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# REACTION OF SUPEROXO Co(III) COMPLEXES WITH 2,6-DI-t-BUTYL-p-BENZOQUINONE METHIDES

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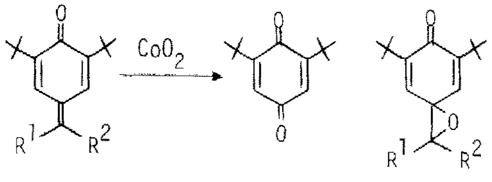
Superoxo Co(III) complexes derived from Co(Salpr) and $[Co(CN)_5]^{3-}$ reacted with 2,6-di-t-butyl-p-benzoquinone methides to give 2,6-di-t-butyl-p-benzoquinone and 2,6-di-t-butyl-2,5-cyclohexadienonespirooxiranes as the main products, which are considered to result from nucleophilic attack by the superoxo species on the exo double bond of the quinone methides.

Superoxo transition metal complexes have currently received much attention with respect to biological oxygenations.[1-3] Since superoxo Co(III) complexes are normally coordinately saturated,[1] their reactions are attributable to the coordinated dioxygen species which possesses radical, anionic, and redox natures. The reactivities of the coordinated dioxygen must be implicated in the natures of ligand in the complex and of the substrate used. Thus, it has previously been found that Co(Salpr)($O_2$) abstracts hydrogen from 2,6-di-t-butylphenols[4] whereas $[Co(CN)_5O_2]^{3-}$ acts as a base to accept proton from these phenols.[5] The latter superoxo complex, on the other hand, couples directly with 2,6-di-t-butylphenoxy radicals,[6] displaying also radical reactivity. Reduction of these radicals by $[Co(CN)_5O_2]^{3-}$ has also been demonstrated under certain conditions.[3,6]

In seeking for the potential reactivities of superoxo Co(III) complexes, we now find that superoxo complexes derived from Co(Salpr) and $[Co(CN)_5]^{3-}$ display nucleophilic reactivity towards 2,6-di-t-butyl-p-benzoquinone methides (1)[7] to give 2,6-di-t-butyl-p-benzoquinone (2) and 2,6-di-t-butyl-2,5-cyclohexadienonespirooxiranes (3) as the main products, although these superoxo complexes are not reactive against unsaturated compounds such as mesityl oxide, 2-cyclohexenone, chalcone, epoxyquinols,[8] and cyclopentadienones.[8]

The reactions were carried out under nitrogen with $[Co(CN)_5O_2]^{3-}$ and under oxygen bubbling with Co(Salpr)($O_2$). Quinone methides 1 ($R^1 = R^2$ = Ph, 9-fluorenylidene) were not reactive. The products were separated by silica gel chromatography. The results are summarized in Table 1.



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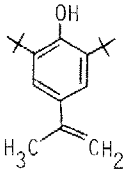

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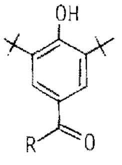

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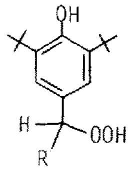

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a; $R^1 = R^2 = H$

b; $R^1 = H$, $R^2 = Me$

c $R^1 = H$, $R^2 =$ i-Pr

d $R^1 = H$, $R^2 = Ph$

e; $R^1 = R^2 = Me$

f; $R^1$, $R^2$ = cyclohexylidene

g; $R^1$, $R^2$ = cyclopentylidene

a; R = H

b; R = Me

c; $R = (CH_2)_3CHO$

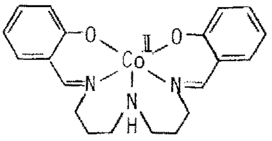
a; R = H

b; R = i-Pr

Table 1. Reaction of Superoxo Co(III) Complexes with Quinone Methides 1.[a]

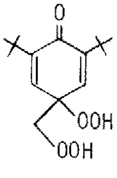
| 1 | $CoO_2$[b] | Solvent | Reaction Temp. (°C) | Reaction Time (h) | Product, Yield (%)[c] | | |
|---|---|---|---|---|---|---|---|
| | | | | | 2 | 3 | Others |
| 1a | A | $CH_2Cl_2$ | 20 | 1.0 | 100 | 0 | 0 |
| 1a | B | DMF | 0 | 0.7 | 8 | 33 | -[d] |
| 1a | C | $CH_2Cl_2$ | 0 | 0.8 | 34 | 42 | -[d] |
| 1b | A | $CH_2Cl_2$ | 20 | 2.0 | 90 | trace | 0 |
| 1c | A | $CH_2Cl_2$ | 0 | 3.0 | 48 | 0 | 6b(15) |
| 1c | B | DMF | 0 | 1.5 | 22 | 18 | 5a(24) |
| 1c | C | $CH_2Cl_2$ | 0 | 0.7 | 61 | 37 | 0 |
| 1d | A | $CH_2Cl_2$ | 30 | 2.0 | 90 | 0 | PhCHO(81) |
| 1d | C | $CH_2Cl_2$ | 0 | 0.5 | 20 | 40 | PhCHO(16) |
| 1e | A | $CH_2Cl_2$ | 0 | 2.0 | 30 | 33 | 5b(8) |
| 1e | B | DMF | 0 | 1.0 | 0 | 0 | 4(100) |
| 1e | C | $CH_2Cl_2$ | 0 | 1.0 | 0 | 61 | 4(13),5b(8) |
| 1f | A | $CH_2Cl_2$ | -20 | 4.5 | 27[e] | 27[e] | |
| 1f | C | $CH_2Cl_2$ | -10 | 0.5 | 15[e] | 44[e] | |
| 1g | C | $CH_2Cl_2$ | -10 | 0.5 | 0 | 24 | 5c(49) |

[a] Reaction conditions: 1 (0.5 mmol), Co complex (1 mmol) in $CH_2Cl_2$(20 ml) or in DMF(100 ml). Conversion, 100% except for 1c with A. [b] A = $Co(Salpr)(O_2)$; B = $[Co(CN)_5O_2][NEt_4]_3$; C = $[Co(CN)_5O_2][Ph_3P{=}\overset{+}{N}{=}PPh_3]_3$. [c] Determined by NMR except for 2 and 3f otherwise by isolation. [d] Decomposition products of 1a itself. [e] Yield by isolation.



Co(Salpr)

Products other than 2 and 3 listed in Table 1 result from migration of the quinone methides under the reaction conditions. The structures of the products are in good agreement with their analytical and spectral data.[9] In the case with Co(Salpr), no reaction took place if either of the complex or $O_2$ was absent. It is therefore no doubt that the dioxygen complex $Co(Salpr)(O_2)$ reversibly formed is the reactive species.[10] As seen from Table 1, the oxidation with $Co(Salpr)(O_2)$ led to the exclusive formation of 2 whereas $[Co(CN)_5O_2]^{3-}$ gave a mixture of 2 and 3. In the oxidation of 1c with $Co(Salpr)(O_2)$, the peroxidic product 6b[11] was obtained in addition to 2, but it did not give 2 under the reaction conditions. This indicates that the peroxidic product 6 may not be the intermediate for the formation of 2. The rearrangement of the quinone methides took place efficiently in DMF. In the reaction of 1e with $[Co(CN)_5O_2]^{3-}$ in DMF, only 2,6-di-*t*-buytl-4-isopropenylphenol (4)[9] was obtained, which is in turn indicative of nonreactivity of $[Co(CN)_5O_2]^{3-}$ against the phenol.[5] From the reaction of 1d, nearly the same amount of benzaldehyde as that of 2 was isolated. The oxygenolysis of 1 giving rise to 2 is therefore seemingly a mimic of dioxygenase reaction, which prompted us to examine reaction mechanism of the oxygenolysis. Thus, it was found that the reaction of 1a with Co(Salpr)($O_2$) in $CH_2Cl_2$ at -20 °C gave the dihydroperoxide 7[12] (47% yield) and 6a[11] (48% yield) along with 2 (5% yield). When the compound 7 was treated with Co(Salpr) or the reaction mixture obtained from 1a with Co(Salpr)($O_2$) at -20 °C was warmed up to 20 °C, 2 was obtained quantitatively. It is therefore reasonable to assume that the intermediate in the formation of 2 is the diperoxy Co(III) complex 10 taking into the results obtained in the Co(Salpr) mediated oxygenation of 2,6-di-*t*-butylphenols,[4] although attempts to isolate 10 was not successful.



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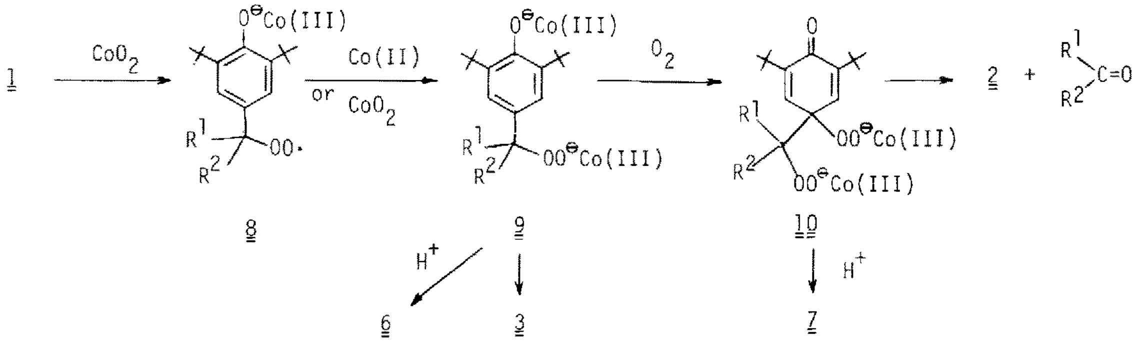
The present results except for those resulting from the migration of 1 are rationalized to involve nucleophilic attack by the superoxo species on the exo double bond in 1 in the initial step followed by further reactions as depicted in the following scheme.[13]



The dihydroperoxide 7 was also obtained in the reaction of 1a with $[Co(CN)_5O_2][Ph_3P{=}\overset{+}{N}{=}PPh_3]_3$ in $CH_2Cl_2$ under nitrogen at -70 °C in 25% yield together with 2 (16%) and 3a (44%). Distribution of these products was not changed when the reaction was carried out under oxygen bubbling. The formation of 7 in the last case may therefore be rationalized by assuming combination in a cage between 9 and $O_2$ which are generated by the reduction of 8 with the superoxo species. The exclusive formation of 2 in the reaction with Co(Salpr) is probably due to that the phenolato Co(III) complex intermediate 9 is susceptible to oxygenation.[4] On the contrary, with $[Co(CN)_5O_2]^{3-}$ the coordination in 9 is so loose that an intramolecular reduction of the peroxy bond in 9 takes place to give 3, finally leading to a mixture of 2 and 3.

## References and Notes

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9) Melting point and NMR($CDCl_3$) data of 3, 4, and 5c are as follows. 3a: 86-88 °C; δ 1.23 (*t*-Bu) 6.14 (C=CH), 3.25 ($R^1$). 3b: δ 1.25 and 1.28 (*t*-Bu), 6.12 and 6.33 (C=CH, d, J = 3 Hz), 1.50 ($R^2$; d, J = 6 Hz), 3.48 ($R^1$; d, J = 6 Hz). 3c: 90-91 °C; δ 1.23 and 1.24 (*t*-Bu), 6.14 and 6.37 (C=CH; d, J = 3 Hz), 3.04 ($R^1$; d, J = 9 Hz), 1.73 ($R^2$, m), 0.91 and 1.19 (Me groups in $R^2$; d, J = 7 Hz). 3d: not purified; δ 1.08 and 1.28 (*t*-Bu), 6.10 and 6.32 (C=CH; d, J = 3 Hz) 4.53 ($R^1$), 7.38 ($R^2$). 3e: 90-91 °C; δ 1.23 (*t*-Bu), 6.41 (C=CH), 1.50 ($R^1$, $R^2$). 3f: 93-95 °C; δ 1.26 (*t*-Bu), 6.47 (C=CH), 1.4-2.0 ($R^1$, $R^2$; m). 3g: 118-119 °C; δ 1.27 (*t*-Bu), 6.26 (C=CH), 1.62-2.1 ($R^1$, $R^2$; m). All the oxiranes 3 except for 3b and 3d, which were not obtained as crystals, gave satisfactory analytical results: C, ±0.3%; H, ±0.3%.
   4: 77-78 °C; δ 1.45 (*t*-Bu), 2.13 (Me, broad s), 5.1-5.3 ($H_2C=C$), 7.3 (ArH), 4.95 (OH). Anal: C, ±0.2%; H, ±0.24%. 5c: not isolated in pure crystalline form; IR(Nujol), 3550, 1713, 1655 $cm^{-1}$; δ 1.50 (*t*-Bu), 2.0-3.1 ($(CH_2)_3$; m), 5.76 (OH), 7.83 (ArH), 9.73 (CHO; t, J = 1.3 Hz).
10) The superoxo complex rather than the μ-peroxo species is reasonably considered to be the case because the interaction of the latter complex with the substrate is sterically hindered.[4]
11) The hydroperoxides 6 could not be crystallized but their NMR spectra are in good agreement with the structure. 6a: δ 1.47 (*t*-Bu), 4.60 ($CH_2$), 7.16 (ArH). 6b: δ 0.73 (Me, d, J = 7 Hz), 1.05 (Me, d, J = 7 Hz), 1.44 (*t*-Bu), 4.54 (O-CH; d, J = 8 Hz), 5.20 (OH), 7.06 (ArH). Iodometric titration of these crude products showed involvement of 88% of the hydroperoxides, respectively.
12) 7: mp 110-112 °C(decomp); IR(Nujol), 3380, 1660, 1630, 1620 $cm^{-1}$; NMR($CDCl_3$), δ 1.23 (*t*-Bu), 4.17 ($CH_2$), 6.68 (C=CH), 7.8-9.0 (OOH). Anal: C, ±0.2%; H, ±0.1%.
13) Nucleophilic attack by various nucleophiles on the exo dougle bond in quinone methides are known well.[7d] Other possible initiation reactions are radical addition and electron transfer by the superoxo species onto the substrate. The facts that 1 was not susceptible to Co(Salpr) itself, nitrogen monooxide, and *t*-butoxy radical generated from *t*-butyl peroxide, however, may exclude these possibilities.

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