

a quintet attributed to the phenoxy radical of **2a** ($a_H = 1.6$ G),¹¹ suggesting that the Co-O₂ 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-O₂ 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-O₂ 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-O₂ 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.

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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-cyclohexadienyldioxy-cobalt(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. Matsuura, unpublished data.
- (14) From a mixture (1:1) of Co(salpr) and the radical of **2a** in CH₂Cl₂ which was allowed to stand at 0 °C for 1 h under nitrogen **2a** was obtained in 40% yield.¹³

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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, Université de Liège, Liège, 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 " $\text{CH}_3\text{OCD}_2(\text{CH}_2)_2\text{CD}_2\text{OCH}_3$ ".

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)₅-MINCCNMt(CO)₅ with Ml = Cr, Mo, W (J. F. Guttenberger, *Angew. Chem., Int. Ed. Engl.*, **6**, 1081 (1967)); [RhCl(CN)₂(P(Ph)₃)₂C₂N₂ and RhClI₂(P(Ph)₃)₂C₂N₂ (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 N₂O₄ \rightleftharpoons NO₂ 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 $\Delta H_1 = 17.8$ kcal, $\Delta S_1 = 43.0$ eu, and $\Delta G_1 = 5.3$ kcal for the dissociation in liquid N₂O₄ as solvent. Our calculated values of $\Delta H_1^\circ = 16.6$ kcal, $\Delta S_1^\circ = 41.3$ eu, and $\Delta G_1^\circ = 4.3$ 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.*