

Formation and reactivity of cobalt(III)–dioxygen complexes promoted by 2-methylpropanal: Oxidation of alkenes and alcohols

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Abstract. 2-Methylpropanal promotes the formation of cobalt(III)-dioxygen species from catalysts 1 or 2 and dioxygen. The cobalt(III)-dioxygen complexes efficiently catalyse the oxidation of various alcohols to carbonyl compounds in the presence of dioxygen and 2-methylpropanal. Similarly substituted alkenes are smoothly transformed to the corresponding monoepoxides under these reaction conditions. EPR study of these reactions indicates that different activated dioxygen species are formed in the presence of catalysts 1 and 2.

Keywords. Dioxygen; 2-methylpropanal; cobalt(III)-superoxo complex; catalytic oxidation; EPR; cobalt(IV)-oxo species.

1. Introduction

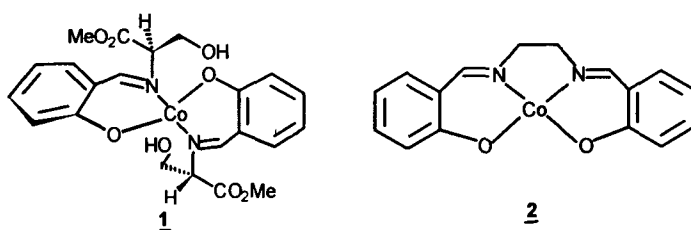
Catalytic oxidation of alcohols and alkenes with dioxygen is gaining (Sheldon and Kochi 1981; Tovrog *et al* 1981; Kanemoto *et al* 1984; Tanaka *et al* 1984; Mimoun 1987; Murahashi *et al* 1993) importance as a viable alternative to the routine metal mediated oxidations. We have recently shown that cobalt(II) Schiff base complexes act as good catalysts for the oxidation of a wide range of alcohols and alkenes with molecular oxygen in the presence of reducing agents like aldehydes or ketoesters (Bhatia *et al* 1993; Punniyamurthy *et al* 1993, 1994; Karla *et al* 1994; Punniyamurthy and Iqbal 1994).

We now show that these cobalt(II) Schiff base complexes can be activated with an aldehyde to form a monomeric cobalt(III)-dioxygen complex and the oxygen atom transfer from the latter to organic substrate is mediated by aldehyde which acts as a reducing agent during this process.

2. Results and discussion

In a typical reaction, alcohol (5 mmol), 2-methylpropanal (10 mmol), cobalt(II) Schiff base complex 1 or 2 (5 mol%) were dissolved in acetonitrile (30 ml) and the reaction mixture was stirred at ambient temperature under a dioxygen balloon for 22–22 hours. Usual workup followed by purification afforded the corresponding carbonyl compounds in good yields. Thus, cyclohexanol, menthol and borneol were oxidised smoothly under these conditions the corresponding carbonyl compounds (table 1, entries 1–3). Similarly allylic alcohols, geraniol and pulegol underwent oxidation to carbonyl compounds. Overoxidation of geraniol to the corresponding carboxylic acid was controlled carefully by monitoring the reaction mixture as corresponding carboxylic

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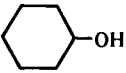
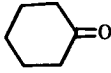
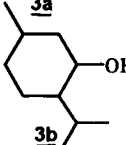
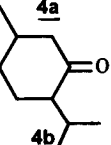
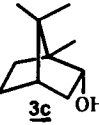
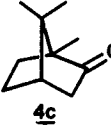
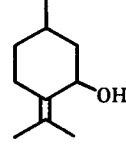
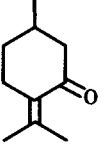
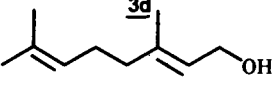
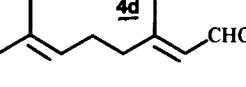
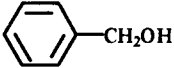
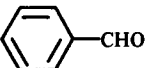
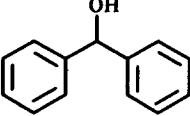
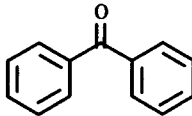
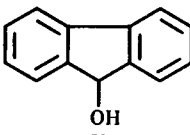
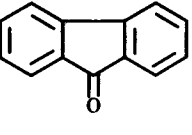
acid is formed by prolonging the reaction (table 1, entry 5). In a similar manner benzyl alcohol can be oxidised to benzaldehyde without concomitant formation of benzoic acid. Benzhydrol and 9-fluorenol underwent clean oxidation to the corresponding carbonyl compounds in high yields (table 1, entries 7 and 8). Carveol is smoothly oxidised to carveone and epoxy ketone in the presence of catalyst 1 in good yields whereas complex 2 fails to catalyse the epoxidation under these conditions (scheme 1). Surprisingly alcohols containing nonconjugated double bonds are quite resistant to these oxidations as 5-norbornene-2-ol and homoallyl alcohol remained unaffected even after 35–40 hours. The reason for the nonreactivity of these alcohols is not clear; however, it appears that the presence of nonconjugated double bonds may be responsible for the sluggish behaviour toward oxidation.

Catalyst 1 is also quite efficient in catalyzing the transfer of an oxygen atom to alkenes to give the corresponding epoxides. Thus a wide range of alkenes can be epoxidised selectively under these conditions as evidenced from the results in table 2. *Trans*-stilbene is smoothly transformed to the corresponding *trans*-stilbene oxide whereas selective epoxidation of linalool acetate, geranyl acetate and β -ionone can be performed to give the monoepoxides exclusively (table 2, entries 2, 3, 5). In the case of linalool acetate and β -ionone more substituted double bond is epoxidised without the formation of other regioisomers or the corresponding diepoxides. Similarly a very highly selective epoxidation of farnesyl acetate can be achieved to give the product resulting from the oxidation of a terminal trisubstituted double bond (table 2, entry 4). These reactions indicate the electrophilic nature of the oxygen atom involved in the epoxidations.

EPR investigation of these reactions indicate the catalyst 1 forms a monomeric cobalt(III)-dioxygen complex 1b only in the presence of aldehyde. It is clearly evident from the EPR that the absence of aldehyde shows a signal due to cobalt(II) at 2666 G (g_{iso} 2.5209) but after the addition of aldehyde we observe the appearance of a sharp signal at 3312 G (g_{iso} 2.0149) which is characteristic of Co–O–O species as reported by Basolo and others (figure 1) (Crumbliss and Basolo 1970; Hoffman *et al* 1970; Jones *et al* 1979; Gubelmann and Williams 1983). Basolo and coworkers (Hoffman *et al* 1970; Crumbliss and Basolo 1970) have already shown that the basic ligand like pyridine coordinates axially with cobalt(II) Schiff base complex to give a pentacoordinated cobalt(II) complex which captures dioxygen spontaneously to give cobalt(III) superoxo complex. In analogy with this it is likely that the basic oxygen atom of aldehyde may act as a good coordinating ligand to complex 1 to give the pentacoordinated complex 1a which may react with dioxygen to give cobalt(III)-superoxo complex 1b.

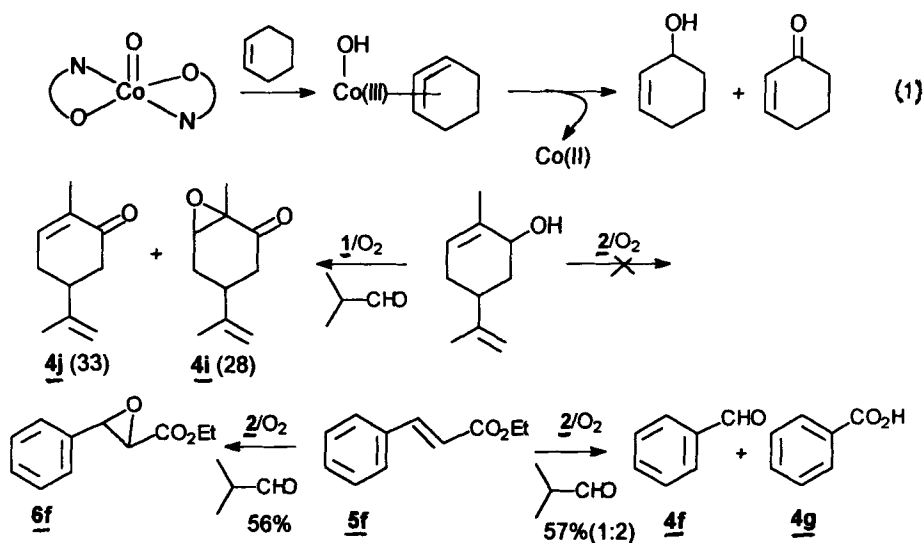
On the other hand no sharp signal corresponding to Co–O–O' species is observed with catalyst 2 after the addition of aldehyde, although catalyst 2 behaves in a similar

Table 1. Cobalt(II) catalysed oxidation of alcohols with dioxygen.

Entry	Alcohol	Product(s)	(Yield %) ^a	
			Catalyst 1	Catalyst 2
1	 3a	 4a	(79) ^b	(57) ^b
2	 3b	 4b	(76)	(91) ^b
3	 3c	 4c	(70)	(15)
4	 3d	 4d	(68)	(90) ^b
5	 3e	 4e	(48) ^b	(48) ^b
6	 3f	 4f	(82) ^b	(68)
7	 3g	 4g	-	(87) ^b
8	 3h	 4h	-	(71) ^b

^a Isolated yield; ^b yield determined by HPLC

manner as catalyst **1** during the oxidation of alcohol and alkene with dioxygen. Since one equivalent of aldehyde is also required as a reducing agent for cobalt(II) complex **2** catalyzed oxidation of alkenes and alcohols the initial reaction of aldehyde with catalyst **2** may be to form a pentacoordinated complex **2a** which may capture dioxygen to give a monomeric cobalt(III)-dioxygen complex **2b**. The latter complex **2b** may undergo reaction with another cobalt(II) complex **2** to give dicobalt(III)- μ -peroxo



Scheme 1.

Table 2. Cobalt(II) catalysed epoxidation of alkenes with dioxygen and 2-methylpropanal.

Entry	Alkene	Product	Yield % ^a
1			70
2			77
3			66
4			32
5			77

^a) Isolated yield

complex 2c (Gubelman and Williams 1983) which may be responsible for oxygen atom transfer to alkenes and oxidation of alcohols. Thus catalysts 1 and 2 may give rise to different types of activated dioxygen species 1b and 2c respectively which will react with

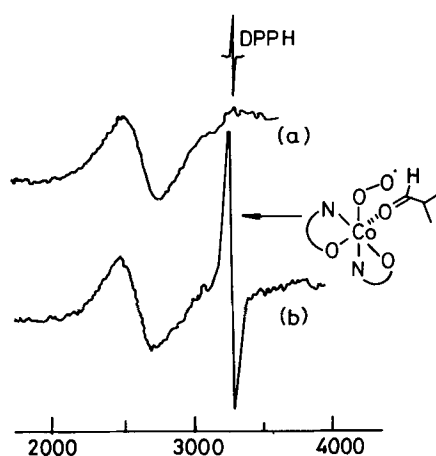
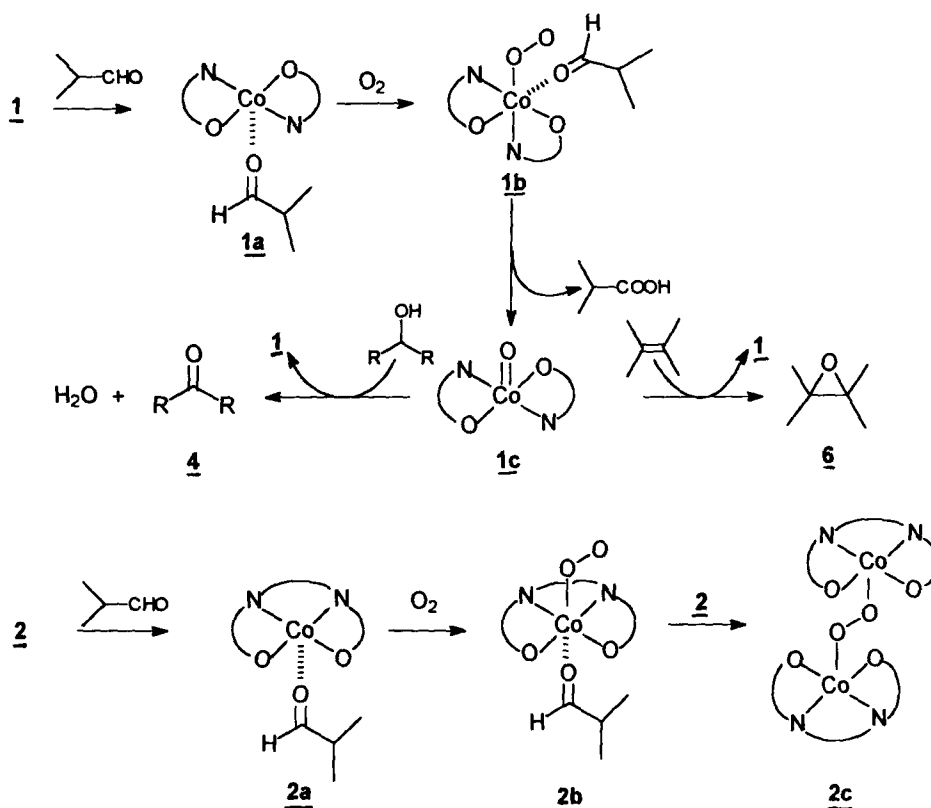


Figure 1. (a) EPR of catalyst 1 in acetonitrile under oxygen atmosphere. (b) EPR after the addition of 2-methylpropanal to catalyst 1 in acetonitrile after 30 min under oxygen atmosphere.

organic substrates leading to same or different products. The diverse nature of the activated dioxygen species in the presence of catalyst 1 and 2 can be established by the oxidation of carveol in the presence of either of these catalysts. Thus catalyst 1 promotes the oxidation of carveol to give a mixture of carvone and epoxy ketone whereas under similar conditions catalyst 2 fails to effect any chemical reaction on carveol. Similarly ethylcinnamate gives a small amount of the corresponding epoxide in the presence of catalyst 1 whereas catalyst 2 promotes the cleavage of carbon-carbon double bond leading to the formation of benzaldehyde and benzoic acid where the latter is formed due to the overoxidation of the former under these conditions (scheme 1). These reactions indicate that different species of activated dioxygen are formed in the presence of catalysts 1 and 2.

In view of the above observation the following mechanism for dioxygen activation by complex 1 and its subsequent reaction with organic substrates may be proposed. The coordination of aldehyde to complex 1 will give a pentacoordinated species 1a which will capture (Busetto *et al* 1971; Vos *et al* 1994) dioxygen to give the monomeric dioxygen complex 1b whose presence can be inferred by EPR spectrum of the reaction mixture (figure 1b). The coordination of aldehyde may take place equatorially (Nishida *et al* 1992) and this would allow the complexed dioxygen and aldehyde to have a *syn* relationship which may facilitate an intramolecular oxygen atom transfer to aldehyde leading to the formation of carboxylic acid. This process would give rise to a highly reactive cobalt(IV)-oxo species 1c which may transfer oxygen atom to alkenes to give epoxides or oxidise alcohol to the corresponding carbonyl compound (scheme 2). Koola and Kochi (1987) have already proposed a similar kind of cobalt(IV)-oxo species during epoxidation of alkenes with iodosylbenzene. The complexed oxygen atom is likely to be electrophilic in nature and that is why the more substituted double bond of alkene is preferentially oxidised under these conditions. The presence of a species of type 1c is also indicated by its reactivity with cyclohexene which leads to the formation of allylically oxidised products (1). This reactivity profile is similar to the corresponding iron(IV)-oxo species proposed earlier for cytochrome P-450 models (Groves *et al* 1978, 1980).



Scheme 2.

The interaction of catalyst **2** with dioxygen in the presence of an aldehyde will provide a monomeric superoxo complex of the type obtained for catalyst **1**, however, it may spontaneously react with another cobalt atom to form the dimeric cobalt(III) complex which is likely to behave as O_2^{2-} species. There is enough evidence in the literature for the formation (Gubelmann and Williams 1983) of this kind of dimeric complexes of cobalt. The propensity of catalyst **2** to form the dimeric dioxygen complex is primarily due to the planar nature of this complex whereas for catalyst **1** the formation of such a dimer may be restricted due to the presence of bulky side chains in the ligands (Busch and Alcock 1994).

In conclusion the studies described here indicate that cobalt(II) Schiff base complexes of type **1** and **2** may be used to capture dioxygen in the presence of 2-methylpropanal leading to the formation of monomeric cobalt(III)-dioxygen complex in one case and dimer for the other. These complexes efficiently react with alkene or alcohol to give the corresponding oxidised products. Interestingly 2-methylpropanal acts as a ligand for inducing dioxygen capture as well as a reducing agent in converting the monomeric superoxo complex to a very highly reactive cobalt(IV)-oxo species. The catalysis **1** and **2** give rise to different activated oxygen species under these conditions which may react differently with certain alkenes and alcohols. Thus, by changing the ligand around the cobalt(II) metal center different types of activated oxygen species can be generated by a combined use of 2-methylpropanal, cobalt(II) complexes **1** or **2** and dioxygen.

3. Experimental

3.1 Materials and methods

Cobalt(II) chloride was purchased from LOBA India (Bombay) and dried at 110°C for 2–3 hours prior to use. Acetonitrile was purified by standard procedures. Aldehydes and alkenes were purchased and purified prior to use. ^1H NMR spectra were recorded at 60 and 80 MHz in CCl_4 or CDCl_3 . UV-Vis spectra were recorded on Perkin–Elmer Lambda-2 spectrophotometer. EPR spectra were recorded on Varian-100 Series Spectrometer in acetonitrile at ambient temperature. Magnetic moment was calculated by Evans (1959) method. Mass spectra were recorded on JEOL SX 102/DA-6000 spectrometer. HPLC was performed on Shimadzu LC-6A. Elemental analysis was conducted using Coleman automatic C, H and N analyzer. All the known compounds were characterized by comparing the data from the literature. Cobalt(II) complex **2** was prepared according to the literature (Chen and Martell 1987) procedure.

Preparation of cobalt(II) complex (1): The Schiff base ligand was prepared by the reaction of salicylaldehyde (0.61 g, 5 mmol) with L-serine methyl ester hydrochloride (5.1 mmol) and triethyl amine (5.5 mmol) in absolute ethyl alcohol (15 ml) at ambient temperature for 5 hours. Removal of ethyl alcohol yields a residue which was dissolved in acetonitrile (10 ml). Triethylamine hydrochloride was filtered and the crude was subjected to column chromatography on silica gel (20:80 EtOAc:petroleum ether) to give the Schiff base ligand as reddish oil. ^1H NMR (CDCl_3): δ 3.6 (s, 3H), 3.7–4.0 (t, 1H, $J = 6.5$ Hz), 3.8–4.0 (d, 2H, $J = 6.5$ Hz), 6.5–7.2 (m, 5H), 8.1 (s, 1H). IR (neat): 3500, 3100, 1740. Anal. Calcd. for $\text{C}_{11}\text{H}_{13}\text{O}_4\text{N}$: C, 59.19; H, 5.83%. Found: C, 59.01; H, 6.01%.

The ligand (1.11 g, 5 mmol) was dissolved in anhydrous acetonitrile (30 ml) and reacted with cobalt(II) chloride (0.33 g, 2.5 mmol) under nitrogen atmosphere for 12 hours at ambient temperature. The solvent was removed under vacuum and the green colored powder was recrystallized using chloroform and petroleum ether. The geometry of this complex was found to be tetrahedral. UV-Vis (CH_2Cl_2): 691, 666, 630, 615 nm. MS(m/z): 504 ($m + 1$), 503 (m^+), 281 (100), 224, 77, 57. Magnetic moment: μ_{eff} 4.39 BM (Lit. μ_{eff} 4.67 BM) (Cotton and Wilkinson 1988). Anal. Calcd. for $\text{C}_{22}\text{H}_{24}\text{O}_8\text{N}_2\text{Co}$: C, 52.49; H, 4.77%. Found: C, 52.47; H, 5.00%.

3.2 General procedure for alcohol oxidation and epoxidation

Alcohol or alkene (5 mmol), 2-methylpropanal (10 mmol) and catalysts **1** or **2** (~ 5 mol%) were stirred in dry acetonitrile (30 ml) at room temperature for 20–22 hours under dioxygen balloon. Removal of acetonitrile under reduced pressure gave the residue which was dissolved in ethyl acetate (30 ml). The organic layer was successively washed with NaHCO_3 solution (3 \times 20 ml) and brine solution (2 \times 15 ml). Drying (Na_2SO_4) and evaporation of the solvent under reduced pressure gave the crude compound which was subjected to HPLC or column chromatography. Allylic oxidation of cyclohexene is also carried out under similar reaction conditions.

2,3-Epoxy carvone (4i): Carveol (0.76 g, 5 mmol), 2-methylpropanal (0.72 g, 10 mmol) and cobalt(II) complex **1** (5 mol%) were subjected to the above described reaction conditions for 24 hours to afford **4i** and **4j** in the ratio of 33:28 (0.48 g, 61%) as an oil. ^1H NMR (CCl_4): δ 1.1–1.3 (m, 5H), 1.7 (s, 3H), 1.8–2.0 (m, 3H), 2.5–2.7 (t, 1H, $J = 6.0$ Hz), 4.6 (s, 2H). IR (neat): 1720, 1365, 1235 cm^{-1} . Anal. Calcd. for $\text{C}_{10}\text{H}_{14}\text{O}_2$: C, 72.00; H, 8.43. Found: C, 72.10; H, 8.40.

3-Acetoxy-3,7-dimethyl-6,7-epoxy-1-octene (6b): Linalool acetate (0.9 g, 2.5 mmol) and 2-methylpropanal (0.36 g, 5 mmol) and cobalt(II) complex **1** (5 mol%) were subjected to the reaction conditions as described in general procedure to give **6** (0.44 g, 84%) as a liquid. $^1\text{H NMR}$ (CDCl_3): δ 1.1 (s, 3H), 1.2 (s, 3H), 1.6 (s, 3H), 1.6–2.0 (m, 4H), 2.0 (s, 3H), 2.4 (t, 1H, $J = 6.5$ Hz), 4.8–5.2 (m, 2H), 5.5–6.0 (m, 1H). IR (neat): 1725, 1360, 1240 cm^{-1} . Anal. Calcd. for $\text{C}_{12}\text{H}_{20}\text{O}_3$: C, 73.40, H, 10.20%. Found: C, 73.44; H, 10.21%.

10,11-Epoxy farnesyl acetate (6d): Farnesyl acetate (0.53 g, 2 mmol), 2-methylpropanal (0.3 g, 4 mmol) and cobalt(II) complex **1** (5 mol%) were subjected to the above reaction conditions for 20 hours to give **6d** (0.4 g, 71%) as an oil. $^1\text{H NMR}$ (CCl_4): δ 0.9 (s, 6H), 1.5 (s, 3H), 1.6 (s, 3H), 1.9–2.2 (m, 11H), 2.55 (t, 1H, $J = 6.0$ Hz), 4.4 (d, 2H, $J = 6.0$ Hz), 4.9–5.5 (m, 2H). IR (neat): 1720, 1365, 1235 cm^{-1} . Anal. Calcd. for $\text{C}_{15}\text{H}_{28}\text{O}_3$: C, 72.85; H, 10.00. Found: C, 72.51; H, 10.07.

1,2-Epoxy β -ionone (6e): β -Ionone (0.95 g, 5 mmol), 2-methylpropanal (0.72 g, 10 mmol) and cobalt(II) complex **1** (5 mol%) were subjected to the above described reaction conditions for 17 hours to afford **6e** (0.63 g, 61%) as an oil. $^1\text{H NMR}$ (CCl_4): δ 0.85 (s, 3H), 1.0 (s, 3H), 1.1 (s, 3H), 1.2–1.9 (m, 6H), 2.1 (s, 2H), 6.0–7.1 (dd), 2H, $J = 12$ Hz). IR (neat): 1690, 1970, 1620, 1375, 1350, 1250 cm^{-1} .

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