recovery is not yet quantitative, this observation is of uncertain significance.

(12) Experimental conditions: water previously boiled, two slides illuminated with GE H100 PSP44-4 Hg Lamp for 425 h.

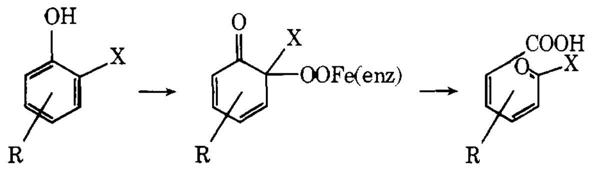
S. J. Valenty,* G. L. Gaines, Jr.*
General Electric Corporate Research and Development
Schenectady, New York 12301

Received December 3, 1976

Novel Peroxycobalt(III) Complexes Derived from 4-Aryl-2,6-di-*tert*-butylphenols. A Model Intermediate of Dioxygenase Reaction

Sir:

Oxidative cleavage of phenolic rings by molecular oxygen, widely seen in nature, is one of the most interesting biological oxygenation reactions. Pyrocatechase and metapyrocatechase are the typical enzymes which catalyze the oxygenation of phenolic substrates leading to the oxidative cleavage of the aromatic rings.[1] These enzymes require ferric or ferrous ion as the cofactor, which is considered to participate in the reaction center.[2] α-Ketoperoxy complex (**1**) involving the metal ion at the reaction center of the enzyme has been postulated as a primary intermediate of the dioxygenase reaction for phenolic substrates.[3] Little is, however, known about such a peroxy complex of type **1**. We now wish to report the synthesis of peroxycobalt(III) complexes of type **1** by the oxygenation of 4-aryl-2,6-di-*tert*-butylphenol with Co(salpr) (salpr = bis(3-salicylideneaminopropyl)amine), a five-coordinated Co(II) Schiff's base complex.[4] This provides a model for the proposed intermediate of the dioxygenase reaction.

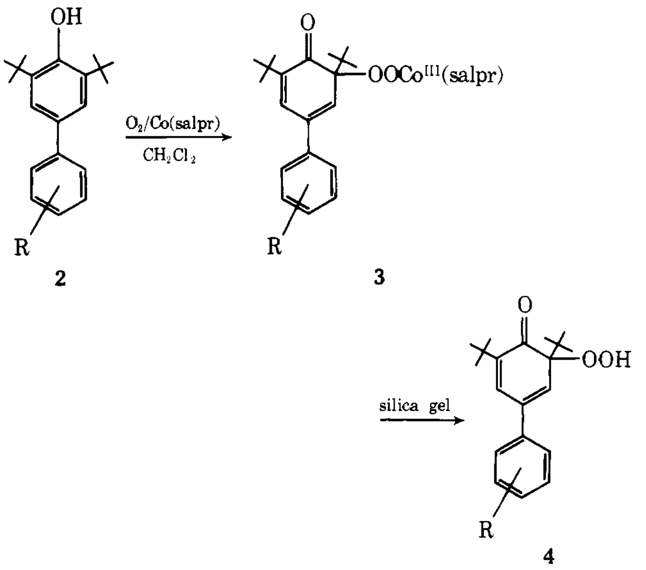


1

X = H or OH

When oxygen is bubbled through a solution of 4-aryl-2,6-di-*tert*-butylphenol (**2**) (0.5 mmol) and Co(salpr) (0.4 mmol) in CH_2Cl_2 (6 ml) at 0 °C the reaction is normally completed within 1 h. The reaction mixture is concentrated (3 ml) and diluted with petroleum ether (20–30 ml) to result in the precipitation of the unreacted Co(salpr). After removal of the precipitates by filtration, the filtrate is kept at −20 °C over night to give the α-ketoperoxycobalt(III) complex (**3**), black prisms.[5] The IR absorption at 1640 cm^{-1} for all complexes, **3**, is referred to the 2,4-cyclohexadienone structure.[6] The NMR spectra are all in good agreement with structure **3** (Scheme I). The signal of one of the *tert*-butyl groups in **3** shifts to considerably higher field compared to that of the corresponding hydroperoxides, **4** (Δ = 0.16–0.22 ppm), reflecting the coordination effect. The magnitude of coupling between the olefinic protones of **3** (J = 2.8 Hz) is characteristic of that between 3-H and 5-H in the 2,4-cyclohexadienone system.[7-9] Structure **3** was further confirmed by the fact that the filtration of a CH_2Cl_2 solution of **3** through a short column of silica gel affords the corresponding α-ketohydroperoxides, **4**, in nearly quantitative yield. Compound **4a** was identical with the sample obtained in the base-catalyzed oxygenation of **2a**.[7]

Scheme I



	a	b	c	d	e	f	g	h
R	4-OMe	3-OMe	2-OMe	4-Me	3-Me	2-Me	H	4-Cl

The NMR spectrum of the reaction mixture resulting from the oxygenation of **2** shows only signals for **2** and **3** but not for **4**, indicating that compound **3** is the sole product in the oxygenation. For the formation of **3**, 1.25 mol/mol of oxygen was taken up against **2** or Co(salpr) incorporated into **3**, and no hydrogen peroxide is detected in the reaction mixture, which shows neutral pH. The stoichiometry of this reaction is therefore depicted as follows:

$$\mathbf{2} + \mathrm{Co(salpr)} + \tfrac{5}{4}O_2 \rightarrow \mathbf{3} + \tfrac{1}{2}H_2O$$

The solution of Co(salpr) in CH_2Cl_2 bubbled with oxygen at room temperature displays the typical ESR signals for the $Co\text{-}O_2$ (1:1) complex (eight lines, a_{Co} = 13 G).[10] Upon addition of a small amount of **2a** under interception of oxygen, the signals were diminished with simultaneous appearance of

Table I. Preparation and Physical Properties of **3**

Compd	Conversion[a] (%)	Yield (%)	Mp (°C)	NMR($CDCl_3$), δ (ppm)						IR (Nujol) (cm^{-1})
				t-Bu		Me	C=CH[c]		Ar	
3a	80	100	131–132	0.83	1.23	3.80	5.85	6.89	6.7–7.6	1640
3b	83	100	123–125	0.82	1.21	3.83	6.00	—[d]	6.6–7.6	1640
3c	76	100	125–127	0.88	1.26	3.81	5.80	6.82	6.7–7.6	1640
3d	67	100	131–133	0.83	1.24	2.35	5.99	6.88	6.7–7.6	1640
3e	62	100	122–124	0.84	1.25	2.40	5.97	—[d]	6.7–7.6	1640
3f	70	100	125–126	0.85	1.25	2.16	5.45	6.63	6.7–7.6	1640
3g	72	100	118–119	0.83	1.24	—	6.03	—[d]	6.7–7.6	1640
3h	37[b]	100	126–127	0.87	1.25	—	5.97	6.88	6.7–7.6	1640

[a] Conversion of **2** to **3**: determined by the yields of the corresponding hydroperoxides **4** which were isolated by filtration of **3** through a short column of silica gel. [b] Determined by isolation of **3h**. [c] A pair of doublets with J = 2.8 Hz. [d] The signal is concealed behind the aromatic signals.

a quintet attributed to the phenoxy radical of **2a** (a_H = 1.6 G),[11] suggesting that the Co–O_2 complex abstracts hydrogen from the phenol. When oxygen was bubbled through the resulting solution the signals of the phenoxy radical disappeared and those of the Co–O_2 complex appeared again. The vicissitudes of these ESR signals can be repeated several times, and the peroxy complex **3a** is obtained from the final solution. These results seem to suggest that the formation of **3** involves the radical combination between the phenoxy radical of **2** and the Co–O_2 complex as the reaction of the phenoxy radical with oxygen is very slow.[12] However, the reaction of the phenoxy radical of **2a** with the Co–O_2 complex under oxygen atmosphere leads to the predominant formation of bis(4-oxo-2,5-cyclohexadienyl) peroxide derivative together with a minor amount of **3a**, indicating that the reaction of the phenoxy radical prefers the para position to the ortho position.[13] Very recently, on the other hand, it has been found that the phenolate anion of **2** can be oxygenated only in associated form with the counter metal ion resulting in the quantitative formation of the hydroperoxide **4**. It should be therefore considered that the formation of **3** is preceded by the equilibrium involving electron transfer from Co(salpr) to the phenoxy radical of **2** affording the Co(III) complex of the phenolate of **2**, to which oxygen is inserted to give **3**. Actually, an ESR study revealed that the phenoxy radical of **2** is reduced by Co(salpr)[14] and the oxygenation of the solution in which the phenoxy radical of **2a** and Co(salpr) are mixed in advance under nitrogen afforded only **3a**.

It is interesting to know the chemical reactivity of the present peroxy complexes in connection with the biological oxygenation of phenols, which is currently investigated.

Acknowledgment. This research was supported by the Japan Society for the Promotion of Science.

References and Notes

(1) M. Nozaki in "Molecular Mechanisms of Oxygen Activation", O. Hayaishi, Ed., Academic Press, New York and London, 1974, p 135.

(2) T. Nakazawa, Y. Kojima, H. Fujisawa, M. Nozaki, O. Hayaishi, and T. Yamano, *J. Biol. Chem.*, **240,** 3224 (1965).

(3) G. A. Hamilton in ref 1, p 443.

(4) We previously reported the oxygenation of 2,4,6-tri-*tert*-butylphenol with Co(salpr) to give 1,3,5-tri-*tert*-butyl-4-oxo-2,5-cyclohexadienyldioxycobalt(III)(salpr); A. Nishinaga, K. Watanabe, and T. Matsuura, *Tetrahedron Lett.*, 1291 (1974).

(5) Satisfactory analytical data for all the complexes were obtained.

(6) The absorption shifts to a little longer wavelength region compared to that of the corresponding hydroperoxides (**4**) (ν_{CO} 1660 cm^{-1}) probably attributed to the coordination effect.

(7) A. Nishinaga and A. Rieker, *J. Am. Chem. Soc.*, **98,** 4667 (1976). The structure of all other hydroperoxides (**4b–4h**) are confirmed by the elemental analyses and by their spectral data.

(8) A. Nishinaga, T. Itahara, and T. Matsuura, *Tetrahedron Lett.*, 2467 (1974).

(9) A. Rieker, W. Rundel, and H. Kessler, *Z. Naturforsch. B*, **24,** 547 (1969).

(10) S. Koda, A. Misono, and Y. Uchida, *Bull. Chem. Soc. Jpn.*, **43,** 3143 (1970).

(11) A. Rieker and K. Scheffler, *Justus Liebigs Ann. Chem.*, **689,** 78 (1965).

(12) E. Müller, A. Schick, and K. Scheffler, *Chem. Ber.*, **92,** 474 (1959).

(13) A. Nishinaga, T. Shimizu, and T. Matsura, unpublished data.

(14) From a mixture (1:1) of Co(salpr) and the radical of **2a** in CH_2Cl_2 which was allowed to stand at 0 °C for 1 h under nitrogen **2a** was obtained in 40% yield.[13]

A. Nishinaga,* K. Nishizawa
H. Tomita, T. Matsuura
Department of Synthetic Chemistry
Faculty of Engineering, Kyoto University
Kyoto, Japan

Received October 19, 1976

Additions and Corrections

Stereochemistry of the Reaction of Strained Olefins with Iron Carbonyls [*J. Am. Chem. Soc.*, **96,** 1622 (1974)]. By JEAN GRANDJEAN, PIERRE LASZLO,* and ARMEL STOCKIS, Institut de Chimie, Universite de Liège, Liege, Belgium.

In the matrix regrouping stereoisomers belonging to the trans series (p 1622), the third-line, first-row symbol should read SXTNS instead of SNTNS. We thank N. Dumont for calling this misprint to our attention.

Chain-Length Effects upon the Interaction of Remote Functional Groups. The Low Energy Electron Impact Mass Spectra of α,ω-Dialkoxyalkanes Examined by Ion Cyclotron Resonance Spectroscopy [*J. Am. Chem. Soc.*, **97,** 2355 (1975)]. By THOMAS HELLMAN MORTON* and J. L. BEAUCHAMP, A. A. Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91109, and Metcalf Research Laboratory, Brown University, Providence, Rhode Island 02912.

The formula for compound **7b** in Table III should read "$CH_3OCD_2(CH_2)_2CD_2OCH_3$".

The Mixed Valence State Based on μ-Cyanogen-bis(pentaammineruthenium) [*J. Am. Chem. Soc.*, **97,** 5310 (1975)]. By GLENN M. TOM and HENRY TAUBE,* Department of Chemistry, Stanford University, Stanford, California 94305.

The title complex is by no means the first complex of cyanogen to have been reported as implied in the paper. Those which have been reported include the series $(CO)_5MlNCCNMt(CO)_5$ with Ml = Cr, Mo, W (J. F. Guttenberger, *Angew. Chem., Int. Ed. Engl.*, **6,** 1081 (1967)); $[RhCl(CN)_2(P(Ph)_3)_2C_2N_2$ and $RhClI_2(P(Ph)_3)_2C_2N_2$ (G. Favero, B. Corain, P. Rigo, and A. Turco, *Gazz. Chim. Ital.*, **103,** 297 (1973)).

Comparison of Equilibrium Reactions in the Gaseous and Liquid Phases. A New, Improved Theoretical Estimate [*J. Am. Chem. Soc.*, **98,** 2046 (1976)]. By SIDNEY W. BENSON and G. DAVID MENDENHALL, Department of Thermochemistry and Chemical Kinetics, Stanford Research Institute, Menlo Park, California 94025.

In our treatment of the $N_2O_4 \rightleftharpoons NO_2$ equilibrium we overlooked a very detailed study of this system by P. Gray and P. Rathbone [*J. Chem. Soc.*, 3550 (1958)]. These workers obtained values of ΔH_1 = 17.8 kcal, ΔS_1 = 43.0 eu, and ΔG_1 = 5.3 kcal for the dissociation in liquid N_2O_4 as solvent. Our calculated values of $\Delta H_1{}^+$ = 16.6 kcal, $\Delta S_1{}^+$ = 41.3 eu, and $\Delta G_1{}^+$ = 4.3 kcal are in better agreement with their data than with data from other sources cited in our paper.

Inelastic Electron Tunneling Spectroscopy of Carbon Monoxide Chemisorbed on Alumina-Supported Transition Metals [*J. Am.*