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OXYGENATION OF p-NITROPHENYLHYDRAZONES WITH Co(II)-SCHIFF BASE COMPLEXES

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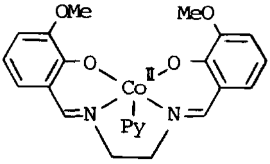
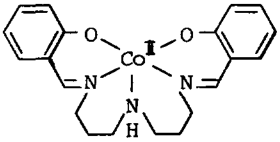
p-Nitrophenylhydrazones, unsusceptible to autoxidation, are readily oxygenated in the presence of a five-coordinate cobalt(II)-Schiff base complex, Co(II)(MeOSalen)(Py) leading to quantitative formation of novel 1-(p-nitrophenylazo)-1-peroxy Co(III) complexes **2**, which were isolated as crystals. A plausible mechanism involving hydrogen abstraction by Co(III)($O_2^{-\cdot}$) from the substrate followed by formation of a substrate anion Co(III) complex intermediate is proposed.

Much attention has been donated to selective oxidations of organic compounds with dioxygen-metal complexes,[1] among which superoxo complexes are of interest particularly in connection with biological oxygenations.[2] Five-coordinate Co(II)-Schiff base complexes such as Co(II)(MeOSalen)(Py) and Co(II)(Salpr) are typical ones capable of binding dioxygen reversibly to form superoxo Co(III) species. These complexes have been demonstrated to mediate oxygenation of 2,6-di-t-butylphenols leading to regioselective formation of hydroperoxycyclohexadienones depending on the nature of substituent at the 4-position of the phenols.[3]

Phenylhydrazones are known to be sensitive to autoxidation to give 1-hydroperoxyazo-1-hydroperoxides,[4] whereas autoxidation of p-nitrophenylhydrazones is very slow.[4a]

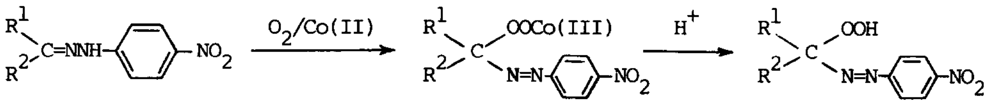


Co(II)(MeOSalen)(Py)



Co(II)(Salpr)

We now find that these five-coordinate Co(II)-Schiff base complexes mediate smoothly the oxygenation of p-nitrophenylhydrazones(1), which are unsusceptible to normal autoxidation,[5] leading to the quantitative formation of 1-(p-nitrophenylazo)-1-peroxy Co(III) complexes of type 2. When oxygen was bubbled through a solution of equimolar amounts of p-nitrophenylhydrazone(1) and Co(II)(MeOSalen) in pyridine at 0 °C, the reaction was normally completed within 3 h ^{1}H NMR and tlc analyses of the mixture showed the quantitative formation of 1-(p-nitrophenylazo)-1-peroxy Co(III)(MeOSalen)(Py) complexes (2), which were isolated as crystals (Table 1). Treatment



1 2 3

a; R^1 = 4-$MeOC_6H_4$, R^2 = Me b; R^1 = 4-MeC_6H_4, R^2 = Me c; R^1 = 4-ClC_6H_4, R^2 = Me

d; R^1 = Ph, R^2 = Me e; R^1 = 4-$MeOC_6H_4$, R^2 = Et f; R^1 = R^2 = Me

g; R^1, R^2 = -(CH_2)-

Table 1. Formation and Physical Data of 1-(p-Nitrophenylazo)-1-peroxy Co(III)(MeOSalen)(Py) Complexes 2.[a]

2	Yield[b]	M.p.[c]	IR(Nujol)	^1H NMR($CDCl_3$)[d] δ (ppm)		
	(%)	(°C)	(cm^{-1})	R^1[e]	R^2	OMe(Schiff base)
2a	40	119-121	1635, 1600	3.61	1.82	3.80
2b	44	105-107	1645, 1605	2.20	1.73	3.80
2c	42	122-123	1645, 1610	-	1.72	3.76 , 3.82[f]
2d	31	112-113	1650, 1610	-	1.68	3.79, 3.81[f]
2e	49	116-118	1640, 1605	3.66	-[g]	-[g]
2f	68	143-145	1635, 1601	1.22		3.84
2g	63	123-124	1635, 1600	1.0-2.0 (m)		3.78, 3.86[f]

[a] Reaction conditions: oxygen was bubbled through a solution of **1** (1 mmol) and Co(II)(MeOSalen) (1 mmol) in pyridine (5 ml) at 0 °C for 3 h. Petroleum ether (2 ml) was added and the mixture was allowed to stand at -20 °C for 24 h. The resulting brown complexes were collected. ^1H NMR and tlc analyses showed the quantitative formation of 2. [b] Isolation yield. [c] Decomposition point. All the products showed satisfactory analytical results: C, ±0.02-0.03%; H, ±0.01-0.24%; N, ±0.02-0.23%. [d] A small amount of pyridine-d_5 was added to avoid the decomposition of 2, measured at -10 °C. [e] Methyl group at the 4-position. Aromatic proton, 6.4-8.2 (m). [f] Observed two peaks are probably due to stereo isomers of 2. [g] Not determined.

of the peroxy complexes with silica gel gave 1-(p-nitrophenylazo)-1-hydroperoxides (**3a-e**) quantitatively, among which **3a-c** were isolated as crystals at low temperature. The hydroperoxides were reduced by dimethyl sulfide to give the original ketones quantitatively, supporting the structure 3, whose data are given in Table 2. The ^1H NMR spectra of 2 in CD_2Cl_2 containing pyridine-$d_5$at -10 °C exhibited clear signals, indicative of a Co(III) state in 2. The signals of R^1 and R^2 in complexes 2a-e are shifted considerably to higher field (Δδ, 0.14-0.26 ppm) compared with those in the corresponding hydroperoxides 3 (Tables 1 and 2). The higher shift may be due to the coordination effect. Complexes 2 are fairly stable in solid state or in pyridine solution, whereas decompose in dichloromethane solution at room temperature, indicating that the coordination of an N-base ligand such as pyridine is essential for the stability of 2. The oxygenation of **1** with Co(II)(MeOSalen) in N,N-dimethylformamide gave the original ketone resulting from de-

Table 2. Physical Data of 1-(p-Nitrophenylazo)-1-hydroperoxides 3.

3	M.p.(decomp) (°C)	IR(Nujol) (cm^{-1})	^{1}H NMR($CDCl_3$), (ppm) R^{1a}	R^2	$PhNO_2$
3a	81-82^b	3430, 1605	3.82	1.97	7.89^c, 8.38^c
3b	66-67^b	3450, 1615	2.37	1.94	8.00^c, 8.42^c
3c	57-59^b	3440, 1620	-	1.90	7.99^c, 8.40^c
3d	-^{d}	-^{e}	-	1.90	8.01^f, 8.43^f
3e	-^{d}	-	3.80	0.97(t)^g, 2.88(q)^g	8.07^c, 8.35^c

[a] Methyl group at the 4-position. Aromatic proton, 6.92-7.98(m).
[b] Satisfactory analytical data were obtained. [c] Doublet, J = 10 Hz.
[c] Decomposed at room temperature. [e] Not determined. [f] Doublet, J = 10 Hz.
[g] J = 7.5 Hz.

composition of the peroxy complex of type 2 intermediately formed.

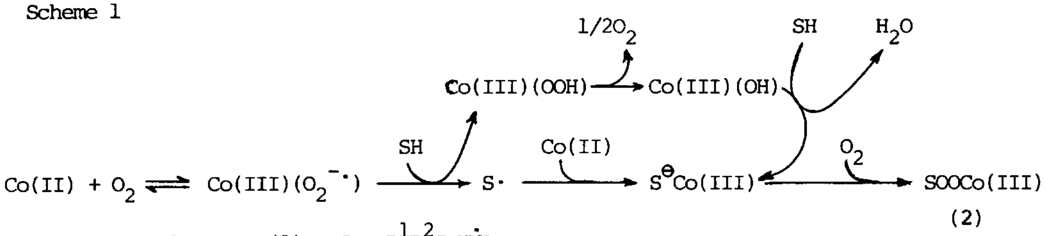
The oxygenation of **1** was also mediated by Co(II)(Salpr) in CH_2Cl_2 at 0 °C. Attempts to isolate peroxy complexes of type 2 were unsuccessful. However, filtration of the reaction mixture through a short column of silica gel gave the corresponding hydroperoxides **3** quantitatively, indicating the quantitative formation of peroxy complexes of type 2.[6]

In the oxygenation of **1** with Co(II)(MeOSalen) in pyridine, 1.25 mol/mol of oxygen was taken up. On the other hand, when **1a** was mixed with an equimolar amount of Co(III)(MeOSalen)(OH)[7] in pyridine under nitrogen, a strong purple color of the substrate anion[8] appeared instantaneously, and **1a** was recovered quantitatively upon acidification of the mixture. However, when the colored mixture was oxygenated, 1 mol/mol of oxygen was taken up and peroxy complex **2a** was obtained quantitatively. Therefore, Co(III)(MeOSalen)(OH), which should be formed during the course of the oxygenation with the Co(II) complex,[3c] does not behave as an oxidant but a base toward the substrate. Rate of the oxygenation of **1** with Co(II)(MeOSalen) in pyridine was in the order **1a** > **1b** > **1c** > **1d** ($t_{1/2}$ = 16, 21, 23, and 33 min, respectively, at 5 °C): the rate increases with increasing electron-donating effect of p-substituent of the phenyl ring in R^1. Furthermore, rate of the oxygenation of **1a** with Co(III)(MeOSalen)(OH) ($t_{1/2}$ = 6 min, at 5 °C) is faster than that of **1a** with Co(II)(MeOSalen). These observations strongly suggest that the mechanism of the present Co(II)-Schiff base complex-mediated oxygenation of **1** involves rate determining hydrogen abstraction by Co(III)($O_2^{-\bullet}$) from the NH group in the substrate to give the corresponding substrate radical, which coordinates rapidly to Co(II) giving rise to a substrate anion Co(III) complex intermediate, into which dioxygen is incorporated to give **2** as depicted in Scheme 1. This mechanism is quite similar to that discussed for the Co(II)-Schiff base complex-mediated oxygenation of 2,6-di-t-butylphenols,[3] although a possibility of direct combination between the substrate radical and Co(III)($O_2^{-\bullet}$) to form **2** may not be negligible.[10]

It is noted that even with 4-methoxyacetophenone phenylhydrazone which is very sensitive to normal autoxidation to give the corresponding hydroperoxide of type 3, the peroxy complex of type 2 was obtained quantitatively when the oxygenation was carried out in the presence of the Co(II)-Schiff base complex. Therefore, one can conclude that the five-coordinate Co(II)-

Schiff base complexes inhibit the normal radical chain autoxidation process and rather activate the substrate in such a way that a substrate anion Co(III) complex intermediate is formed.

Scheme 1



where SH; Substrate (1)   S•; $R^1R^2C{=}N\dot{N}Ar$

$S^{\ominus}Co(III)$; $R^1R^2C{=}NN^{\ominus Co(III)}_{Ar} \longleftrightarrow R^1R^2C^{\ominus Co(III)}_{N=NAr}$ Ar = 4-$NO_2C_6H_4$

Since some stable hydroperoxides obtained from autoxidation of phenylhydrazones have been demonstrated to act as a hydroxylation reagent like Fenton's reagent,[11] it is interesting to know chemical reactivity of the present unstable hydroperoxides **3** and peroxy complexes **2**, which is currently investigated.

References and Notes

1) Abstracts of the First International Symposium on Oxygen Activation and Selective Oxidation Catalyzed by Transition Metals, J. Mol. Catal., **7**, 1-320 (1980).

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3) (a) A. Nishinaga, K. Nishizawa, H. Tomita, and T. Matsuura, J. Am. Chem. Soc., **99**, 1287 (1977). (b) A. Nishinaga, H. Tomita, and T. Matsuura, Tetrahedron Lett., 2893 (1979). (c) A. Nishinaga, H. Tomita, K. Nishizawa, T. Matsuura, S. Ooi, and K. Hirotsu, J. Chem. Soc. Dalton Trans., 1504 (1981).

4) (a) K. H. Pausacker, J. Chem. Soc., 3478 (1950). (b) A. J. Bellamy and R. D. Guthrie, J. Chem. Soc., 2788 (1965).

5) Actually, no appreciable oxidation took place when solutions of p-nitrophenylhydrazones (**1a-1e**) in CH_2Cl_2 were exposed to air or oxygen at room temperature for 10 h. Autoxidation of p-nitrophenylhydrazones of aliphatic ketones (**1f, 1g**) proceeded faster than those of the aromatic ketones. However, the reaction was not clean.

6) ^1H NMR spectrum of the oxygenated mixture from **1a-d** is complicated, including more than two signals assignable to the methyl group in peroxy complex 2 Co(III) = Co(III)(Salpr). This is probably due to a mixture of stereo isomers of the peroxy complex, which may be implicated in failure in isolation of these peroxy complexes.

7) Co(III)(MeOSalen)(OH) was prepared in good yield by the reaction of Co(III)(MeOSalen)($OOBu^t$) with triphenylphosphine.

8) M. Kambe, Y. Hasegawa, and E. Shindo, Bunseki Kagaku, **12**, 63 (1963).

9) Interestingly, no reaction took place when oxygen was bubbled through a solution of **1a** in DMF containing t-BuOK at 0 °C for 5 h. This indicates that the free anion of **1** is not susceptible to oxygenation. It is therefore evident that the complexation of the anion of **1** to the Co(III) species accelerates the dioxygen incorporation into the substrate to form **2**.

10) Radical coupling between stable phenoxy radicals and a superoxo Co(III) complex gives peroxyquinolato Co(III) complexes: A. Nishinaga, H. Tomita, and T. Matsuura, Tetrahedron Lett., 3407 (1980).

11) T. Tezuka, N. Narita, W. Ando, and S. Oae, J. Am. Chem. Soc., **103**, 3045 (1981).

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