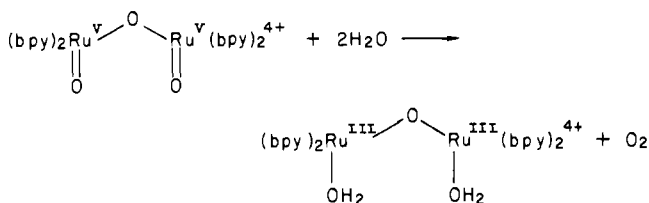RuORu(OH)$_2$(bpy)$_2$$^{4+}$ or its mononuclear precursor, large amounts of O$_2$ can be obtained (runs 6-10), with the catalytic process probably occuring on two sites, with simultaneous exchange of protons and electrons, as earlier postulated:[7]

Finally, the experimental results of homogeneous catalysis of water oxidation by ruthenium complexes must be regarded with great caution. The decomposition products of the compounds are often ruthenium oxides, and thus they are likely to be catalytically active.[38,39] Knowing how difficult it is to definitely prove that a reacting medium remains homogeneous, one should exercise great care when drawing conclusions.

Conclusion

Several complexes of ruthenium(II), containing two molecules of sterically hindering diimine as ligands, have been prepared and

characterized. None of these complexes display catalytic activity for O$_2$ formation from water, in the presence of excess cerium(IV). In these compounds, the presence of methyl substituents prevents condensation to μ-oxo polynuclear ruthenium complexes. On the contrary, the dinuclear complex (bpy)$_2$(H$_2$O)RuORu(H$_2$O)-(bpy)$_2$$^{4+}$ acts as an efficient catalyst. With this compound, up to 13.2 mol of O$_2$/mol of μ-oxo complex have been obtained. It seems therefore clear that a multimetallic system is required to promote water oxidation to oxygen, in analogy with the postulated mechanism of the manganese-containing enzyme of photosystem II in natural photosynthesis.[3]

(38) Lehn, J. M.; Sauvage, J. P.; Ziessel, R. *Nouv. J. Chim.* **1979**, *3*, 423; Collin, J. P.; Lehn, J. M.; Ziessel, R. *Nouv. J. Chim.* **1982**, *6*, 405.
(39) Kalyanasundaram, K.; Grätzel, M. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 701.
(40) Newkome, G. R.; Pantaleo, D. C.; Pucket, W. E.; Ziefle, P. L.; Deutsch, W. A. *J. Inorg. Nucl. Chem.* **1981**, *43*, 1529.

Contribution from the Department of Chemical Engineering, Faculty of Engineering, Kobe University, Nada, Kobe 657, Japan

Cobalt(II) Chelate Catalyzed Oxidation of 3,5-Di-*tert*-butylcatechol

Shigeru Tsuruya,* Shun-ichi Yanai, and Mitsuo Masai

Co(II) chelate catalyzed oxidation of 3,5-di-*tert*-butylcatechol (3,5-DtBC) has been studied in the nonaqueous phase under O$_2$ atmosphere at room temperature. The only oxidation product is a corresponding *o*-benzoquinone, 3,5-di-*tert*-butyl-*o*-benzoquinone (3,5-DtBQ), irrespective of the Co(II) chelate catalyst used. The following overall stoichiometric equation without H$_2$O$_2$ accumulation is suggested for the Co^{II}(acac)$_2$ catalyzed oxidation of 3,5-DtBC by O$_2$ absorption measurements and analysis of the oxidation product and H$_2$O$_2$: 3,5-DtBC + ^{1}/$_2$O$_2$ → 3,5-DtBQ + H$_2$O. Variation in cobalt(II) chelates is found to appreciably affect the catalytic activity in 3,5-DtBC oxidation. The effect of the addition of amine on the oxidation activity is discussed in connection with the behavior of the electronic absorption spectra of the cobalt-amine catalytic systems. By observation of the catalytic activity of Co(II) chelate-pyridine derivative systems, the importance of the affinity of the Co(II) chelate toward the oxygen molecule is suggested. The rate of Co^{II}(acac)$_2$ catalyzed oxidation is found to be first order with respect to the concentrations of Co^{II}(acac)$_2$ and 3,5-DtBC, respectively, and also first order in the partial pressure of molecular oxygen. The kinetic parameters for the 3,5-DtBC oxidation are estimated in the temperature range 286-309 K. A reaction scheme is proposed to account for these results. It involves the reaction of a Co^{II}(acac)$_2$-3,5-DtBC complex with O$_2$ to give a ternary 3,5-DtBC-Co^{II}-O$_2$ complex and the intramolecular reaction of the ternary oxygenated Co complex to give 3,5-DtBQ in the rate-determining step.

Introduction

Liquid-phase oxidation of catechol and its derivatives catalyzed by metal complexes has been the subject of considerable interest in recent years. A variety of metal complexes, e.g. Cu(II),[1-6] Fe(III),[7-13] Ru(II),[14] and V(IV)[15] complexes, that effect the ox-

idative cleavage of catechol have been reported. Oxidases or enzymes catalyzing reactions of oxygen are a particularly intriguing area in the field of reaction mechanisms. Some of the most interesting oxidases are in the group exemplified by the enzyme pyrocatechase, in which entire oxygen molecules are incorporated into an enzyme molecule in what appears to be a single reaction.[16] The metal ion catalyzed oxidation of 3,5-di-*tert*-butylcatechol by

(1) Tsuji, J.; Takayanagi, H. *J. Am. Chem. Soc.* **1974**, *96*, 7349.
(2) Tsuji, J.; Takayanagi, H.; Sakai, I. *Tetrahedron Lett.* **1975**, *16*, 1245.
(3) Rogic, M. M.; Demmin, T. R.; Hammond, W. B. *J. Am. Chem. Soc.* **1976**, *98*, 7441.
(4) Rogic, M. M.; Demmin, T. R. *J. Am. Chem. Soc.* **1978**, *100*, 5472.
(5) Tsuji, J.; Takayanagi, H. *Chem. Lett.* **1980**, 65.
(6) Demmin, T. R.; Swendorff, M. D.; Rogic, M. M. *J. Am. Chem. Soc.* **1981**, *103*, 5795.
(7) Funabiki, T.; Sakamoto, H.; Yoshida, S.; Tarama, K. *J. Chem. Soc., Chem. Commun.* **1979**, 754.
(8) Laffer, R. B.; Heistand, R. H.; Que, L., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 3947.
(9) Weller, M. G.; Weser, U. *J. Am. Chem. Soc.* **1982**, *104*, 3752.

(10) Que, L., Jr. *Coord. Chem. Rev.* **1983**, *50*, 73.
(11) Funabiki, T.; Mizoguchi, A.; Yoshida, S. *Chem. Lett.* **1983**, 917.
(12) White, L. S.; Nilsson, P. V.; Pignolet, L. H.; Que, L., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 8312.
(13) Nishida, Y.; Shimo, H.; Kida, S. *J. Chem. Soc., Chem. Commun.* **1984**, 1611.
(14) Matsumoto, M.; Kuroda, K. *J. Am. Chem. Soc.* **1982**, *104*, 1433.
(15) Tatsuno, Y.; Tatsuno, M.; Otsuka, S. *J. Chem. Soc., Chem. Commun.* **1982**, 1100.
(16) Hayaishi, O.; Hashimoto, K. *J. Biochem.* (*Tokyo*) **1950**, *37*, 371.

O_2 has been carried out in the presence of metal salts in slightly alkaline aqueous methanol in which the main product was 3,5-di-*tert*-butyl-*o*-benzoquinone.[17] Martell and co-workers have reported kinetic studies on the autoxidation of 3,5-di-*tert*-butylcatechol in 50% methanol by manometric, ESR, and spectrophotometric methods.[18] Also, studies of the metal chelate catalyzed oxidation of pyrocatechol to *o*-benzoquinone in which bidentate chelating agents such as 4-nitrocatechol and tetrabromocatechol have been used as auxiliary ligands have been reported.[19] The metal chelate catalyzed oxidations of catechol derivatives have been compared to free Mn(II) and base catalyzed autoxidations. It would be considered that such a study as metal catalyzed oxidation could be significant in providing new information on the activation of oxygen by metal ions, a subject of interest to synthetic organic chemists.

From the point of view of the activation of an oxygen molecule, the ability of transition-metal ions to reversibly coordinate O_2 (synthetic oxygen carriers) has attracted the interest of chemists for their possible relationship to natural oxygen carriers such as hemoglobin and myoglobin. A number of reviews deal with the structures, binding, and reactivities of dioxygen complexes.[20,21] Some of the first synthetic systems reported to bind O_2 were cobalt(II) complexes.[22] However, only 10 years ago it was demonstrated that a wide variety of ligand environments about cobalt(II) result in reversible systems.[23-28]

In this paper we describe the oxidation of 3,5-di-*tert*-butylcatechol (3,5-DtBC) in a nonaqueous solution catalyzed by a variety of cobalt chelate complexes, in which only 3,5-di-*tert*-butyl-*o*-benzoquinone (3,5-DtBQ) is the oxidation product. The effect of amine addition on the oxidation activity is investigated in connection with the oxygenation of the cobalt(II) complex and the role of the cobalt(II)–O_2 adduct to the oxidation of 3,5-DtBC. On the basis of the kinetic results obtained, a plausible reaction scheme for the oxidation of 3,5-DtBC catalyzed by the Co(II) complex is presented.

Experimental Section

Measurements. ¹H NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as an internal standard on a JEOL PS 100 (100-MHz) spectrometer. IR spectra were measured by a KBr method using a Hitachi EPIG-2 spectrophotometer, unless otherwise stated. Electronic absorption spectra were taken on a JASCO UVIDEC-420 spectrophotometer using a 1-cm quartz cell at room temperature. Melting points were measured on a Mitamura Riken melting point apparatus and were uncorrected. GLC analyses were carried out on a Shimazu GC-6A instrument with a FID using a 2-m glass column (diameter 3 mm) of 10% silicone SE-30 on Uniport B operating at 473 K with nitrogen as a carrier gas (20 mL/min). Elemental analyses were performed at the Microanalysis Center, Kyoto University.

Materials. 3,5-Di-*tert*-butylcatechol (3,5-DtBC) was recrystallized from *n*-hexane and dried under vacuum. Pyridine and piperidine were reagent grade products used after distillation. α-Picoline, γ-picoline, 4-cyanopyridine, 4-aminopyridine, diethylamine, and triethylamine were reagent grade products and were used without further purification. Chloroform and methanol were purified by distillation. Bis(acetylacetonato)cobalt(II) was purchased commercially (reagent grade) and used after drying under vacuum. The seven cobalt chelate complexes used as catalysts were prepared by the same procedures mentioned in the literature. All Co(II) complexes synthesized gave satisfactory elemental analyses. The following materials were used: chloro(pyridine)cobal-

Table I. Oxidation of 3,5-DtBC Catalyzed by Co(II) Chelate Complexes[a]

catalytic system Co(II) complex (mM)	amine added (mM)	yield of 3,5-DtBQ, %[b]
bis(*N*-phenylsalicylaldiminato)cobalt(II)	pyridine (25)	97
bis(benzoylacetonato)cobalt(II) (1.0)		96
bis(acetylacetonato)cobalt(II) (0.6)	imidazole (0.6)	97
cobaloxime–bis(pyridine) (1.0)		98

[a] 100 mM 3,5-DtBC; solvent 50 mL of $CHCl_3$; 303 K; O_2 atmosphere. [b] Based on 3,5-DtBC.

oxime(III),[29] bis(salicylaldehydato)cobalt(II),[30] bis(*N*-phenylsalicylaldiminato)cobalt(II),[31] bis(*N*-cyclohexylsalicylaldiminato)cobalt(II),[31] bis(benzoylacetonato)cobalt(II) dihydrate,[32] cobaloxime(II)–pyridine adduct,[29] and bis(ethyl benzoylacetato)cobalt(II).[32]

Oxidation Methods. Reactions were run in 50-mL round-bottom flasks connected to a mechanical stirrer, a gas-inlet tube, a condenser with a drying tube, and a dropping funnel under an oxygen atmosphere at a controlled temperature. In a typical experiment, prescribed amounts of Co(acac)₂ complex (0.026 g, 0.1 mmol) and pyridine (0.396 g, 5 mmol) were dissolved in 40 mL of chloroform. The oxidation reaction was started by adding a chloroform solution (10 mL) of 3,5-DtBC (1.11 g, 5 mmol) to the catalytic solution by means of a dropping funnel attached to the reaction vessel. Once the reaction was started, aliquots (0.1 mL) were removed and transferred to capped samle tubes for a known time interval and stored in a dry ice–methanol bath for later analysis by GLC. Initial rates were determined by using six to ten points per run. The only reaction product found was 3,5-di-*tert*-butyl-*o*-benzoquinone (3,5-DtBQ), which was obtained in essentially quantitative yield and characterized by elemental analysis, melting point, IR, and NMR data. Anal. Calcd for $C_{16}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.26; H, 9.22. Mp: 386 K (lit. mp 386.2–386.8 K).[18] ¹H NMR: δ 1.26 (s, 1 H, ring), 6.21 (1 H, ring), 6.98 (18 H, *tert*-butyl).

Oxygen Absorption Measurements. Oxygen absorption measurements were conducted in a constant-pressure gas absorption apparatus consisting of a reaction vessel with a magnetic stirrer connected to a gas buret and a U-tube manometer. The vessel, thermostated at 303 K, was attached to a pressure-equalized dropping funnel into which a chloroform solution of 3,5-DtBC was added. The whole reaction system was saturated with oxygen for 40–60 min under vigorous stirring. When equilibrium was obtained, the 3,5-DtBC solution was added to the catalytic solution in the reaction vessel. Oxygen consumption at a constant pressure was measured at regular time intervals. This pressure was regulated by the evolution of gas in the electrolysis of water and controlled by an electric relay.

Analytical Procedure for Hydrogen Peroxide. Reaction mixtures, after being quenched with acid to stop further oxidation, were extracted twice with water, and the aqueous layer was analyzed by the usual method of iodometry.[33] The extracted aqueous layer was transferred into 100 mL of 2 N H_2SO_4 solution containing 1 g of potassium iodide and titrated with 0.1 N sodium thiosulfate with starch solution as an indicator.

Results

Data on the catalyzed oxidation of 3,5-DtBC are shown in Table I. The yields of 3,5-DtBC have been measured under conditions of changing Co(II) chelate complex systems and of varying concentrations of the Co(II) chelate complex. Chloroform was used as solvent, and the tabulated yields are based on initial 3,5-DtBC. No attempt has been made to optimize the yield of 3,5-DtBC in a commercial sense. It is apparent from Table I that only 3,5-DtBC was produced almost quantitatively, irrespective of the catalytic system used, and that any other oxidation products, such as carbon–carbon bond cleavage products, were not obtained. Thus, the principal product seems to be only 3,5-DtBC for the

(17) Grinstead, R. R. *Biochemistry* **1964**, *3*, 1308.
(18) Tyson, C. A.; Martell, A. E. *J. Phys. Chem.* **1970**, *74*, 2601.
(19) Tyson, C. A.; Martell, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 939.
(20) McLendon, G.; Martell, A. E. *Coord. Chem. Rev.* **1976**, *19*, 1.
(21) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 139.
(22) Bailes, R. H.; Calvin, M. *J. Am. Chem. Soc.* **1947**, *69*, 1886.
(23) Hoffman, B. M.; Diemente, D. L.; Basolo, F. *J. Am. Chem. Soc.* **1970**, *92*, 61.
(24) Crumbliss, A. L.; Basolo, F. *J. Am. Chem. Soc.* **1970**, *92*, 55.
(25) Walker, F. A. *J. Am. Chem. Soc.* **1970**, *92*, 4235.
(26) Ochiai, E.-I. *J. Inorg. Nucl. Chem.* **1973**, *35*, 1727.
(27) Wayland, B. B.; Minkiewiez, J. V.; Abd-Elmageed, M. E. *J. Am. Chem. Soc.* **1974**, *96*, 2795.
(28) Wayland, B. B.; Abd-Elmageed, M. E. *J. Am. Chem. Soc.* **1974**, *96*, 9809.

(29) Schrauzer, G. N. *Inorg. Synth.* **1968**, *11*, 61.
(30) Pfeiffer, P.; Breith, E.; Lubbe, E.; Tsumaki, T. *Justus Liebigs Ann. Chem.* **1933**, *503*, 84.
(31) Sacconi, L.; Ciamplini, M.; Maggio, F.; Cavasino, F. P. *J. Am. Chem. Soc.* **1962**, *84*, 3246.
(32) Cotton, F. A.; Holm, R. H. *J. Am. Chem. Soc.* **1960**, *82*, 2979.
(33) Vogel, A. I. "A Text Book of Quantitative Inorganic Analysis", 3rd ed.; Wiley: New York, 1961; p 343.
(34) Sakamoto, H.; Funabiki, T.; Yoshida, S.; Tarama, K. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2760.
(35) "International Critical Table"; McGraw-Hill: New York, 1928; Vol. III, p 271.
(36) "Kagaku Benran (Kiso-hen II)"; Maruzen: Tokyo, 1966; p 627.

Table II. Stoichiometry of Co(II) Chelate Catalyzed Oxidation of 3,5-DtBC[a]

| catalytic system	% O₂ consumed[b]	% 3,5-DtBQ produced[c]	% H₂O₂ produced[d]
bis(acetylacetonato)cobalt(II)[e]	104	100	5.7
	21	19	0.0
bis(*N*-phenylsalicylaldiminato)cobalt(II)[f]	102	100	0.0
bis(*N*-cyclohexylsalicylaldiminato)cobalt(II)–pyridine[g]	96	100	2.3
	79	84	0.0
bis(ethyl benzoylacetato)cobalt(II)–pyridine[h]	100	100	1.1

[a] Solvent 20 mL of CHCl₃. [b] Conforms to the equation 3,5-DtBC + ¹/₂O₂ → 3,5-DtBQ + H₂O. [c] Determined by GLC. [d] Determined titrimetrically by the iodometry method. [e] 293 K; 0.4 mM Co(II); 29.3 mM 3,5-DtBC. [f] 288 K; 1.7 mM Co(II); 17.3 mM 3,5-DtBC. [g] 288 K; 0.6 mM Co(II); 45.4 mM 3,5-DtBC; 600 mM pyridine. [h] 303 K; 0.6 mM Co(II); 44.5 mM 3,5-DtBC; 600 mM pyridine.

oxidation of 3,5-DtBC catalyzed by cobalt(II) chelate complexes according to the following reaction:
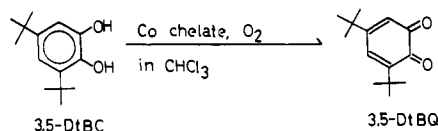

The reaction of 3,5-DtBC with $Co^{II}(acac)_2$ in chloroform or chloroform + CH₃OH solvent was performed under a nitrogen atmosphere to study the role of oxygen (100 mM 3,5-DtBC; 3.8–8.5 mM $Co^{II}(acac)_2$; 303 K; 4–6 h). However, no oxidation product was formed, and the starting 3,5-DtBC was recovered quantitatively. Also, the $Co^{III}(acac)_3$–pyridine system under a N₂ atmosphere (100 mL 3,5-DtBC; 12 mM $Co^{III}(acac)_3$; 200 mM pyridine; 50 mL of CHCl₃; 303 K) was tried as a catalyst for 3,5-DtBC oxidation in place of $Co^{II}(acac)_2$. It was found that $Co^{III}(acac)_3$ under a nitrogen atmosphere had no catalytic activity for 3,5-DtBC oxidation, just as for the $Co^{II}(acac)_2$ system under a nitrogen atmosphere. This result may suggest that oxygen must participate directly in the oxidation of 3,5-DtBC.

Stoichiometry of Co(II) Chelate Catalyzed Oxidation of 3,5-DtBC. Figure 1 shows the relationship between the amounts of oxygen absorption vs. reaction time during the oxidation of 3,5-DtBC catalyzed by $Co^{II}(acac)_2$ and bis(*N*-phenylsalicylaldiminato)cobalt(II). Both dotted straight lines in Figure 1 show the oxygen amount calculated based on the equation 3,5-DtBC + ¹/₂O₂ → 3,5-DtBQ + H₂O. The stoichiometries of both Co(II) chelate catalyzed oxidations were determined by product analysis and O₂-uptake experiments. The results are given in Table II. The reactions produce 100% of the quinone and require a 3,5-DtBc:O₂ ratio of 2:1. Also, there was little H₂O₂ accumulation during the 3,5-DtBC oxidation. Thus with the Co(II) chelate complex catalysts, the stoichiometry for the oxidation of 3,5-DtBC seems to conform to the equation
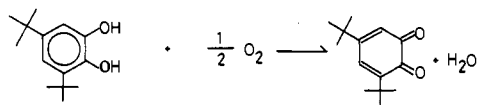
rather than
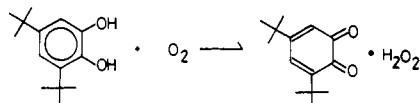
Oxidation Activity of Co(II) Chelate Complexes. Data on the Co(II) chelates and simple Co(II) salts that catalyzed the oxidation of 3,5-DtBC are shown in Table III. The initial catalytic activity for the oxidation of 3,5-DtBC was due to the rate of oxygen absorption. It is apparent that the oxidation activity of simple Co(II) salts, like cobalt(II) nitrate, was lower than that of the corresponding chelate complexes. Particularly, only cobalt(II) nitrate without amine had no catalytic activity under the present reaction conditions. The addition of pyridine to the cobalt(II) nitrate catalyst induced catalytic activity, though it was rather low. The effect of the formal charge of the Co ions on the catalytic activity in the oxidation is significant. When Co(III) catalsyts were used, the initial rates were lower than those for the corresponding Co(II) catalysts. In the cobalt(II) chelates, the com-
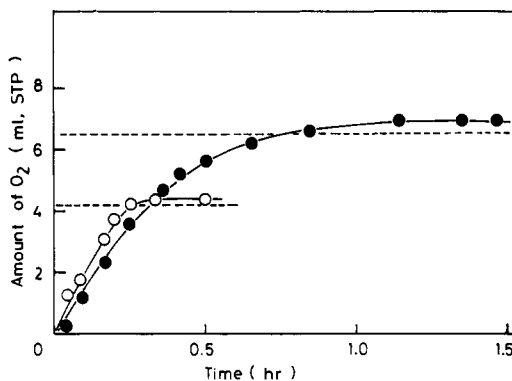

Figure 1. Plot of absorbed O₂ vs. reaction time: ●, 29.3 mM 3,5-DtBC; 0.4 mM Co(acac)₂, 20 mL of CHCl₃, 288 K; ○, 18.1 mM 3,5-DtBC, 3.68 mM bis(*N*-phenylsalicylaldiminato)cobalt(II), 20 mL of CHCl₃; 288 K; ---, theoretical O₂ amount calculated on the basis of 3,5-DtBC + ¹/₂O₂ → 3,5-DtBQ + H₂O.

Table III. Catalytic Activity of Co(II) and Co(III) Complexes for 3,5-DtBC Oxidation[a]

catalyst	$r_{3,5-DtBQ}$, mol/(L s)
bis(acetylacetonato)cobalt(II)	1.6 × 10⁻³
bis(benzoylacetonato)cobalt(II)	1.6 × 10⁻³
bis(ethyl benzoylacetato)cobalt(II)	1.8 × 10⁻³
bis(*N*-cyclohexylsalicylaldiminato)cobalt(II)	1.2 × 10⁻³
bis(*N*-phenylsalicylaldiminato)cobalt(II)	8.6 × 10⁻⁴
cobaloxime(II)–bis(pyridine)	2.1 × 10⁻⁴
tris(acetylacetonato)cobalt(III)	1.3 × 10⁻⁴
chloro(pyridine)cobaloxime(III)[b]	0
cobalt(II) acetate	4.0 × 10⁻⁵
cobalt(II) nitrate	0
cobalt(II) nitrate–pyridine[c]	2.8 × 10⁻⁶

[a] 100 mM 3,5-DtBc; 300 K; 1.0 mM Co(II) or Co(III) catalyst. [b] 3.2 mM. [c] 250 mM pyridine.

plexes in which cobalt(II) ion is chelated by four oxygen atoms, such as $Co^{II}(acac)_2$, have been found to be the most active, and the chelates in which the cobalt(II) ion is surrounded by two oxygen and two nitrogen atoms have intermediate activity. Cobaloxime(II)–bis(pyridine), in which the cobalt(II) ion was surrounded by four nitrogen atoms, had the lowest activity for 3,5-DtBC oxidation, though a part of the cobalt(II) ion of the cobaloxime(II)–bis(pyridine) complex might be oxidized to the cobalt(III) ion because of its ease of oxidation.

The cobalt(III) chelates, $Co^{III}(acac)_3$ and chloro(pyridine)cobaloxime(III), were also used as catalysts for 3,5-DtBC oxidation, as shown in Table III. At first it is evident that the cobalt(III) chelate had lower catalytic activity for 3,5-DtBC oxidation than did the corresponding Co(II) chelate (1.6 × 10⁻³ mol/(L s) for $Co^{II}(acac)_2$ and 1.3 × 10⁻⁴ mol/(L s) for $Co^{III}(acac)_3$). Also, the cobalt(III) chelate in which the cobalt(III) ion was surrounded by oxygen atoms ($Co^{III}(acac)_3$) had higher activity than that in which the cobalt(III) ion was surrounded by nitrogen atoms (chloro(pyridine)cobaloxime(III)). A similar trend was observed with the cobalt(II) chelate catalytic systems.

Effect of Amine Addition of 3,5-DtBC Oxidation. Generally, addition of amine derivatives was found to increase the activity

Table IV. Effect of Amine on 3,5-DtBC Oxidation[a]

catalyst	catalyst concn, mM	amine added (mM)	$r_{3,5\text{-DtBQ}}$, mol/(L s)
bis(acetylacetonato)cobalt(II)	0.48		3.8×10^{-5}
	0.48	α-picoline (10)	3.9×10^{-5}
	0.48	γ-picoline (10)	5.1×10^{-5}
	0.48	ethylenediamine (3.0)	0
	0.60		4.9×10^{-5}
	0.60	pyridine (2.5)	6.0×10^{-5}
	0.60	imidazole (0.6)	9.0×10^{-5}
bis(benzoylacetonato)cobalt(II)	1.0		8.0×10^{-5}
	1.0	pyridine (2.5)	1.7×10^{-4}
cobaloxime(II)–bis(pyridine)	1.0		1.0×10^{-6}
	1.0	piperidine (1.0)	4.4×10^{-5}
chloro(pyridine)cobaloxime(III)	3.2		0
	3.2	4-aminopyridine (100)	0
	0.3	piperidine (230)	4.9×10^{-5}

[a] 100 mM 3,5-DtBC; 300 K; 50 mL of CHCl₃ solvent.
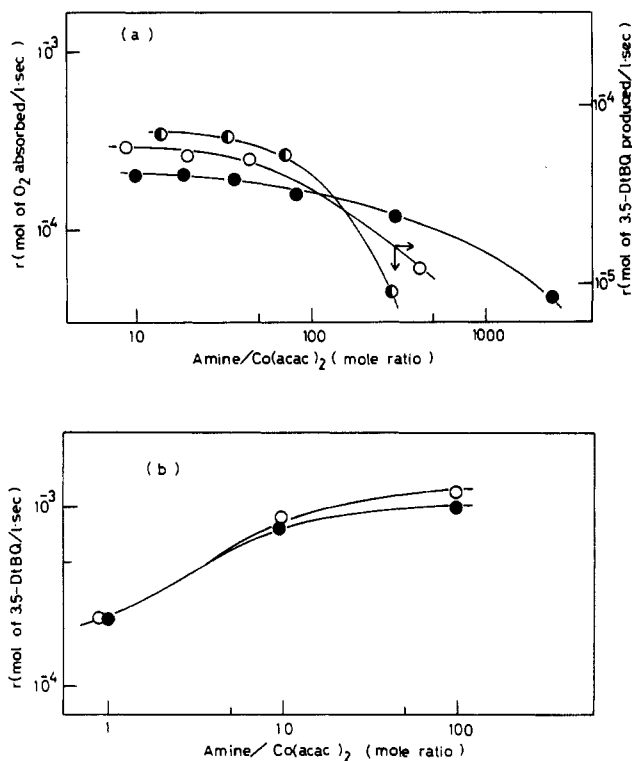
Figure 2. Effect of amine addition on the oxidation activity of 3,5-DtBC:
(a) 58 mM 3,5-DtBC, 0.30 mM Co(acac)₂, 20 mL of CHCl₃, and 293 K for (●) pyridine and (◐) 4-aminopyridine; 100 mM 3,5-DtBC, 0.48 mM Co(acac)₂, 50 mL of CHCl₃, and 303 K for (○) γ-picoline; (b) 100 mM 3,5-DtBC, 1.0 mM Co(acac)₂, 50 mL of CHCl₃, and 303 K for (●) diethylamine and (○) triethylamine.
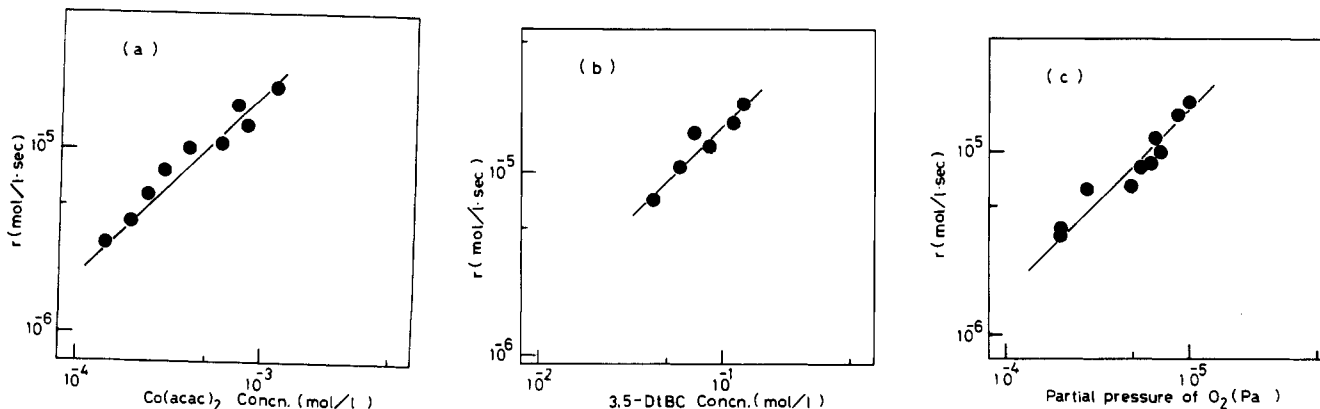
of cobalt chelate in 3,5-DtBC oxidation, as shown in Table IV. However, it must be noted that the Co^{II}(acac)₂ catalyst was almost inactivated by adding ethylenediamine, a typical chelating reagent. Figure 2a illustrates the influence of the mole ratio of pyridine derivative to Co^{II}(acac)₂ on 3,5-DtBC oxidation activity. It is evident that the oxidation activity tended to decrease at mole ratios greater than about 50, irrespective of the pyridine derivatives added. Thus, an excess of pyridine derivatives in the cobalt chelate catalyst was found to decrease the catalytic activity for 3,5-DtBC oxidation catalyzed by cobalt(II) chelate. Figure 2b indicates the relationship between the formation rate of 3,5-DtBC and the mole ratios of triethylamine and/or diethylamine to Co^{II}(acac)₂. It is of interest to note that, in contrast to the addition of pyridine derivatives (Figure 2a), the formation rate of 3,5-DtBC tended to increase with increasing mole ratios of both amines to Co^{II}-(acac)₂. The rate did not decrease even at a mole ratio of 100.

Kinetics of Oxidation of 3,5-DtBC Catalyzed by Co^{II}(acac)₂.
Oxygen absorption rates for the oxidation of 3,5-DtBC were measured under various reaction conditions using Co^{II}(acac)₂ as a catalyst. The dependence of the rate on the concentrations of Co^{II}(acac)₂ and 3,5-DtBC and the partial pressure of oxygen is illustrated in Figure 3a–c as log–log plots. From the slopes of the straight lines shown in Figure 3, the oxygen absorption rate was found to be first order with respect to the concentrations of Co^{II}(acac)₂ and 3,5-DtBC and also the partial pressure of oxygen. (The slopes in Figure 3a–c, calculated from the least-squares method, were 0.97, 0.99, and 1.00, respectively.) Thus, the rate describing the oxidation is expressed in the form of eq 1.

$$r = k_e(3,5\text{-DtBC})(Co^{II}(acac)_2)(O_2) \qquad (1)$$

Arrhenius plots for oxygen absorption rates in the temperature range 285–310 K were prepared for both the Co^{II}(acac)₂–pyridine and bis(N-phenylsalicylaldiminato)cobalt(II) catalytic systems (Figure 4) in order to obtain the apparent activation energies.

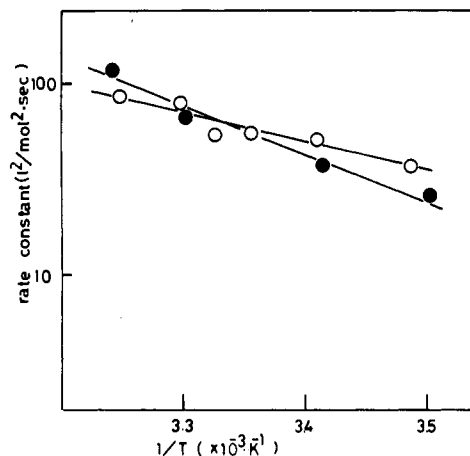**Figure 3.** Log–log plots of the O₂ absorption rate vs. the concentrations of Co(acac)₂ and 3,5-DtBc and the partial pressure of O₂; (a) 57.8 mM 3,5-DtBC, 20 mL of CHCl₃, 293 K; (b) 0.6 mM Co(acac)₂, 20 mL of CHCl₃, 293 K; (c) 57.7 mM 3,5-DtBC, 0.6 mM Co(acac)₂, 20 mL of CHCl₃, 293 K.

Figure 4. Arrhenius plots for oxidation of 3,5-DtBC to 3,5-DtBQ (60 mM 3,5-DtBC, 20 mL of CHCl₃: O, Co(acac)₂–pyridine; ●, bis(*N*-phenylsalicylaldiminato)cobalt(II).

Table V. Kinetic Parameters of 3,5-DtBC Oxidation

catalytic system	temp, K	rate const k, $L^2/(mol^2 s)$	$H,^a$ kJ/mol	$S,^a$ J/(mol K)
Co^{II}(acac)₂–pyridine	286	37.0		
	293	53.9		
	298	55.3	27.0	−120
	303	82.4		
	308	86.9		
bis(*N*-phenylsalicyl-	286	29.5		
aldiminato)cobalt(II)	293	37.9		
	303	64.8	41.1	−73
	309	127.0		

^{a}Calculated on the basis of the assumption that the Ostward solubility parameter, β (β = 0.217 at 289.3 K[25]), of oxygen in CHCl₃ varies according to the variation[26] of the β of oxygen in CCl₄ with temperature.

These were calculated to be 29.5 and 43.6 kJ/mol, respectively, from the straight lines in Figure 4. Table V shows the kinetic parameters obtained for these two catalytic systems.

Discussion

A variety of oxidation products of 3,5-DtBC, including the oxygenation products, obtained by using a number of catalysts and/or oxidants has been reported. However, results reported herein found that cobalt(II) chelate complex catalysts yielded only 3,5-DtBQ selectively. From the stoichiometry of the oxidation of 3,5-DtBC catalyzed by Co(II) chelate complexes was proposed eq 1, with no apparent hydrogen peroxide, on the basis of oxygen absorption data and 3,5-DtBQ and H₂O₂ analyses. Martell and Tyson have studied the kinetics and mechanisms of metal chelate catalyzed oxidation of pyrocatechols in an aqueous medium.[19] Their analyses of the products and yields from the Co(II)–4-nitrocatechol catalyzed oxidation of 3,5-DtBC confirmed the equation 3,5-DtBC + $^1/_2$O₂ → 3,5-DtBQ + H₂O as the overall stoichiometry and suggested that the Co(II)–4-nitrocatechol–3,5-DtBC system is worthy of further study, since it is one of the few nonenzymatic reactions so far reported to give *o*-quinone without H₂O₂ accumulation.[19,37] It is of interest to note that the overall stoichiometry of 3,5-DtBC oxidation catalyzed by Co(II) chelates investigated herein was also found to be without H₂O₂ accumulation, though both systems are fairly different from each other. This is because the former reaction system earlier reported was in aqueous system, whereas the system reported herein was a nonaqueous system.

It has been found that the addition of some amine to the Co(II) complex catalyst caused an increase in the oxidation activity of 3,5-DtBC (Table IV). However, the oxidation activity of 3,5-DtBC was found to be different, depending on the amine added.

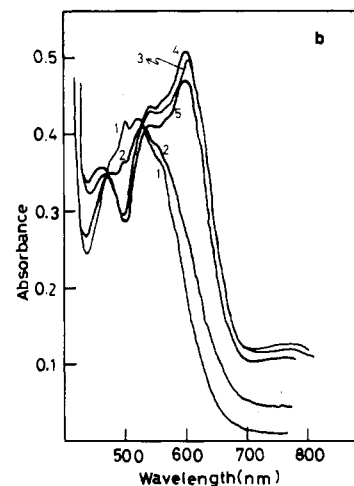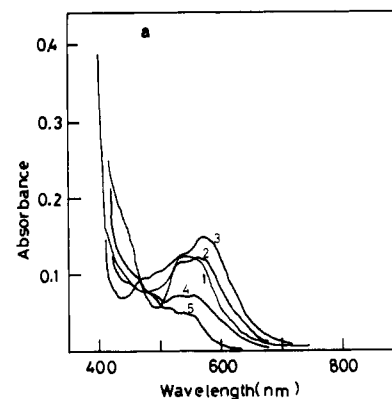(37) Rabani, J.; Nielson, S. O. *J. Phys. Chem.* **1969**, *73*, 3736.

Figure 5. Absorption spectra in CHCl₃ for Co(acac)₂–amine complexes. (a) 3.38 mM Co(acac)₂; pyridine:Co(acac)₂ mole ratio = (1) 0.0; (2) 0.37; (3) 3.7, (4) 37, and (5) 370; (b) 14.2 mM Co(acac)₂; diethyl-amine:Co(acac)₂ mole ratio = (1) 0.0, (2) 2.5, (3) 5.0, (4) 10, (5) 50.

thus, too much of a pyridine derivative tended to decrease the rate of O₂ absorption during the oxidation of 3,5-DtBC, as illustrated in Figure 2a. On the other hand, the rate did not decrease with an amine:Co(II) complex mole ratio of 100 in the case of adding a typical alkylamine such as diethyl- or triethylamine (Figure 2b). Figure 5a illustrates the variation in the visible spectra of the Co^{II}(acac)₂–pyridine system in chloroform solvent with the mole ratio of pyridine:Co^{II}(acac)₂. Fackler[38] has reported earlier the variation in the visible spectra of the Co^{II}(acac)₂–pyridine system in benzene solvent with differing mole ratios of pyridine to Co^{II}(acac)₂. It has been suggested[38] that the increase in this pyridine:Co^{II}(acac)₂ mole ratio caused the formation of Co(II)–pyridine species such as Co^{II}(acac)₂·py and/or [Co^{II}-(acac)₂]₂·py at mole ratios of less than ca. 3. The Co(II)–pyridine species, such as Co^{II}(acac)₂·2py, were formed at mole ratios of more than 10, on the basis of the variation in the visible spectra. The decrease in the absorbance of the Co^{II}(acac)₂–pyridine system in CHCl₃ solvent with increasing pyridine:Co^{II}(acac)₂ mole ratios greater than 10 may be due to the formation of Co^{II}(acac)₂·2py species in accordance with the result of Fackler. It is reasonable to consider that the Co^{II}(acac)₂·2py species are not active for the oxidation of 3,5-DtPB because of the difficulty of the access of 3,5-DtBC to the Co^{II}(acac)₂·2py species. Thus, the decreasing trend in the oxidation activity of 3,5-DtBC at mole ratios of pyridine derivatives to Co^{II}(acac)₂ greater than 10–50 may be

(38) Fackler, J. P. *Inorg. Chem.* **1963**, *2*, 266.
(39) Walker, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 1150.
(40) Stynes, D. V.; Stynes, H. C.; James, B. R.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 1796.
(41) Schwarzenbach, G. *Helv. Chim. Acta* **1949**, *32*, 839.
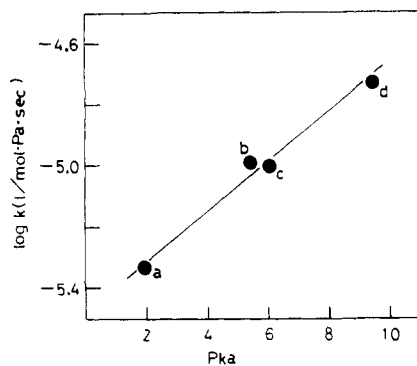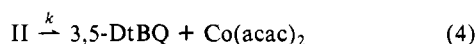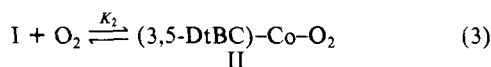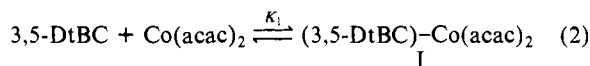(42) Kucharkowski, R.; Doege, H. G. *Fresenius' Z. Anal. Chem.* **1968**, *238*, 241.

Figure 6. Relationship between log k and pK_a (58 mM 3,5-DtBC, 0.30 mM Co(acac)$_2$, 20 mL of CHCl$_3$, 283 K): a, 4-cyanopyridine; b, pyridine; c, γ-picoline; d, 4-aminopyridine.

caused by the formation of inactive Co^{II}(acac)$_2$·2py species. The variation in the visible spectra of the Co^{II}(acac)$_2$–diethylamine system in CHCl$_3$ solvent with the mole ratio of diethylamine: Co^{II}(acac)$_2$ is illustrated in Figure 5b. In contrast to the pyridine ligand effect described above (Figure 5a), the decrease in the absorbance near 600 nm with increasing mole ratio of diethylamine:Co^{II}(acac)$_2$ was not as high as that in the Co^{II}(acac)$_2$–pyridine system. Also, the absorption peak near 600 nm appreciably remained even at a mole ratio of 50. If the absorption peak is assumed to be identified as the active species, such as Co^{II}-(acac)$_2$–diethylamine for the oxidation of 3,5-DtBC, the different behavior of diethylamine addition from that of pyridine addition with respect to the oxidation activity (Figure 2) seems to be understood in terms of the formation of the active and/or inactive Co(II) species for 3,5-DtBC oxidation. Another factor affecting the different behavior between diethylamine and pyridine additions may be pointed out.[43] Thus, the considerable difference in basicities of these amines (e.g.: diethylamine, pK_a = 10.9; pyridine, pK_a = 5.2) will also affect the binding to the Co complex of 3,5-DtBC. In addition, since at high concentration diethylamine deprotonates 3,5-DtBC, the great addition of diethylamine may facilitate the oxidation of 3,5-DtBC by producing the more easily oxidized 3,5-DtBC anion.

The log–log plots between oxygen absorption rate constants vs. pK_a values of the pyridine derivatives added (Figure 6) shows a reasonably straight-line correlation. Thus, the observed linear free energy relationship (LFER) may be compared to the log K_{O_2} and the pK_a of the protonated pyridine bases, for which a good correlation has been found.[20,21,39,40] From the comparison, it may be suggested that the increase in the activity of the Co(II) catalytic systems for 3,5-DtBC oxidation can be partly rationalized in terms of a greater affinity of the Co(II) complexes toward an oxygen molecule. Thus, one of the major factors affecting the oxidation activity is the O$_2$ affinity for the Co(II) complex catalysts.

The rate of Co^{II}(acac)$_2$ catalyzed oxidation of 3,5-DtBC shows first-order dependence on the concentrations of cobalt catalyst, 3,5-DtBC, and oxygen, respectively (Figure 3). Thus, the rate law for the reaction is given by eq 1 and is comparable to the reaction mechanism involving the steps shown in Scheme I. The

Scheme I

$$3,5\text{-DtBC} + \text{Co(acac)}_2 \underset{}{\overset{K_1}{\rightleftharpoons}} (3,5\text{-DtBC})\text{--Co(acac)}_2 \quad (2)$$
$$\text{I}$$

$$\text{I} + \text{O}_2 \underset{}{\overset{K_2}{\rightleftharpoons}} (3,5\text{-DtBC})\text{--Co--O}_2 \quad (3)$$
$$\text{II}$$

$$\text{II} \xrightarrow{k} 3,5\text{-DtBQ} + \text{Co(acac)}_2 \quad (4)$$

(43) We extend our thanks to a reviewer for helpful comments on this matter.

first step is the interaction between 3,5-DtBC and Co(II) catalyst (eq 2). Prior to the first step (eq 2), the reactant, 3,5-DtBC, may be partly dissociated in the presence of amine
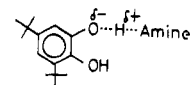
in which these species are considered to interact more easily with the Co(II) catalyst. The formed species (I) can interact with oxygen molecules to generate species II, a kind of ternary Co–oxygen adduct, prior to electron transfer (eq 3). The intramolecular electron transfer of the ternary complex generates the corresponding quinone. If this step (eq 4) is assumed to be rate-determining, the rate (r) can be expressed as follows:

$$r = k(\text{II}) \quad (5)$$

Assuming the existence of species II and III as intermediates

$$(\text{I}) = K_1(3,5\text{-DtBC})(\text{Co(acac)}_2) \quad (6)$$

$$(\text{II}) = K_2(\text{I})(\text{O}_2) \quad (7)$$

$$(\text{II}) = K_1 K_2 (3,5\text{-DtBC})(\text{Co(acac)}_2)(\text{O}_2) \quad (8)$$

where K_1 and K_2 are the equilibrium constants of eq 1 and 2, respectively. By substitution of eq 8 into eq 6

$$r = k K_1 K_2 (3,5\text{-DtBC})(\text{Co(acac)}_2)(\text{O}_2) \quad (9)$$

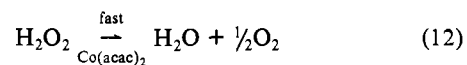$$r = k'(3,5\text{-DtBC})(\text{Co(acac)}_2)(\text{O}_2) \quad (10)$$

where

$$k' = k K_1 K_2 \quad (11)$$

The rate expression of eq 10 is in agreement with the experimentally obtained rate law in eq 1, by assuming $k' = k_e$.

The reaction assumed here includes associative oxygen species adsorbed on cobalt ions. The LFER between oxidation activity and the measure of O$_2$ affinity described (Figure 6) is line with the reaction mechanism assumed here. The kinetics and/or the stoichiometry obtained here, however, give no information about the number of electrons transferred in the rate-determining step.

Finally, some comments may be made on H$_2$O$_2$ accumulation. As evidenced from the stoichiometry obtained experimentally, the apparent H$_2$O$_2$ accumulation can be neglected. Since Co(II) complexes, however, are known to catalyze H$_2$O$_2$ decomposition,[29,41,42] the H$_2$O$_2$ once generated in the rate-determining step might be decomposed to H$_2$O by the Co(II) chelate complexes under a fast step:

$$\text{H}_2\text{O}_2 \xrightarrow[\text{Co(acac)}_2]{\text{fast}} \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \quad (12)$$