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## Cobalt(II) Catalyzed Biomimetic Oxidation of Hydrocarbons in the Presence of Dioxygen and 2-Methylpropanal

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Abstract: Cobalt(II) Schiff base complex 1 catalyses the oxidation of aliphatic and aromatic hydrocarbons in the presence of 2-methylpropanal under 1 atmosphere of dioxygen to give corresponding ketones and alcohols.

Metal catalyzed oxidation of organic compounds with dioxygen is rapidly gaining importance<sup>1</sup> as a viable alternative to the environmentally hazardous metal promoted stoichiometric oxidations. Recent studies have shown<sup>2</sup> that transition metals in combination with various oxidizing agents convert a wide range of hydrocarbons to the corresponding oxidized products. These metal catalyzed oxidations are modelled<sup>3</sup> on certain enzymes which perform the oxidation of hydrocarbons in natural systems. In spite of many studies, there are very few which use dioxygen directly as a source of oxygen atom in the oxidation of hydrocarbons. We now report that cobalt(II) Schiff base complex 1 efficiently catalyses the oxidation of cyclic hydrocarbons to the corresponding alcohols and carbonyl compounds in the presence of dioxygen and 2-methylpropanal.



Our earlier studies have indicated<sup>5</sup> that complex 1 and related Schiff base complexes are extremely versatile in catalyzing the oxidation of a wide range of organic compounds in the presence of dioxygen and 2-methylpropanal at ambient pressure. The oxidation of hydrocarbons does not proceed to any appreciable extent under these reaction conditions, however, increasing the pressure of oxygen to 1 atm afforded good yields of the oxidized products at ~20% conversion. Thus, stirring a mixture of hydrocarbon (10 mmol), catalyst 1 (5 mol%) and 2-methylpropanal (20 mmol) in acetonitrile (15 mL) at 1 atm of dioxygen at ambient temperature for 12-15 h gave a mixture of alcohols and ketones in good yields (Table 1). According to this protocol, cyclohexane can be converted into a mixture of cyclohexanol and cyclohexanone in 1:4 ratio whereas cyclooctane afforded a 1:2 mixture of the corresponding alcohol and ketone in moderate yields (Table 1, entries 1-2). Methyl cyclohexane can also be oxidized to give 1-methyl cyclohexan-1-ol as the major

 entry	hydrocarbon	conversion(%)a	products yi	eld(%)c,d
1	Cyclohexane	17	Cyclohexanol Cyclohexanone	21 79
2	Cyclooctane	13	Cyclooctanol Cyclooctanone	33 67
3	Methylcyclohexane	20	1-Methylcyclohexan-1-o	ol 70
4	Decalin	25	9-Hydroxy 1-decalone	60
5	Benzene	21 <sup>b</sup>	1,4-Benzoquinone	71e
6	Anthracene	65 <sup>b</sup>	9,10-Anthraquinone	67b

Table 1.	. Cobalt(II) catalysed oxidation of hydrocarbons in the presence of
	dioxygen and 2-methylpropanal

<sup>a</sup>Determined by GC analysis.<sup>b</sup>Determined by HPLC analysis.<sup>c</sup>Determined by GC analysis based on the converted substrate.<sup>d</sup>Reaction condition: hydrocarbon (10 mmol), 2-methylpropanal (20 mmol) and 1 (~5mol%) were stirred in acetonitirle (15mL) for 12-15h under dioxygen (1atm) at ambient temperature. In these reactions, 2-methylpropanal was oxidised to 2-methylpropanoic acid. <sup>e</sup>Determined by HPLC based on converted substrate.

entry	cyclohexane : 2-methylpropanal	dioxygen pressure	conversion(%)a	<u>vield %<sup>b,c,d</sup></u> cyclohexanol : cyclohexanone
1	1:2	ambient	5	7:93
2	1:1	1 atm	13	10:90
3	1:2	1 atm	17	21:79
4	1:3	1 atm	20	29:61
5	1:2	2 atm	21	64:34

## Table 2. Oxidation of Cyclohexane at Different Conditions

<sup>a</sup>Determined by GC analysis. <sup>b</sup>Determined by GC analysis based on converted cyclohexane. <sup>c</sup>2-methylpropanal was oxidised to the corresponding carboxylic acid.<sup>d</sup>Reaction condition: Same as mentioned in footnote d of table 1.

product, however, the reaction mixture also consisted of some unidentifiable products ( $\sim 15$  %) (Table 1, entry 3). Interestingly, a mixture of *cis* and *trans*-decalins underwent oxidation to give 9-hydroxy 1-decalone as the major product(Table 1, entry 4). Similarly, benzene and anthracene can also be oxidized to the corresponding quinones under these conditions (Table 1, entries 5 and 6). In order to optimize the yield of oxidized products, the oxidation of cyclohexane was carried out under a different oxygen pressure and quantity of 2-methylpropanal. Thus, reaction of cyclohexane in the presence of 2 equiv of 2-methylpropanal, at ambient pressure of dioxygen gave a very poor percentage of conversion (Table 2, entry 1), however, in the presence of 1 equiv of aldehyde and increasing the pressure (1 atm) of dioxygen showed some improvement in the yield was not substantial and further attempts to enhance the extent of conversion of hydrocarbon by increasing the quantity of 2-methylpropanal did not bring about any significant improvement

in conversion and the yield of oxidized products (Table 2, entries 3-4). Further increase in the pressure (2 atm) of dioxygen did not have any effect on the yield of these reactions (Table 2, entry 5). These studies thus indicate that increasing the quantity of aldehyde or pressure of dioxygen beyond 1 atm has very little effect on the extent of conversion of hydrocarbon. It is known that Co(II) SALEN catalyzes the oxidation of



aldehydes to peracids under aerobic conditions and thus the reaction catalyzed by 1 may also be proceeding via the formation of peroxy isobutyric acid. However, this pathway is ruled out as no oxidation of hydrocarbon is observed in the presence of Co(II) SALEN catalyst.



Thus, these oxidations may be proceeding via the reaction of hydrocarbons with a highly active cobalt (1V)-oxo species (1b) which is likely to be generated from the initially formed cobalt (1II)-superoxo complex (1a) (Scheme 1). An EPR investigation on catalyst 1 in the presence of 2-methylpropanal and dioxygen in acetonitrile has indicated the formation of cobalt (1II)-superoxo complex (1a) and the formation of the latter is promoted by aldehyde as no EPR signal corresponding to 1a appeared in the absence of it. Thus, the initial EPR spectrum of the complex 1 at 2662 G (Fig. 1a) changes to a sharp signal at 3332 G (Fig. 1b) after adding 2-methylpropanal in the presence of dioxygen. The sharp signal at 3332 G indicates the formation of a Co-O-O species which has already been reported<sup>5</sup> earlier by Basolo *et al.* on related cobalt complex in the presence of pyridine. The formation of Co(III) species is also inferred from the electronic spectra of the reaction mixture as indicated in Fig. 2 where the initial Co(II) spectra (2a) changes to Co(III) spectra (2b) after 1.25 hours. The formation of Co(III)-O-O species from 1 may be facilitated by the intramolecular hydrogen bonding between the terminal oxygen atom of bound O<sub>2</sub> and the hydroxy group present in the ligand

(e.g. 2). A similar stabilization of superoxo complex from cobalt and iron has been proposed<sup>6</sup> recently. Participation of -OH group in this stabilization is further supported by studying the EPR of the cobalt catalyst derived from the corresponding acetate which showed no such EPR signal under these conditions. Similarly, no EPR was observed in the case of Co catalyst derived from methyl ester of phenyl alanine. It is noteworthy, though not particularly surprising, that neither of these cobalt complexes acted as a good catalyst during the oxidation of hydrocarbons. Subsequently, cobalt (IV)-oxo species 1b may be formed from cobalt(III)-superoxo complex (1a) by the reducing action of aldehyde present in the latter complex (Scheme 1). Kochi and coworkers have also proposed7 the intermediacy of a cobalt-oxo complex of type 1b during the oxidation of alkenes with iodosyl benzene. This mechanism is not proceeding via Fenton type chemistry as our earlier results indicate that the active species derived from catalyst 1, dioxygen and aldehyde is extremely versatile as it oxidizes alkenes, alcohols, benzylic and aromatic substrates with remarkable facility. If a Fenton like species is formed then it is unlikely that it could oxidize a wide range of organic substrates as mentioned above. Also, the oxidation of benzene is not occurring via the corresponding phenol, as the oxidation of latter under these conditions affords no benzoquinone. Thus, this mechanism has some similarity<sup>3,8</sup> with the iron (IV)-oxo complex proposed during the oxidation promoted by cytochrome P-450 systems. It is evident that aldehyde plays a dual role as initiator in the formation of superoxo<sup>4(,5</sup> complex 1a and subsequently by a reducing action in the formation of cobalt (IV)-oxo species 1b. In view of the chiral nature of complex 1, we have attempted the enantioselective hydroxylation of n-hexane. However, no enantioselectivity was observed in this reaction.

In conclusion, the studies described here indicate that the cobalt complex 1 catalyses the oxidation of hydrocarbons in the presence of dioxygen and 2-methylpropanal via the formation of cobalt (III)-superoxo species. Studies related to the mechanism and improvement in the yields of this oxidation is currently underway in our laboratory.

## **References and Notes**

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