

Equatorial and Axial Ligand Effects in Square Planar Co(II) Complexes Catalysing the Oxidation of 1-Phenylethan-1-ol to Acetophenone

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There is great interest in metal complex catalysed homogeneous oxidations of organic substrates, and research activity in this area has focussed on three central themes: (i) the discovery of new oxidation catalysts, and new catalytic oxidation reactions, (ii) the elucidation of mechanisms through kinetic studies, and (iii) the 'tailoring' of the catalyst and reaction conditions for maximum catalytic activity [1]. It is the latter theme which we have investigated in this paper.

Square planar Co(II) complexes of tetradentate ligands (CoL_4) have been reported [2] to catalyse the oxidation of secondary alcohols to ketones in the presence of an axial ligand (B) and dioxygen at normal temperature and pressure. Kinetic studies of this reaction have demonstrated that the oxidation proceeds via the labile pre-reaction complex depicted in Fig. 1, with reduction of the coordinated dioxygen by hydrogen abstraction in the rate determining step [2, 3]. We now report how varying both the axial and equatorial ligands changes the activity of the Co(II) catalyst in the oxidation of 1-phenylethan-1-ol to acetophenone, and discuss the implications for the reactivity of coordinated dioxygen.

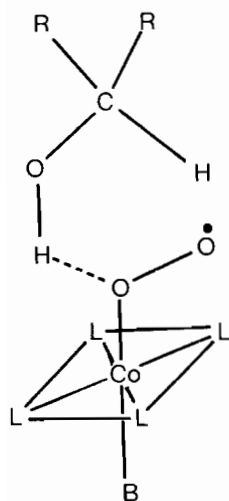


Fig. 1. Schematic drawing of the labile pre-reaction complex composed of CoL_4 , axial base (B), O_2 , and alcohol. The alcohol is hydrogen bonded to the coordinated dioxygen.

Experimental

Cobalt(II) complexes were prepared by standard methods, and the abbreviations used for the ligands are given in ref. 4. In a typical reaction the axial base (100 mg) was dissolved in 1-phenylethan-1-ol (10.0 ml) in a water-jacketed flask at $40.0 \pm 0.2^\circ\text{C}$. The CoL_4 complex (50 mg) was then added and the reaction mixture stirred vigorously under an O_2 atmosphere maintained with a balloon assembly for 18 h. After this period the yield of acetophenone was determined by GLC as previously described [3]. The results are expressed as turnover numbers, defined as (mol of product)/(mol of cobalt(II) catalyst) under the above conditions.

Results and Discussion

The effects of axial bases on the catalytic oxidation of 1-phenylethan-1-ol to acetophenone were assessed by measuring turnover numbers using Co(benacen) as the square planar, tetradentate, cobalt(II) catalyst. The results are depicted in Fig. 2. Changing the axial ligand from 1-methylimidazole to triphenylphosphine resulted in a 4.3 fold increase in the yield of acetophenone. An explanation for this behaviour was initially sought in the role of the axial ligand in promoting dioxygen binding, as previous work had demonstrated that in related systems $\text{Co}(\text{salen})(\text{PPh}_3)(\text{O}_2)$ is the catalytically active species [2, 3]. However, the $\text{Co}(\text{benacen})(\text{B})$ complex with the highest dioxygen affinity ($\text{B} = 1\text{-methylimidazole}$)

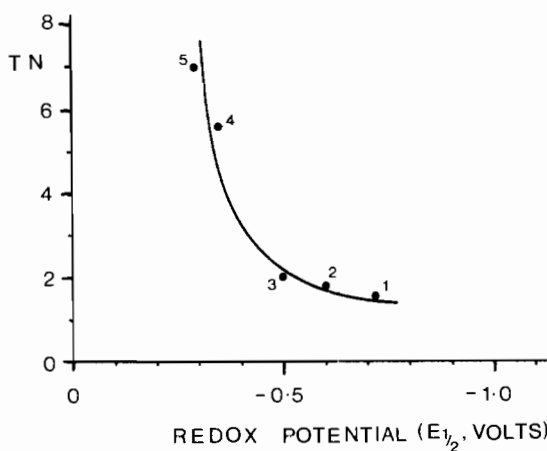


Fig. 2. Plot of turnover number observed for the $\text{Co}(\text{benacen})(\text{B})$ catalysed oxidation of 1-phenylethan-1-ol to acetophenone against $E_{1/2}$ (from ref. 5) for the $\text{Co}(\text{benacen})(\text{B})_2$ complexes with B as follows: 1, 1-methylimidazole; 2, piperidine; 3, pyridine; 4, 4-cyanopyridine; 5, triphenylphosphine.

[5] has the lowest catalytic activity and the complex with the highest catalytic activity (B = triphenylphosphine) has the lowest affinity for dioxygen [5]. These results imply that it is the changing reactivity of the coordinated dioxygen which is crucial here, as the catalytic activity must depend on both the concentration and reactivity of the dioxygen complex.

Using the spin pairing model [6] to describe the bonding of dioxygen in these complexes (in which one of the unpaired antibonding electrons of O_2 pairs with the d_{z^2} electron of cobalt(II)) the reduction of dioxygen in the rate determining step would be favoured by a low extent of electron transfer (ET) to the coordinated dioxygen. Two measures are available for this, the ET values determined from EPR data [6], and electrochemical measurements. The most relevant available data for the present series of complexes are the polarographic half-wave potentials of $Co(benacen)(B)_2$ complexes [5], these measure the ease of electron removal from the cobalt d_{z^2} orbital and thus give a guide to the magnitude of ET in the corresponding $Co(benacen)(B)(O_2)$ complexes. Figure 2 shows the turnover numbers plotted against these half-wave potentials, and demonstrates that the turnover number increases as the potential of the complex becomes less negative. Thus the most reactive complex (B = triphenylphosphine) is that in which ET is least, supporting the hypothesis advanced above.

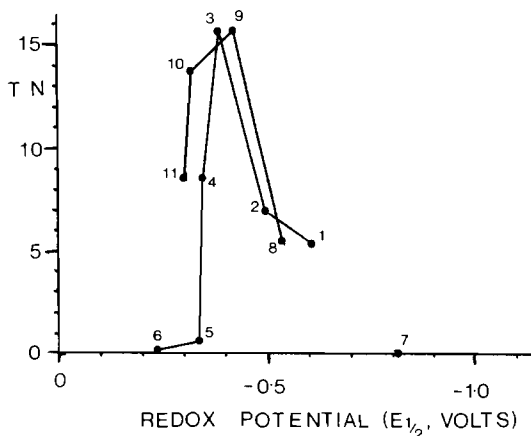


Fig. 3. Plot of turnover number observed for the CoL_4 - (triphenylphosphine) catalysed oxidation of 1-phenylethan-1-ol to acetophenone, against $E_{1/2}$ (from refs. 5, 7) for the CoL_4 (pyridine) $_2$ complexes (data points 1 to 6), and against $E_{1/2}$ (from ref. 8) for the CoL_4 (dimethylformamide)(O_2) complexes (data points 8 to 11), with L_4 as follows: 1 and 8, acacen; 2, benacen; 3 and 9, salen; 4 and 11, saloph; 5, (dmg) $_2$; 6, pMeO-TPP; 10, 3-MeOsalen. Point 7 is $E_{1/2}$ for O_2 [8].

The results of varying the equatorial ligand are shown in Fig. 3, where turnover numbers for a variety of tetradentate cobalt(II) complexes, with triphenyl-

phosphine as axial ligand, are again plotted against half-wave potential. In this case half-wave potentials are available for the cobalt(II) complexes of these equatorial ligands with both axial positions occupied by pyridine [5, 7], or with dioxygen and dimethylformamide as axial ligands [8]. Where data are available for complexes in both series, e.g. for acacen, salen, and saloph as equatorial ligands, the potentials for both the bis-pyridine and dioxygen complex have similar values, but this is probably fortuitous as both solvent and reference electrode differ between the two series. However, it is significant to note that the relative orders of the potentials of the two series of complexes are the same, and it is this, rather than the similarity in the potentials, which validates the inclusion of the data for the bis-pyridine complexes in Fig. 3 as a measure of ET to coordinated dioxygen. On coordination dioxygen is more readily reduced ($E_{1/2} = -0.81$ for O_2^-/O_2 [8] is included in Fig. 3), thus we would expect the reactivity of the dioxygen complexes to increase as $E_{1/2}$ becomes less negative, as established above for the variation in axial ligand, and this is borne out by the increase in turnover number in the series of ligands: acacen < benacen < salen. However, maximum catalytic activity is attained with the salen complex ($TN = 15.4$), and as $E_{1/2}$ becomes less negative than -0.4 the catalytic activity decreases sharply. Clearly another effect unconnected with the inherent activity of the coordinated dioxygen must be coming to the fore, this we believe to be the decreasing affinity of the complexes for dioxygen. It is well established [5, 9] that as the ease of oxidation of a square planar $Co(II)$ complex increases, the dioxygen affinity of the complex also increases, and there is ample evidence for the low dioxygen affinity of tetraphenylporphyrin complexes of $Co(II)$ [10].

Drago's group have recently shown [1b] that in the $Co(II)$ -Schiff's base complex catalysed oxidation of phenols the catalysts became more effective as ET (measured from EPR data) to dioxygen increased. This is contrary to our observations on alcohol oxidation. Although the details of the extraction of ET values from EPR data have been criticised [11], where such data are available [6] for the complexes used in this work they indicate a similar order for ET (greater for an N_4 donor ligand set than for an N_2O_2 set) to that inferred from the electrochemical measurements.

The explanation for the opposing sensitivities of these two reactions to electron density on the catalyst must lie in the differing requirements of the two rate determining steps. In the oxidation of alcohols it is reduction of coordinated dioxygen by the abstraction of a hydrogen atom in the complex shown in Fig. 1, [2, 3] whereas in the oxidation of phenols the initial hydrogen atom abstraction is fast, and it is the break-

down of a metallo-peroxide which is considered to be the slow step [1b].

Conclusions

The reactivity of coordinated dioxygen in $\text{CoL}_4(\text{B})(\text{O}_2)$ complexes towards hydrogen atom abstraction is controlled by *ET* from the cobalt to the dioxygen moiety, with low *ET* enhancing the reactivity. However low *ET* is associated with a low dioxygen affinity, and the catalytic activity in the oxidation of secondary alcohols is dependent upon a balance between these two opposing factors.

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