for 3d and 3e were identical with authentic samples. Yields were determined by <sup>1</sup>H NMR and TLC. <sup>c</sup> Crystalline radical dimer was added. <sup>d</sup> New compound whose analytical and spectral data are in good agreement with the structure. Mp: 3d, 88 °C(decomp); 3e, 81 °C(decomp). <sup>1</sup>H NMR( $\text{CDCl}_3$ )  $\delta$ , C=CH: 3d, 6.63 (s); 3e, 6.67 (

The formation of the hydroperoxides 3 and 5 obviously indicates the direct radical combination between 1 and the superoxo complex leading to peroxyquinolato Co(III) complexes one of which is depicted as  $3^-\text{Co}(\text{III})$  in the scheme, although they were not isolated. The radical coupling also occurs in DMF at -70 °C. The reaction with 1c-e around 0 °C resulted predominantly in the electron transfer from the superoxo complex to 1. The electron transfer also takes place quantitatively when the mixture obtained from the reaction with 1c-e in DMF at -70 °C was warmed up to 0 °C. These results strongly suggest that the reaction involves a  $\pi$ -complex intermediate 2, analogous to that in base-catalyzed reaction of hydroperoxides 3 and 5 leading to the formation of the parent phenols 4.<sup>4</sup> This is due to a strong ionic nature of the Co-O bond in the peroxyquinolato Co(III) complexes.<sup>3</sup> In the reaction with 1a, on the contrary, the combination takes place predominantly at the *ortho* position. This fact and the exclusive formation of 3c from 1c provide decisive evidence that superoxo Co(III) complex mediated regioselective dioxygen incorporation into 4, where 4a and 4c give 3a and 5c, respectively.<sup>1,2</sup> does not involve the radical combination between 1 and  $\text{Co}(\text{III})\cdot\text{O}_2^-$ . The present reaction also provides a unique method for preparation of peroxy-*p*-quinols with an electron withdrawing group R in 3.

### References

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(Received in Japan 28 May 1980)