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Kinetics of the Co(II)(Salen) Catalysed Hydration of Styrene to 1-Phenylethan-1-ol in Ethanol Solution

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Abstract

In aerobic ethanol solution Co(Salen), in the presence of PPh_3, was found to catalyse the hydration of styrene. Turnovers of *ca.* 25 were obtained within 3 h, but by the end of that period reaction had ceased. The reaction was regiospecific and the Markovnikov addition product was obtained. Stoichiometric co-oxidation of the ethanol solvent to acetaldehyde and of PPh_3 to $OPPh_3$ also occurred. Kinetic studies indicate that the rate determining step of the reaction was hydrogen abstraction from the solvent by the coordinated dioxygen ligand of (O_2)-Co(Salen)(PPh_3). A mechanism has been proposed for the remaining steps of the reaction which involve an oxymetallation of the C=C of the styrene by HOO–Co(Salen)(PPh_3). Secondary phenylcarbinols were found to be catalytically oxidised to the corresponding ketones by the Co(Salen)/PPh_3 system in toluene solution and yields of up to 94% were obtained.

Introduction

The selective oxidation of organic substrates by dioxygen in homogeneous reactions catalysed by transition metal complexes is of interest in both chemistry and biology [1–4]. Research activity in this area has focussed on three central themes: (i) the discovery of new catalytic oxidation reactions and new catalysts, (ii) the elucidation of mechanisms through kinetic studies, and (iii) the 'tailoring' of catalyst and conditions for maximum activity [5–8]. A reaction of both academic and industrial importance is the selective oxygenation of alkenes [9–11]. This paper reports a mechanistic study by means of a kinetic investigation into the catalytic oxygenation, under mild conditions, of styrene in ethanol solution. A re-investigation from a synthetic viewpoint of the related catalytic oxidation of alcohols to carbonyl compounds has also been undertaken [12]. The catalyst for these oxygenation/oxidation reactions is the square planar cobalt(II) complex, Co(Salen)*.

Experimental

General

Co(Salen) and PPh_3 were obtained commercially. Ethanol, propan-2-ol, t-butanol, and toluene were distilled before use, whilst other solvents were used as supplied. Styrene was distilled at reduced pressure to obtain it free from inhibitor, 4-t-butylcatechol. H_2O_2 (100 volumes) and the secondary phenylcarbinols 1-phenylethan-1-ol, indan-1-ol, benzoin, benzhydrol, and 9-fluorenol were obtained commercially and were used without further purification. GC analyses were performed on a Perkin-Elmer F11 dual column instrument fitted with a flame ionization detector, using a 5% FFAP on diatomite column. Propiophenone was used as an internal standard to calibrate 1-phenylethan-1-ol and acetophenone signals. The purity of PPh_3/$OPPh_3$ was determined by ^{31}P NMR on a JEOL FX90Q spectrometer operating at 36 MHz. ^1H spectra were recorded at 90 MHz.

Kinetic Experiments

A stock ethanol solution (250.0 cm^3) containing styrene (25.00 cm^3) and propiophenone (0.152 g) was prepared and aliquots (10.00 cm^3) of this solution were used to study the time course of the reaction and for the kinetic runs. These experiments were performed in a two-necked 25 cm^3 flask (equipped with a reflux condenser, a septum, and a magnetic follower) immersed in a constant temperature oil bath (40.0 ± 0.2 °C). The Co(Salen) and PPh_3 were added to the reaction solution, which was open to air, and stirred vigorously. GC samples were taken periodically (0.25 h intervals) to determine the extent of reaction. The standard reaction system consisted of Co(Salen) (1.5×10^{-3} M), PPh_3 (38×10^{-3} M), and styrene (0.87 M). Each component was varied in turn and the initial rate of the reaction was determined from plots of yield (1-phenylethan-1-ol + acetophenone) against time, e.g. Fig. 1. Initial rate data at variable Co(Salen) and PPh_3 concentrations are given in Figs. 2 and 3 respectively. Other experiments noted in the text were performed under similar conditions.

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*N,N'-Bis(salicylidene)ethylenediaminocobalt(II).

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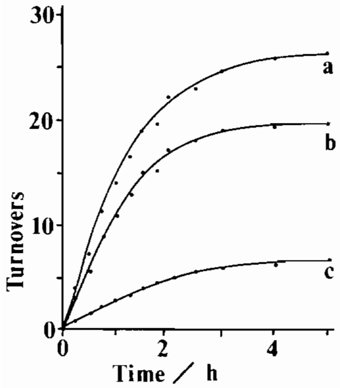

Fig. 1. Time course for the oxygenation of styrene (8.7 × 10^{-3} mol) in ethanol solution (10 cm^3) with Co(Salen) (1.5 × 10^{-5} mol) and PPh_3 (3.8 × 10^{-4} mol) as additives. (a) Production of total oxygenated product, 1-phenylethan-1-ol + acetophenone, (b) production of 1-phenylethan-1-ol and (c) production of acetophenone.

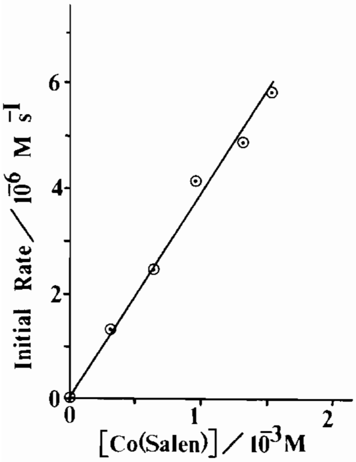

Fig. 2. Plot of initial reaction rate against Co(Salen) concentration: PPh_3 38 × 10^{-3} M and styrene 0.87 M. The line drawn is the theoretical line with k_1 and K_a at 5.3 × 10^{-3} s^{-1} and 85 dm^{-3} mol^{-1} respectively.

Oxidation of Secondary Alcohols

For the investigation of the effects of solvent and temperature upon the oxidation of 1-phenylethan-1-ol the following procedure was used. 1-Phenylethan-1-ol (0.610 g, 5.00 mmol) and PPh_3 (0.262 g, 1.00 mmol) were dissolved in the appropriate solvent (10.00 cm^3). To this solution was added Co(Salen) (0.082 g, 0.25 mmol). The reaction mixture was then stirred vigorously in a flask open to air at 40 °C for 24 h, and the yield of acetophenone was determined by GC analysis. Results (% yield) from reactions in various solvents at 40 °C were: DMF, 1.4%; acetone, 1.6%; acetonitrile, 3.0%; THF, 3.0%; chloroform, 3.9%; carbon tetrachloride, 5.1%; benzene, 10.7%; hexane, 11.1%; chlorobenzene, 11.6%; toluene, 13.0%. Results from reactions run in toluene at other temperatures were: 50 °C, 15.7%; 60 °C, 15.4%; 70 °C, 11.2%. The conditions for the catalytic oxidations found in Table 1 were as follows: the secondary alcohol (1.00 mmol), Co(Salen) (0.25 mmol), and PPh_3 (1.00 mmol) were stirred vigorously in a flask open to air in toluene solution (2.00 cm^3) at 50 °C for 48 h. Preparative t.l.c. (Silica, Kieselgel GF 254) with chloroform/60–80 °C light petroleum (60:40) as the eluant was used to isolate the products which were then identified by comparison of melting points, t.l.c. properties, and NMR properties with those of authentic samples.

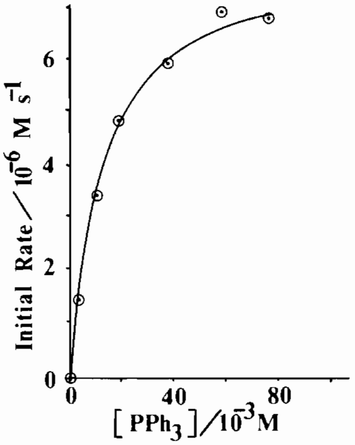

Fig. 3. Plot of initial reaction rate against PPh_3 concentration: Co(Salen) 1.5 × 10^{-3} M and styrene 0.87 M. The line drawn is the theoretical line with k_1 and K_a at 5.3 × 10^{-3} s^{-1} and 85 dm^{-3} mol^{-1} respectively.

TABLE 1. Oxidation of Secondary Alcohols Catalysed by Co(Salen)/PPh_3 in Toluene Solution at 50 °C

Substrate	Product	Yield (%)[a]
Propan-2-ol	acetone	33[b]
1-Phenylethan-1-ol	acetophenone	52[b]
Indan-1-ol	indan-1-one	56
Benzoin	benzil	70
Benzhydrol	benzophenone	75
9-Fluorenol	9-fluorenone	94

[a] From preparative TLC after 48 h reaction in air. [b] From GC analysis.

Results and Discussion

Styrene, in the presence of PPh_3 and Co(Salen) in aerobic ethanol solution, was found to be hydrated in a regiospecific manner to give the Markovnikov product, 1-phenylethan-1-ol (eqn. (1)). Acetophenone was also produced in smaller yields in this reaction but styrene oxide, 2-phenylethan-1-ol and

2-phenylethan-1-al were not detected in the reaction mixture. The oxygenation was not inhibited by the chain stopping reagent, 4-t-butylcatechol, and is similar to that reported by Drago and co-workers [13, 14] who have observed hexan-2-one as the major product from the oxygenation of hex-1-ene/ethanol solutions containing Co(SMDPT).

$$PhCH{=}CH_2 \longrightarrow PhCH(OH)CH_3 \qquad (1)$$

The time course for the production of oxygenated styrenes at 40 °C for a 10.00 cm^3 ethanol solution containing 8.7×10^{-3} mol styrene, 1.5×10^{-5} mol Co(Salen), and 3.8×10^{-4} mol PPh_3 was followed and is shown in Fig. 1. The oxygenation was found to be catalytic with respect to Co(Salen) and turnovers (moles of 1-phenylethan-1-ol + acetophenone/moles of cobalt catalyst) of *ca.* 25 were obtained within 2–3 h. By the end of this period, the reaction had ceased, and 4.0×10^{-4} mol of oxygenated styrenes had been produced. Addition of a further 3.8×10^{-4} mol of PPh_3 to this reaction solution re-started the oxygenation of the styrene, but again the reaction stopped, 2–3 h later, after a total of 7.3×10^{-4} mol of 1-phenylethan-1-ol/acetophenone had been produced. Removal of the solvent and volatiles from this reaction mixture followed by extraction of the residue with warm hexane yielded $OPPh_3$ (6.9×10^{-4} mol). These observations indicate that the catalytic hydration of styrene had occurred with stoichiometric co-oxidation of PPh_3.

Primary and secondary alcohols containing Co(Salen) and PPh_3 as solutes are known to be slowly catalytically oxidised under aerobic conditions to the corresponding aldehyde or ketone [12]. Since the hydration of styrene occurred in ethanol solution, it was of interest to determine whether acetaldehyde was produced as a co-product of the reaction. Acetaldehyde was detected in the reaction mixture but its high volatility precluded its quantitative GC analysis. When the reaction was attempted in t-BuOH solution, neither the solvent nor the PPh_3 were oxidised and the styrene was not hydrated. These results indicated that the oxidation of the alcohol and the hydration of the styrene were interlinked and that Co(Salen) was catalysing the reaction shown in eqn. (2), with acetophenone being formed in a side reaction from the catalytic oxidation of 1-phenylethan-1-ol.

$$PhCH{=}CH_2 + PPh_3 + CH_3CH_2OH + O_2 \longrightarrow PhCH(OH)CH_3 + OPPh_3 + CH_3CHO \qquad (2)$$

A kinetic investigation of this system using initial reaction rates was performed in order to further understand this interesting hydration reaction. As the Co(Salen) concentration was increased there was a proportionate increase in the initial reaction rate, indicating first order dependence upon the Co(Salen), Fig. 2. The rate of production of oxygenated styrenes was found to be independent of the styrene concentration in the concentration range 1.0 to 0.2 M. Below this lower concentration, the conversion of styrene to its oxygenated products was too great for initial reaction rate data to be meaningful. As the PPh_3 concentration was increased, the initial reaction rate also increased, until a plateau was reached, Fig. 3. Similar behaviour was observed for the Co(Salen)/PPh_3 catalysed oxidation of neat propan-2-ol to acetone [12], and for the oxidation 1-phenylethan-1-ol to acetophenone in chlorobenzene solution [15]. In these cases a dioxygen complex of Co(Salen)(PPh_3) was proposed as the catalytically active species. The rate law derived by Savitskii [12] for the catalytic oxidation of propan-2-ol was of the form Rate = k_1x, in which x is the equilibrium concentration of Co(Salen)(PPh_3). The value of x is dependent upon the formation constant of the complex, K_a. The data in Figs. 2 and 3, obtained at 40 °C, were fitted by the constants 5.3×10^{-3} s^{-1} and 85 dm^3 mol^{-1} for k_1 and K_a respectively. The corresponding values obtained by Savitskii for the catalytic oxidation of propan-2-ol at 40 °C were 6.2×10^{-4} s^{-1} and 350 dm^3 mol^{-1} [4]. The formation constant obtained here in ethanol solution is lower than that measured by Savitskii in isopropanol, but solvation effects may be important as an even lower value of 15 dm^3 mol^{-1} has been reported at the same temperature with chlorobenzene as solvent [15]. The applicability of the rate law and the similarity in the magnitude of the constants for k_1 and K_a respectively would suggest that the rate determining step in the oxidation of alcohols, as determined by Savitskii, and the rate determining step of the hydration of styrene in ethanol, is the same. For the case of the oxidation of propan-2-ol this was attributed to the abstraction of a hydrogen atom from the alcohol by coordinated dioxygen (Fig. 4) [12]. By inference the rate determining step for the hydration of styrene is shown in eqn. (3).

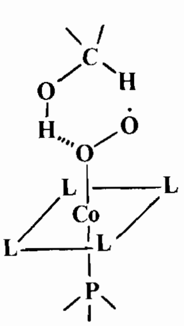

Fig. 4. Schematic drawing of the labile pre-reaction complex composed of Co(Salen), PPh_3, O_2 and the alcohol. The alcohol is hydrogen bonded to the coordinated dioxygen. The rate determining step of the reaction is the abstraction of the hydrogen atom by the dioxygen molecule.

$$(PPh_3)Co(Salen)(OO^{\bullet}) + CH_3CH_2OH \longrightarrow (PPh_3)Co(Salen)(OOH) + CH_3CH^{\bullet}OH \quad (3)$$

A catalytic cycle has been proposed for the oxidation of alcohols which involves H_2O_2 as an intermediate [15, 16]. This is of interest since the regiospecific hydration of the styrene could be explained by heterolytic addition of H_2O_2 across the double bond to give the hydroperoxide, $PhCH(OOH)CH_3$. The hydroperoxide would then be reduced by PPh_3 to $PhCH(OH)CH_3$ producing an equivalent of $OPPh_3$. To test whether hydrogen peroxide was a possible intermediate in the hydration reaction, its reaction with styrene was studied under a nitrogen atmosphere. Styrene (8.7×10^{-3} mol) in ethanol solution (10.00 cm^3) was found to be unreactive towards hydrogen peroxide (3.0×10^{-3} mol) at 40 °C. Furthermore, the styrene remained uneffected when Co(Salen) (1.5×10^{-5} mol) and PPh_3 (3.8×10^{-4} mol) were added to the reaction mixture. Therefore H_2O_2 was not an intermediate in the hydration reaction.

A possible mechanism which could account for the regiospecific nature of the reaction involves addition of the hydroperoxide of cobalt(III) to the styrene (eqn. (4)). This is similar to an oxymetallation type reaction and has been cited previously [13, 17] as a possible step in the reaction for the oxidation of hex-1-ene to hexan-2-one. The reaction could then proceed according to eqns. (5) and (6) with the overall stoichiometry as in eqn. (2).

$$(PPh_3)Co(Salen)(OOH) + PhCH{=}CH_2 \longrightarrow (PPh_3)Co(Salen)[CH_2CH(OOH)Ph] \quad (4)$$

$$(PPh_3)Co(Salen)[CH_2CH(OOH)Ph] + CH_3CH^{\bullet}OH \longrightarrow (PPh_3)Co(Salen) + CH_3CH(OOH)Ph + CH_3CHO \quad (5)$$

$$PPh_3 + CH_3CH(OOH)Ph \longrightarrow OPPh_3 + CH_3CH(OH)Ph \quad (6)$$

As the catalytic oxidation of the ethanol solvent was of importance in the hydration reaction the oxidation of alcohols was re-investigated to determine whether synthetically useful yields of ketones can be obtained from secondary alcohols using the Co(Salen)/PPh_3 system. In order to find conditions which would maximise conversions/yields of ketones the catalytic oxidation of 1-phenylethan-1-ol was studied as a model system for other alcohols. Experiments to optimise the yield of acetophenone were performed by varying the reaction solvent, reaction temperature, and catalyst:1-phenylethan-1-ol ratio. The highest yield of acetophenone was obtained in toluene solution at 50 °C at a Co(Salen):1-phenylethan-1-ol ratio of 4:1. Under these conditions a yield of 52% of acetophenone was obtained after 48 h reaction. Oxidations of other secondary alcohols were attempted under the same conditions and yields ranged from 33–94% (Table 1). Co-oxidation of PPh_3 also occurred in these reactions. Synthetically useful yields of ketones were obtained from phenylcarbinols in toluene solution using this catalyst system. The yields of the ketones produced in the oxidation parallel kinetic observations of initial reaction rates which correlate with the ease of abstraction of the hydrogen atom from the carbinol [12, 15].

References

1 J. M. Davidson, *Catalysis,* Vol. 2, The Chemical Society, John Wright, London, 1978, Ch. 8.
2 C. Masters, *Transition-metal Catalysis,* Chapman and Hall, London, 1981.
3 A. Nishinaga and H. Tomita, *J. Mol. Catal., 7* (1980) 179.
4 R. S. Drago, B. B. Corden and A. Zombeck, *Comments Inorg. Chem., 1* (1981) 53.
5 B. B. Corden, R. S. Drago and R. D. Perito, *J. Am. Chem. Soc., 107* (1985) 2903.
6 M. A. Beckett and R. B. Homer, *Inorg. Chim. Acta, 118* (1986) L11.
7 A. Nishinaga, H. Tomita, K. Nishizawa, T. Matsuura, S. Ooi and K. Hirotsu, *J. Chem. Soc., Dalton Trans.,* (1981) 1504.
8 A. Zombeck, R. S. Drago, B. B. Corden and J. H. Gaul, *J. Am. Chem. Soc., 103* (1981) 7580.
9 H. Mimoun, M. Mignard, P. Brechot and L. Saussine, *J. Am. Chem. Soc., 108* (1986) 3711.
10 M. Bresson, F. Morandini, A. Morvillo and P. Rigo, *J. Organomet. Chem., 280* (1985) 139.
11 M. Roussel and H. Mimoun, *J. Org. Chem., 45* (1980) 5387.
12 A. V. Savitskii, *J. Gen. Chem. USSR, 44* (1974) 1518.
13 D. E. Hamilton, R. S. Drago and A. Zombeck, *J. Am. Chem. Soc., 109* (1987) 374.
14 A. Zombeck, D. E. Hamilton and R. S. Drago, *J. Am. Chem. Soc., 104* (1982) 6782.
15 M. A. Beckett and R. B. Homer, *Inorg. Chim. Acta, 115* (1986) L25.
16 M. A. Beckett and R. B. Homer, *Inorg. Chim. Acta, 122* (1986) L5.
17 R. S. Drago, A. Zuzich and E. D. Nyberg, *J. Am. Chem. Soc., 107* (1985) 2898.