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The Kinetics of the Oxidation of 1-Phenylethanol Catalysed by Co(II)(salen) with Triphenylphosphine

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The selective oxidation of organic substrates by dioxygen in homogeneous reactions catalysed by transition metal complexes is of current interest in both chemistry and biology. The dioxygen molecule in its triplet ground state is kinetically inert, but this can be overcome by coordination to a metal centre. Transition metal complexes containing dioxygen as a cyclic bidentate ligand have been prepared for most of the heavier late transition elements, and their stoichiometric and catalytic reactions have been thoroughly investigated [1]. Cobalt and rhodium are also capable of forming bent unidentate dioxygen complexes, but the catalytic potential of this class of compounds has been little explored. Nishinga [2] has reported a number of synthetically useful oxidations utilizing cobalt dioxygen complexes and Drago [3] has investigated the oxidation of phenols by similar catalysts.

This paper elucidates the mechanism of the oxidation of alcohols by Co(II)(salen) in the presence of triphenyl phosphine, a reaction first described by Savitskii [4], who measured the initial rates of oxygen consumption employing alcohols as both solvents and substrates. We have studied the time course of product formation, and have further investigated the mechanism in the inert solvent, chlorobenzene.

Experimental

Cobalt complexes were prepared by standard methods [6]. The purity of the solvents and substrates obtained commercially was checked by GLC analysis on a Perkin-Elmer F11 dual column instrument using carbowax 20M/chromosorb W as the packing material. Synthetic standards of the products were used to determine yields by comparison of peak heights and areas. The kinetic runs in chlorobenzene were performed in a 15 ml water jacketed reaction flask, kept at constant temperature (40 ± 0.2 °C), Co(salen) was added and an O_2 filled balloon assembly secured above the solution to start the reaction. The solution was vigorously stirred and GLC samples were taken periodically (0.5 hour intervals) to determine the extent of reaction. The standard reaction system consisted of 50 mg Co(salen) (15.4×10^{-3} M), 500 mg, PPh_3 (0.191 M), and 1.00 ml 1-phenylethanol (0.83 M) made up to 10.00 ml with chlorobenzene. Each component was varied in turn and the initial rate of reaction determined from plots of yield against time; data are shown in Figs. 1, 2 and 3. Other reactions were run under similar conditions. Distillation of the reaction mixtures followed by extraction of the residues with hexane yielded triphenylphosphine oxide upon evaporation.

Results and Discussion

When a solution of Co(salophen) (4 g) and triphenylphosphine (8 g) in 1-phenylethanol (75 ml) is stirred under air at room temperature an 8% yield (6 g) of acetophenone is produced after 24 h, at which stage the reaction has ceased. However,

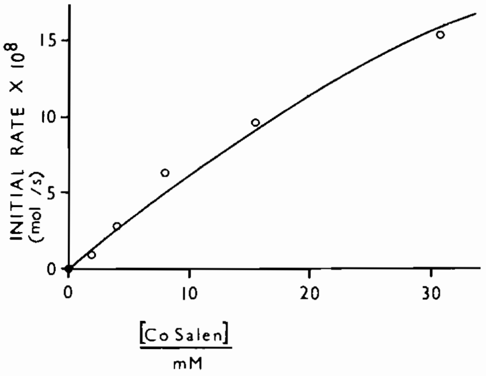

Fig. 1. Plot of initial reaction rate against Co(salen) concentration: triphenylphosphine 0.191 M and 1-phenylethanol 0.83 M. The line drawn is the theoretical line assuming Co(salen) dimerises at high concentrations ($K_d = 6$ l mol^{-1}).

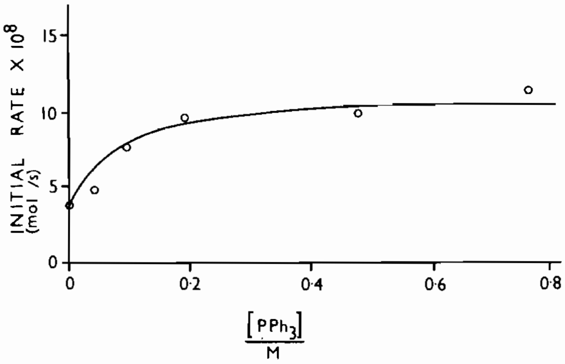

Fig. 2. Plot of initial reaction rate against triphenylphosphine concentration: Co(salen) 15.4×10^{-3} M and 1-phenylethanol 0.83 M. The line drawn is based on the value of 15 l mol^{-1} for K_a, the association constant for PPh_3 with Co(salen).

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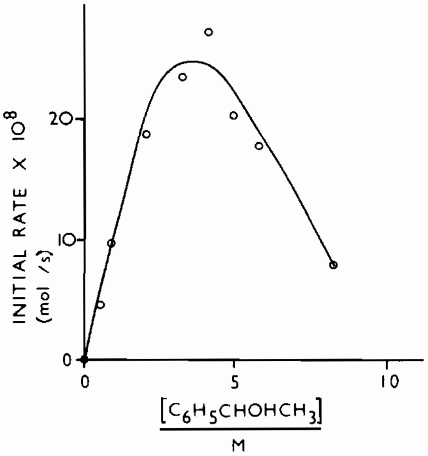

Fig. 3. Plot of initial reaction rate against 1-phenylethanol concentration: Co(salen) 15.4×10^{-3} M and triphenylphosphine 0.191 M. Neat 1-phenylethanol is 8.3 M.

further additions of similar quantities of triphenylphosphine are followed by proportionate increases in the accumulated yield of acetophenone.

Similar results with Co(salen) as catalyst showed that the production of acetophenone obeyed first order kinetics, and the rate constant increased 1.7 times when oxygen replaced air. When the reaction had ceased, 87% of the triphenylphosphine originally added was recovered as triphenylphosphine oxide. Savitskii [4] demonstrated that the catalytic oxidation of propan-2-ol to acetone using Co(salen)/triphenylphosphine as catalyst was a non-chain process. This makes it probable that hydrogen peroxide is an intermediate reduction product of dioxygen. However, attempts to detect hydrogen peroxide colorimetrically during the reaction using Cr(VI) and Ti(III) were unsuccessful, although hydrogen peroxide added at the end of the reaction, at 10% of the original triphenylphosphine concentration, could be detected. The failure to detect hydrogen peroxide could be understood when it was shown to react efficiently with both 1-phenylethanol and triphenylphosphine. Large amounts of triphenylphosphine (2 g) in 1-phenylethanol (10 ml) prevented oxidation of the alcohol by hydrogen peroxide (1.2 mmol), the only detectable product being the phosphine oxide. The production of hydrogen peroxide in the catalytic oxidation can thus account for the destruction of triphenylphosphine, and, as this is an essential component of the catalyst, the cessation of the catalytic reaction.

In order to gain more control over reaction conditions, further investigation of the catalytic reaction was made using initial rates of product formation obtained in the inert solvent chlorobenzene. Figure 1 shows that the rate of reaction is not linear in catalyst concentration, such curvature can be explained by dimerisation of Co(salen), with $K\alpha$ 6 l mol^{-1}, to yield an inactive dimer, such dimerisation has been observed in other solvents [6]. As the triphenylphosphine concentration is increased the reaction rate increases until a plateau is reached, Fig. 2. Savitskii [4] observed similar behaviour in the catalytic oxidation of neat propan-2-ol, and attributed it to the enhanced activity of the triphenylphosphine–Co(salen) complex, for which he obtained a formation constant of 350 l mol^{-1} at 40 °C. The data in Fig. 2 are fitted by a much lower formation constant, 15 l mol^{-1} at 40 °C, which is probably due to the change in solvent polarity, as it is similar to that reported for Co(salophen)/triophenylphosphine in dichloromethane [7]. The kinetic data presented here and by Savitskii [4] suggest that the same ternary catalytic species, involving a monomeric cobalt complex to which triphenylphosphine and dioxygen are coordinated, operates in both alcohols and chlorobenzene as solvent.

Savitskii [4] proposed that the alcohol substrate was hydrogen bonded to the catalytic species before oxidation occurred. It was thus of interest to determine the substrate dependence of the reaction, as Michaelis–Menten kinetics, observed for the Co(3MeOsalen) catalysed oxidation of hydrazobenzene [8], would lend strong support to Savitskii's proposal. The data in Fig. 3 show that the initial reaction rates are proportional to alcohol concentration up to 1.5 M-phenylethanol, and then start to become less than first order in substrate. However, instead of becoming independent of substrate concentration, which would indicate saturation of the catalyst with substrate, the rate peaks where the mole fractions of 1-phenylethanol and chlorobenzene are about equal, and then declines sharply. Any evidence for association between the substrate and catalyst is being overwhelmed by a solvent effect as the composition of the reaction medium changes; the association constant cannot exceed 1 l mol^{-1}. Interestingly similar solvent effects have been reported [9] for the oxidation of cyclohexanol in chlorobenzene by $\mathrm{Co(acac)_3}$. The work of Drago *et al* [10] who have shown that 1,1,1-trifluoroethanol can form strong hydrogen bonds to coordinated dioxygen provides another test of Savitskii's proposal. When the reaction mixture was made 0.64 M in 1,1,1-trifluoroethanol the rate of oxidation of 0.83 M 1-phenylethanol was reduced by 50% and the 1,1,1-trifluoroethanol wa not oxidized. Trifluoroethanol is a stronger hydrogen bond donor than 1-phenylethanol, it can thus inhibit the reaction by displacing the latter from the proposed catalytic complex.

Savitskii's suggestion [4] that the rate determining step was abstraction of the α-hydrogen atom from the alcohol was based on qualitative work using the alcohols as solvents, where the strong solvent effects demonstrated above could be paramount. Initial rate measurements in chlorobenzene, corrected for

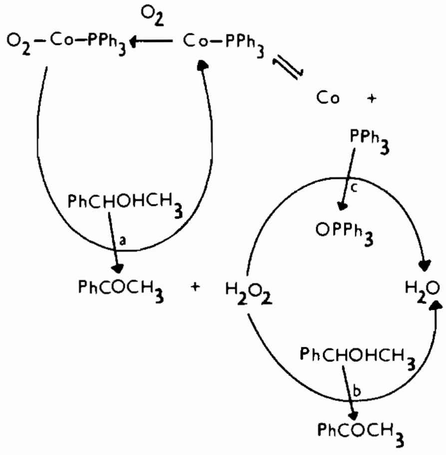

Fig. 4. Proposed catalytic cycle. Reaction (a) is catalysed by Co(salen)(PPh_3) and produces acetophenone and H_2O_2. The fate of H_2O_2 is reduction to H_2O via reactions (b) and (c) with reaction (b) being dominant. Reaction (c) renders the catalyst inactive and eventually stops reaction (a).

the number of α-hydrogen atoms on the substrate, for the oxidation of propan-2-ol, benzyl alcohol and 1-phenylethanol (each at 0.83 M), were in the ratio 1:1.5:2.8. This is in accord with the expected reactivity of such hydrogen atoms in hydrogen abstraction reactions [11].

Conclusions

The oxidation of alcohols, whether as neat liquids or as solutes in chlorobenzene, catalysed by Co(II) Schiff's base complexes in the presence of triphenylphosphine, proceeds through a ternary complex in which the alcohol is hydrogen bonded to the coordinated dioxygen, and triphenylphosphine is the other axial ligand to cobalt. The rate determining step is the abstraction of the α-hydrogen atom from the alcohol by the activated dioxygen moiety. Turnover numbers (mol product/mol catalyst) of at least 20 can be achieved, the reaction ceasing when all the triphenylphosphine has been oxidised. This occurs in a side reaction with the hydrogen peroxide which is produced in the catalytic step. These reactions are summarised in the catalytic cycle, Fig. 4.

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