Autoxidation of Thiols Catalysed by a Tetraaza[14]-annulene–Cobalt(II) Complex

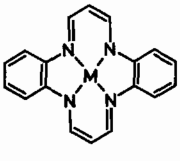
KAZUNORI SAKATA*, SHIGERU WADA
and MAMORU HASHIMOTO

Department of Chemistry, Faculty of Engineering, Kyushu Institute of Technology, Tobata-ku, Kitakyushu 804, Japan

(Received March 4, 1988)

Since most of the research for tetraaza[14]-annulene complexes has been concerned with structural and spectroscopic studies [1], very little attention has been paid to the potential use of these complexes as catalysts for the oxidation of thiols.

Many methods have been described for the catalytic oxidation of thiols to the corresponding disulfide with sodium hydroxide, iodine, bromine and phenyl dimedonyl iodone [2]. Although iron(III) chloride and potassium hexacyanoferrate(III) relating to a transition metal complex have been employed as catalysts in order to obtain a disulfide [3], there is no example of a cobalt complex. Therefore, we now report the result of an investigation for the autoxidation of a variety of thiols using tetraaza-[14]annulene–cobalt(II) complex, dibenzo[b,i]-[1,4,8,11]tetraazacyclotetradecinato)cobalt(II) (**1-Co**).



1-M
M = Co(II), Ni(II)

Experimental

Physical Measurements

Mass spectral measurements were performed on a JEOL JMS-DX 300 gas chromatograph-mass spectrometer at 70 eV. Melting points were measured on a Yamato hot-stage apparatus. Infrared spectra in the area of 400–4000 cm^{-1} were carried out with a Hitachi 260-10 spectrophotometer at room temperature by a KBr disk and neat methods. Proton NMR measurements were recorded on a JEOL JNM-FX 60 spectrometer operating in the Fourier transform mode. The NMR spectra were run in chloroform-d. Electronic spectra covering the 300–600 nm region were taken on a Shimadzu UV-200S double beam spectrophotometer for chloroform at room temperature.

Preparation of Tetraaza[14]annulene–Metal Complexes

(Dibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)cobalt(II) (1-Co) and (dibenzo[b,i]-[1,4,8,11]tetraazacyclotetradecinato)nickel(II) (1-Ni)

The preparative procedures for **1-Co** and **1-Ni** have been described previously [1e, 1g].

Autoxidation of Various Thiols

Usual procedure for the autoxidation of various thiols utilizing 1-Co or 1-Ni

A mixture of the thiols (10 mmol) and the complex (0.25 mmol) in chloroform (100 ml) is stirred at 25.0 ± 1.0 °C for 2 h, while air (3.5–4.5 dm^3 min^{-1}) is conducted into it. After that, the solvent is removed under reduced pressure. When the product

TABLE I. Autoxidation Products for Various Thiols in Chloroform Utilizing **1-Co**[a] Maintained at 25.0 ± 1.0 °C

Substituent group (R)	Yield of thiols (%)	Molecular weight[b] found (M^+)	Molecular weight[b] calculated (M)	Melting point (°C) this work	Melting point (°C) literature	Reference
4-H	71	218	218.02	55.5–56.0	62	2d
4-CH_3	49	246	246.05	45.0–46.0	46–48	2f
4-NO_2	66	308	307.99	180.0–181.0	182	4
4-Cl	54	286	285.94	68.5–69.5	70–71	5
4-NH_2	43	248	248.04	70.0–71.5	75–76	6
4-OCH_3	73	278	278.04	43.0–44.0	44	7
3-NH_2	39	248	248.04	c		8
2-CH_3	91	246	246.05	39.0–41.0	38–39	7
2-COOH	29	306	306.00	298.0–299.0	287–289	2f

[a] 1-Co, (dibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)cobalt(II). [b] The molecular weight was determined by the mass spectral method. [c] Viscous liquid.

---

*Author to whom correspondence should be addressed.

0020-1693/88/$3.50

© Elsevier Sequoia/Printed in Switzerland

TABLE II. Autoxidation for Thiophenol in Chloroform on Addition of 4-Aminopyridine Maintained at 25.0 ± 1.0 °C

Catalyst of 1-Co[a] (mmol)	Added 4-amino-pyridine (mmol)	Yield of diphenyldisulfide (%)
0.25	none	71
0.25	0.25	49

[a] 1-Co, (dibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)-cobalt(II).

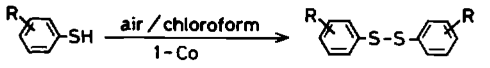
is a solid, it is recrystallized from methanol or dichloromethane to give the pure disulfide. On the other hand, when the product is in a liquid state, it is distilled *in vacuo* to give the pure disulfide. Melting points and parent peaks of mass spectra for all compounds are summarized in Table I with others obtained from the literature. The structure of these products has also been confirmed by IR and NMR spectroscopies.

Usual procedure for the autoxidation of thiophenol utilizing 1-Co and 4-aminopyridine

The autoxidation reaction of **1-Co** (0.25 mmol), thiophenol (10 mmol) and 4-aminopyridine (0.25 mmol), following the above manner, gives rise to the pure diphenyldisulfide with the yields given in Table II.

Results and Discussion

We have found that, in an atmosphere of air, under mild conditions, the cobalt(II) complex, **1-Co**, functions as an efficient catalyst for the air oxidation of various thiols. This oxidation reaction is described by eqn. (1).



(1)

The reaction was carried out by stirring a chloroform solution of the thiol in the presence of **1-Co** (2.5 mol%) at 25.0 ± 1.0 °C. The color of the reaction mixture changed during the reaction from dark red to black, exhibiting irreversible oxidation of a part of the catalyst, too. Under these conditions, the yield of the disulfide is good in most cases as shown in Table I. The catalytic effect of **1-Co** is clearly demonstrated by the yield of the disulfide in comparison with that of the blank practice listed in Table III. The present investigation has shown that no product other than that given in eqn. (1) is detectable during the reaction. According to the data in Table I, it can be presumed that with **1-Co**, substituent groups in the aromatic ring affect the rate of oxidation of thiols due to electronic and/or steric effects. However, it is not clear at present whether the electronic or the steric effect contributes to the oxidation reaction of thiols.

TABLE III. Autoxidation for Thiophenol in Chloroform Maintained at 25.0 ± 1.0 °C under Various Conditions

Catalyst[a]	Gas used	Yield of diphenyldisulfide (%)
1-Co	air	71
1-Ni	air	0
1-Co	nitrogen	~0
No catalyst added	air	0

[a] 1-Co, (dibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)-cobalt(II); 1-Ni, (dibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)nickel(II).

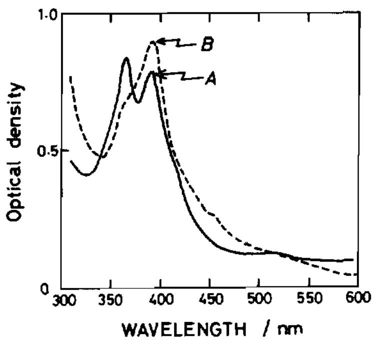
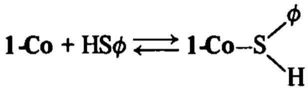


Fig. 1. Electronic spectra for (dibenzo[b,i][1,4,8,11]tetraazacyclotetradecinato)cobalt(II) complex (1-Co) in chloroform at room temperature. A, 1-Co; B, 1-Co (4-aminothiophenol was added, an equal mol relative to 1-Co).

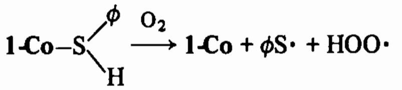
To gain further insight into the character of the cobalt(II) complex-catalysed oxidation, the reaction is performed as follows. The nickel(II) complex, **1-Ni**, used in this work does not catalyse the oxidation of thiols under the mild conditions as given in Table III. The visible spectrum of **1-Ni** does not change upon addition of 4-aminothiophenol. Under surrounding nitrogen, the thiophenol also does not convert to any product using **1-Co** as a catalyst. The addition of 4-aminopyridine as an axial base to **1-Co** makes the yield of disulfide lower as seen in Table II. The spectral change of **1-Co** in the range of 300–600 nm upon addition of 4-aminothiophenol is shown in Fig. 1. This spectral behavior is similar to that observed for the interaction of **1-Co** with pyridine [1g]. It is not difficult to appreciate that 4-aminopyridine coordinates the axial site of **1-Co** and interferes with the coordination of the thiol to the cobalt(II) complex. Accordingly, the catalytic activity of the complex rests upon the nature of the axial site.

The interaction of **1-Co** with the thiol involves the initial equilibrium

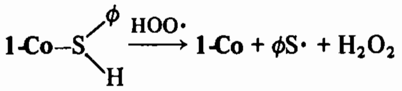


$$\mathbf{1\text{-}Co} + \mathrm{HS}\phi \rightleftharpoons \mathbf{1\text{-}Co}\text{–}\mathrm{S}\begin{smallmatrix}\phi\\ \mathrm{H}\end{smallmatrix} \qquad (2)$$

The catalytic oxidation mentioned in this work appears to involve dehydrogenation, although no conclusive proof of this step can be presented. The dehydrogenation of the thiol can be visualized by postulating the stepwise hydrogen-atom transfer to dioxygen, being brought to the formation of a disulfide. In this system the oxidation of the thiol to its corresponding disulfide may be described by the following mechanistic paths



$$\mathbf{1\text{-}Co}\text{–}\mathrm{S}\begin{smallmatrix}\phi\\ \mathrm{H}\end{smallmatrix} \xrightarrow{O_2} \mathbf{1\text{-}Co} + \phi\mathrm{S}\cdot + \mathrm{HOO}\cdot \qquad (3)$$



$$\mathbf{1\text{-}Co}\text{–}\mathrm{S}\begin{smallmatrix}\phi\\ \mathrm{H}\end{smallmatrix} \xrightarrow{\mathrm{HOO}\cdot} \mathbf{1\text{-}Co} + \phi\mathrm{S}\cdot + \mathrm{H_2O_2} \qquad (4)$$

$$2\phi\mathrm{S}\cdot \longrightarrow \phi\text{–S–S–}\phi \qquad (5)$$

ϕ = aryl

followed by

$$\mathrm{H_2O_2} + 2\phi\mathrm{SH} \longrightarrow \phi\text{–S–S–}\phi + 2\mathrm{H_2O} \qquad (6)$$

In conclusion, in an atmosphere of air, under mild conditions, the cobalt(II) complex, **1-Co**, catalyses the oxidation of thiols, added in 2.5 mol%. The oxidation mechanism is presumed to follow eqns. (2)–(6). The substituent groups in the aromatic ring of thiols do not indicate clearly whether the influence on the rate of oxidation is due to electronic and/or steric effects. This is one of the most convenient methods for obtaining disulfides.

References

1 (a) H. Hiller, P. Dimroth and H. Pfitzner, *Liebigs Ann. Chem., 717*, 137 (1968); (b) F. A. L'Eplattenier and A. Pugin, *Helv. Chim. Acta, 58*, 917 (1975); (c) R. Mueller and D. Woehrle, *Makromol. Chem., 176*, 2775 (1975); (d) M. C. Weiss, G. Gordon and V. L. Goedken, *J. Am. Chem. Soc., 98*, 8021 (1976); (e) K. Sakata, M. Hashimoto, N. Tagami and Y. Murakami, *Bull. Chem. Soc. Jpn., 53*, 2262 (1980); (f) K. Sakata, H. Nakamura and M. Hashimoto, *Inorg. Chim. Acta, 83*, L67 (1984); (g) K. Sakata, M. Hashimoto and H. Yoshino, *Inorg. Chim. Acta, 99*, 231 (1985).

2 (a) A. L. Vogel, 'A Textbook of Practical Organic Chemistry', Longmann, Green and Co., London, 1959; (b) F. Kurzer and P. M. Sanderson, *J. Chem. Soc.*, 1058 (1959); (c) T. J. Wallace and A. Schriesheim, *J. Org. Chem., 27*, 1514 (1962); (d) T. J. Wallace, A. Schriesheim and W. Bartok, *J. Org. Chem., 28*, 1311 (1963); (e) T. J. Wallace, N. Jacobson and A. Schriesheim, *Nature, 201*, 609 (1963); (f) G. F. Koser, S.-M. Linden and Y.-J. Shih, *J. Org. Chem., 43*, 2676 (1978).

3 (a) V. O. Lukashevich and M. M. Sergeeva, *Zh. Obshch. Khim., 19*, 1493 (1940); *Chem. Abstr., 44*, 3452 (1950); (b) A. Alcalay, *Helv. Chim. Acta, 30*, 578 (1947); (c) A. H. Herz and D. S. Tarebell, *J. Am. Chem. Soc., 75*, 4657 (1953); (d) C. S. Marvel, T. H. Shepherd, C. King, J. Economy and E. D. Vessel, *J. Org. Chem., 21*, 1173 (1956); (e) P. M. Pojer and I. D. Rae, *Aust. J. Chem., 25*, 1737 (1972).

4 E. Vinkler and F. Klivenyi, *Acta Chim. Acad. Sci. Hung., 5*, 271 (1954).

5 E. Vinkler and F. Klivenyi, *Acta Chim. Acad. Sci. Hung., 5*, 159 (1954).

6 C. C. Price and G. W. Stacy, *Org. Synth., Coll. 3*, 86 (1955).

7 R. C. Weast (ed.), 'CRC Handbook of Chemistry and Physics', 65th edn., Chemical Rubber Publishing Co., Cleveland, Ohio, 1984.

8 *Beilstein, 13*, 426 (1930).