

Oxygenation of 2,6-Di-*t*-butylphenol Catalysed by a New Cobalt(II) Complex [Co(babp)]: a Salen Analogue having Higher Catalytic Activity, Selectivity, and Durability

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The deprotonated form of the cobalt(II) complex of 6,6'-bis(benzoylamino)-2,2'-bipyridine [Co(babp)] shows excellent catalytic activity in the selective oxygenation of 2,6-di-*t*-butylphenol (DTBP) to 2,6-di-*t*-butyl-*p*-benzoquinone (DTBQ) in the presence of an appropriate base. The durability of [Co(babp)] as an oxygenation catalyst is much higher than that of [Co(salen)] and, furthermore, the reduced catalytic activity of the complex after repeated use can easily be improved to a certain extent by heating at 200 °C under reduced pressure.

Oxygenation of organic substrates with molecular oxygen catalysed by square-planar cobalt(II) complexes has been intensely studied,¹ and selective oxygenation of phenols to give the corresponding *p*-benzoquinones without formation of by-products such as diphenoquinone derivatives is regarded as one of their attractive uses.² Square-planar cobalt(II) complexes of Schiff base-type ligands,³⁻⁹ phthalocyanines,⁷ porphyrines,⁸⁻¹⁰ and oximes^{8,9} have been used for the reactions, and cobalt(II) complexes of *N,N'*-di(salicylidene)ethylenediamine [Co(salen)] and its analogues have been recognized to be efficient catalysts for the oxygenation.^{2-5,7-10} However, [Co(salen)] is not durable enough, and its turnover number seldom exceeds 200 due to the oxidative degradation of the ligand, and/or some other processes.^{4,11} Many attempts have been made to improve the durability of the catalyst by structural modification of the diamine and/or phenoxy units of salen.^{4,6,8,9}

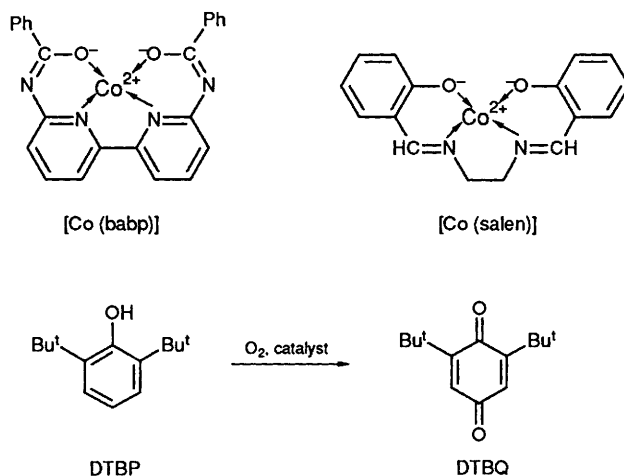
We adopted a different strategy to overcome this problem, *i.e.* the N_2O_2 co-ordination sites of salen were reconstructed by using entirely different building blocks, 2,2'-bipyridine and amide structures, to form 6,6'-bis(acylamino)-2,2'-bipyridines. The ligands can be synthesized conveniently from 6,6'-diamino-2,2'-bipyridine¹² and carboxylic acid chlorides. The 1:1 complexes of these ligands with several divalent transition metal ions have the same N_2O_2 -type square-planar structure as that of salen.^{13,14}

In a previous communication,¹⁵ we reported the excellent catalytic activity of [Co(babp)], where babp represents the deprotonated form of 6,6'-bis(benzoylamino)-2,2'-bipyridine (babpH₂), in selective oxygenation of 2,6-di-*t*-butylphenyl (DTBP) to 2,6-di-*t*-butyl-*p*-benzoquinone (DTBQ). The oxygenation product was substantially exclusively DTBQ, with <1% of 3,3',5,5'-tetra-*t*-butyldiphenoquinone (DPQ). Here, we present full details of the properties of the complex and its catalytic activity in the oxygenation of phenols to quinones.

Experimental

The complex [Co(babp)] was prepared as previously described.¹⁴ [Co(salen)] was obtained commercially from Tokyo Kasei Kogyo Co., Ltd and was used without further purification. Other chemicals were also obtained commercially, and some of them were purified by conventional methods prior to use, if necessary. IR spectra were recorded on a JASCO IR-700 spectrophotometer with KBr disks.

Oxygenation of DTBP.—Oxygenation of DTBP was



performed in a 50-cm³ flask with oxygen bubbling (1 atm, *ca.* 5 cm³ min⁻¹) through a solution of DTBP (5 × 10⁻¹ mol dm⁻³) and [Co(babp)] (2.5 × 10⁻³ mol dm⁻³) {initial molar ratio of DTBP and [Co(babp)], [DTBP]₀/[Co(babp)]₀, was 200} in pyridine or toluene containing pyridine (20 cm³) for 24 h. The amounts of DTBP and DTBQ were monitored by GLC (YANACO G-2800; Shimadzu Silicon DC550/Chromosorb W; 3 mm × 2 m) during the reaction, and the initial rate of the reaction was determined from the steepest slope of the time-course of the consumption of DTBP after the induction period. The amount of DPQ was determined by high-performance liquid chromatography (HPLC) (JASCO TWINCLE; Merck LiChro CART 254-1; MeOH). DTBQ was also isolated from the reaction mixture by conventional column chromatography, and its melting point (70–71 °C) and IR spectrum were identical with those of an authentic sample.

Thermal Analyses of the Complexes.—Analysis of volatile products from the complexes was performed by gas chromatography (GC) [Shimadzu GC-4C; Molecular Sieve 5A 30/60; 3 mm × 2 m equipped with a flush thermolysis unit (temp. 300 °C)]. Thermogravimetric (TG) and differential thermal analytical (DTA) curves were recorded simultaneously on a Shimadzu DTG-30 Thermal Analyzer with a heating rate of 5 °C min⁻¹ under aerobic conditions.

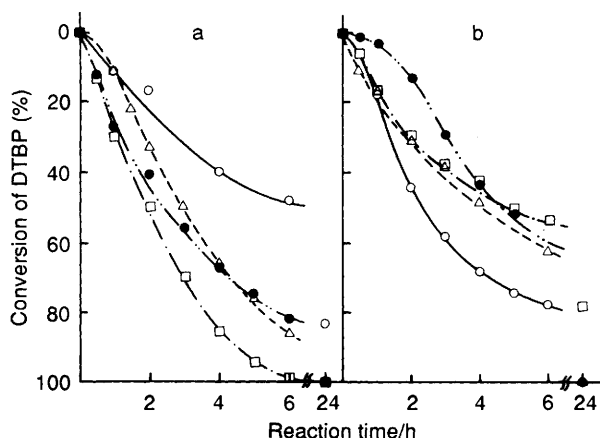
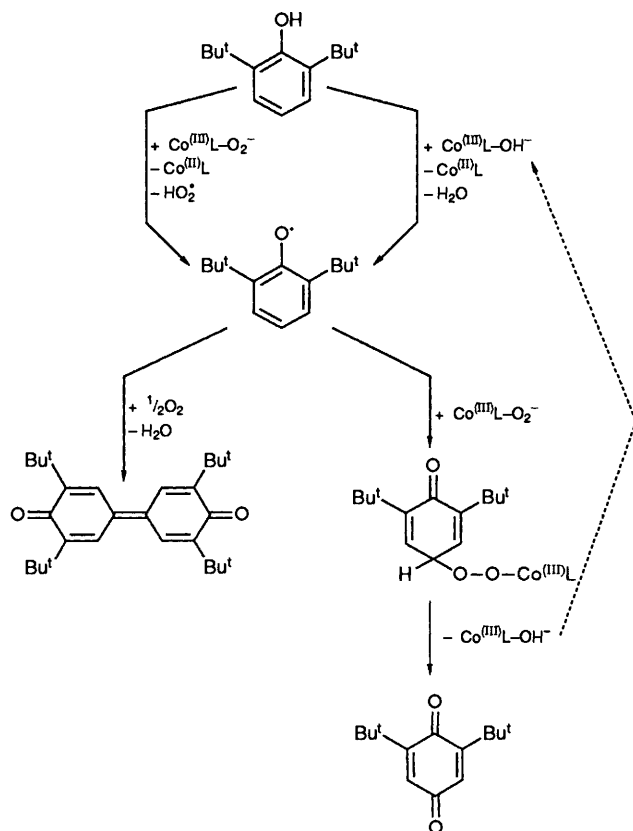


Figure 1. Time-course plot of oxygenation of DTBP catalysed by [Co(babp)]. (a) in pyridine at 5 °C (O), at 20 °C (Δ), at 40 °C (□), and at 60 °C (●); (b) in toluene at 20 °C in the presence of pyridine (O), 4-MEPY (Δ), 4-DMAP (□), and ABCO (●). Initial conditions, see Experimental section.

Results and Discussion

Activity and Selectivity.—Oxygenation of DTBP catalysed by [Co(babp)] {[DTBP]₀/[Co(babp)]₀ 200} was complete within 24 h in the presence of >1% v/v of pyridine in toluene at room temperature.¹⁵ No reaction took place in the absence of any one of [Co(babp)], oxygen, or pyridine. The product was almost exclusively DTBQ. The yield of DPQ was <0.5%, demonstrating that [Co(babp)] was an efficient and highly selective catalyst for this reaction. The superoxide-type oxygen-adduct of [Co(babp)] was shown to be formed in solution at room temperature when pyridine was added as an axial ligand.^{15,16} Therefore, we conclude



Scheme 1.

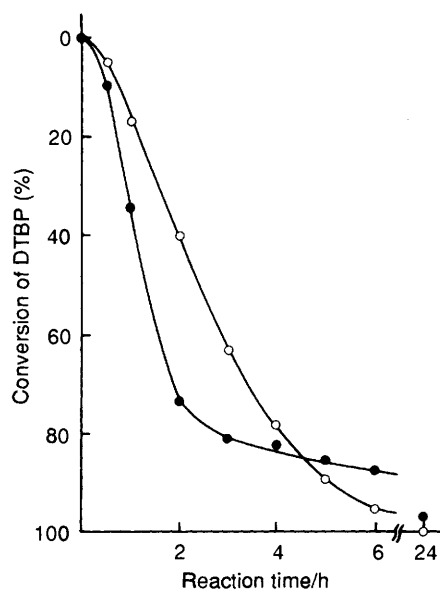


Figure 2. Time-course plot of oxygenation of DTBP catalysed by [Co(babp)] (O) and [Co(salen)] (●) in pyridine at room temperature.

that the oxygenation of DTBP proceeds through activation of molecular oxygen by the pyridine-co-ordinated [Co(babp)], which was essentially the same situation as that of the [Co(salen)]-catalysed oxygenation (Scheme 1).^{2,4,8,9}

The effect of reaction temperature on the oxygenation of DTBP in pyridine is summarized in Table 1 and Figure 1a. When the temperature was raised from 5 to 40 °C, the initial rate became faster and the half-decay time of DTBP ($t_{1/2}$) became shorter (entries 1–3). However, no further acceleration of the reaction was observed at 60 °C and, instead, conversion of DTBP into DTBQ became slower as the reaction proceeded, probably due to deterioration of the catalytic activity (entry 4). The temperature effect on the [Co(babp)]-catalysed oxygenation of DTBP observed here was similar to that of cobalt porphyrin-catalysed reaction reported by Martell and co-workers.¹⁰

Two pyridine derivatives, 4-methylpyridine (4-MEPY) and 4-(dimethylamino)pyridine (4-DMAP), were also effective as the axial ligand (Table 2, Figure 1b). The stronger the basicity of the pyridine derivatives, the higher the initial rate of oxygenation. However, the half-decay times of DTBP in the presence of 4-MEPY (entry 3) and 4-DMAP (entry 4) were longer than that in the presence of pyridine, and the oxygenation in the presence of 4-DMAP was not complete even after 24 h, indicating deterioration of catalytic activity during the reaction. In the case of 4-DMAP, the selectivity for DTBQ as the product was also decreased. In addition, the reaction rate in the presence of a strong aliphatic amine, 1-azabicyclo[2.2.2]octane (ABCO), was slower than that in the presence of pyridine, indicating that ABCO was inferior to pyridine as an axial ligand although its basicity is much higher (entry 5).

Durability.—Time courses of the oxygenation catalysed by [Co(babp)] and [Co(salen)] in pyridine at room temperature are shown in Figure 2. Though the initial rate in the presence of [Co(babp)] was slightly slower than that in the presence of [Co(salen)], higher conversion of DTBP was attained after 5 h in the former case. In the case of [Co(salen)], the reaction was not complete even after 24 h. Thus, [Co(babp)] was shown to be more resistant to the deterioration of its catalytic activity than was [Co(salen)].

Table 1. Oxygenation of DTBP catalysed by [Co(babp)] in pyridine at various temperatures.^a

Entry	Temperature (°C)	$t_{\frac{1}{2}}$ (min) ^b	% DTBQ ^c	[DPQ]/[DTBQ] ^d
1	5	380	83	0.005
2	20	185	100	0.004
3	40	120	100	0.009
4	60	150	100	0.058

^a Initial conditions: see Experimental section. ^b Half-decay time of DTBP. ^c Yield of DTBQ after 24 h. ^d Molar quotient of DPQ to DTBQ after 24 h.

Table 2. Oxygenation of DTBP catalysed by [Co(babp)] in toluene containing various axial ligands at 20 °C.^a

Entry	Base ^b	pK _a of base	$t_{\frac{1}{2}}$ (min) ^c	% DTBQ ^d	[DPQ]/[DTBQ] ^e
1	Pyridine	5.2	185	100	0.005
2	Pyridine ^f	5.2	185	100	0.004
3	4-MEPY	6.0	250	100	0.005
4	4-DMAP	9.7	320	80	0.022
5	ABCO	11	270	100	0.002

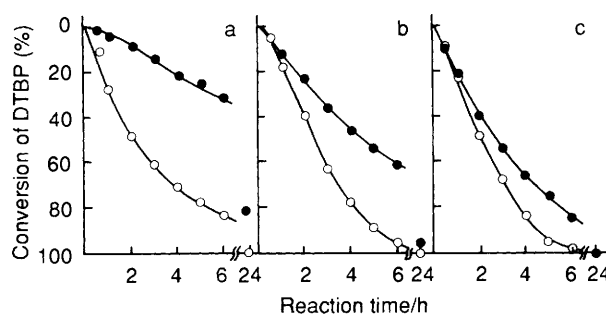
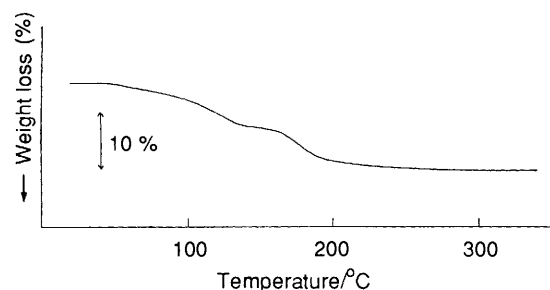
^a Initial conditions: see Experimental section. ^b [base] 2.5×10^{-2} mol dm⁻³; abbreviation of base, see text. ^c Half-decay time of DTBP. ^d Yield of DTBQ after 24 h. ^e Molar quotient of DPQ to DTBQ after 24 h. ^f In 100% pyridine.

Table 3. Oxygenation of DTBP catalysed by [Co(babp)] in the second run, without removal of the first reaction products, at room temperature for 24 h.^a

Entry	Solvent ^b	2nd reaction ^c		
		1st reaction % DTBQ (turnover)	% DTBQ (turnover) ^d	Relative rate ^e
1	1% Pyridine-toluene	100(200)	82(364)	0.24
2	10% Pyridine-toluene	100(200)	98(396)	0.35
3	Pyridine	100(200)	96(392)	0.53
4 ^f	Pyridine	100(200)	100(400)	0.76
5 ^g	Pyridine	97(194)	14(222)	0.02
6 ^{f,g}	Pyridine	98(196)	23(242)	0.10

^a Initial conditions: see Experimental section. ^b See Experimental section. ^c The second reaction was performed by addition of the initial amount of DTBP (1.0×10^{-2} mol) to the mixture from the first reaction. ^d Total turnover number of first and second reactions. ^e Initial rate relative to that of the first reaction. ^f In the presence of anhydrous sodium carbonate. ^g Catalysed by [Co(salen)].

The higher durability of the catalytic activity of [Co(babp)] shown above was more clearly demonstrated in a repeated-use experiment. After completion of the first reaction, the initial amount of DTBP was again fed into the reaction mixture without removal of the reaction products. The results are summarized in Table 3 and Figure 3. >80% of DTBP was converted into DTBQ after another 24 h in the second run (entry 1). The initial rate of the second run was slower than that of the first one, indicating that deactivation of the catalyst had taken place during the first reaction. The deactivation was found to be suppressed to some extent on increasing the pyridine content (entries 1–3). Addition of anhydrous sodium carbonate (entry 4) was also effective for this purpose.⁴ Judging from the relative initial rates, [Co(babp)] retained 76% of its catalytic activity in the second run in pyridine in the presence

**Figure 3.** Time-course plot of the first (○) and second (●) reactions catalysed by [Co(babp)] at room temperature: (a) in 1% pyridine-toluene; (b) in pyridine; (c) in pyridine in the presence of anhydrous sodium carbonate. Initial conditions of first reactions; see Table 3.**Figure 4.** TG curve of the black powder (see text). Heating rate 5 °C min⁻¹, under aerobic conditions.

of anhydrous sodium carbonate.* It is worth noting that only 14 and 23%, respectively, of the DTBP was converted into DTBQ when [Co(salen)] was used in the second run in the absence and presence of sodium carbonate, respectively (entries 5 and 6).

Thermal Reactivation of the Catalyst.—As [Co(babp)] was shown to retain its catalytic activity during the oxygenation reaction, the ligand moiety of the complex was thought to be relatively stable against oxidative degradation under the reaction conditions, where the oxygen-adduct of the complex^{15,16} was indicated to be involved. Furthermore, the cobalt(III)-superoxide-type oxygen-adduct formed by reversible co-ordination of oxygen in pyridine was found to retain its characteristic ESR signal^{15,16} for more than 1 day without undergoing irreversible oxidation at room temperature. Therefore, [Co(babp)] must be sufficiently stable under these oxidative conditions. To test further the stability of [Co(babp)] under the reaction conditions, the thermal stability of the oxygen-adduct of the complex was studied.

Addition of light petroleum (b.p. range 30–70 °C) to an oxygen-bubbled, 1% v/v pyridine-toluene solution of [Co(babp)] at –78 °C caused precipitation of a black powder. GC analysis of the powder following flash thermolysis at 300 °C indicated the evolution of oxygen in addition to release of the co-ordinated pyridine. TG analysis showed that the weight of the powder decreased twice, between 46–136 °C and between 154–215 °C (Figure 4); this is accounted for by elimination of the co-ordinated molecular oxygen and pyridine, respectively. These results suggested that the black powder was the oxygen-adduct of [Co(babp)-pyridine]. The residual orange powder

* When the initial concentrations of [Co(babp)] and DTBP were changed to 0.5 mmol dm⁻³ and 2.0 mol dm⁻³, respectively ([DTBP]₀/[Co(babp)]₀ 4 000), under the same conditions, the turnover number of the catalyst exceeded 760 in a single run after 7 days.

Table 4. Oxygenation of DTBP in 1% pyridine-toluene catalysed by re-used [Co(babp)] after heating at reduced pressure.^a

Entry	Heating temperature (°C)	2nd Reaction		3rd Reaction	
		% DTBQ (turnover) ^b	Relative rate ^b	% DTBQ (turnover) ^b	Relative rate ^b
1	200	100(400)	0.70	99(598)	0.52
2	50	82(364)	0.27		
3 ^c		82(364)	0.24		

^a First reactions: see entry 1 in Table 1. ^b See Table 3. ^c Entry 1 in Table 3.

obtained after elimination of the co-ordinated oxygen and pyridine by heating to 300 °C showed an endothermic DTA peak at 333 °C. This temperature was identical with the m.p. of the starting material [Co(babp)].¹⁴ The IR spectrum of the residual powder confirmed that the residue was the starting material [Co(babp)]. Thus, the molecular structure of the new salen analogue, babp, was highly resistant against thermal decomposition even in the presence of co-ordinated molecular oxygen. However, slow deterioration of its catalytic activity was observed in the oxygenation reactions (Table 3, Figure 3). Therefore, this deterioration of its catalytic activity might well not be due to irreversible degradation of the complex but rather to other reasons such as interference by trace amounts of unidentified reaction products in the oxygenation process. To test this hypothesis, we took advantage of the high thermal stability of the complex, and tried to recover [Co(babp)] from the reaction mixture by heating it under reduced pressure in order to remove solvent, unchanged substrate, and products. Thus, after completion of the first reaction, the solvent was removed by evaporation, and the residue was heated under reduced pressure in order to remove reaction products (ca. 2 mmHg). Then the same amount of DTBP was subsequently added to the mixture and the second run was carried out under the same conditions (Table 4). When the heating temperature was 50 °C, DTBQ was recovered quantitatively as a sublimate. The IR spectrum of the residual solid was slightly different from that of the oxygen-adduct of [Co(babp)-pyridine], showing a small additional peak at 1 660 cm⁻¹. The residual solid obtained did not restore the catalytic activity of the complex (entry 2). When the heating temperature was increased to 200 °C,* a trace amount of unidentified yellow powder was obtained as a sublimate. The IR spectrum of the residual solid was almost identical with that of [Co(babp)],¹⁴ and no additional peak was observed at 1 660 cm⁻¹. The recovered residue was subjected to repeated use as the catalyst in another batch (entry

1), which converted ca. 100% of the substrate DTBP into DTBQ within 24 h in both the second and third usage without deterioration of its selectivity, though the initial rates decreased to 70 and 52% of the initial value (first use) in the second and third reactions, respectively (entry 1). These results demonstrated that the complex [Co(babp)] was capable of repeated use as the catalyst for oxygenation.

In conclusion, the Co^{II} complex of a new salen analogue, [Co(babp)], whose N₂O₂ co-ordination sites were reconstructed by use of bipyridine and amide units, was demonstrated to be an efficient catalyst with high durability, selectivity, and activity for oxygenation of DTBP to DTBQ. Furthermore, the high thermal stability of [Co(babp)] allow us to restore its catalytic activity by heating it to 200 °C under reduced pressure.

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* When the heating temperature was increased above 200 °C, a small amount of [Co(babp)] was definitely obtained as a sublimate.