The Oxidation of Hydrazobenzene Catalyzed by Cobalt Complexes in Nonaqueous Solvents

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The oxidation of hydrazobenzene by molecular oxygen in the polar solvent methanol is catalysed by a Schiff's base complex Co(3MeOsalen) which is a synthetic oxygen carrier. The products are *trans*-azobenzene and water. The rate of the reaction has been studied spectrophotometrically and the rate law established. A mechanism involving a ternary complex of catalyst, hydrazobenzene and molecular oxygen has been proposed. The kinetic studies show that a ternary complex $CoL{\cdot}H_2AB{\cdot}O_2$ is involved in the rate determining step. The reactions are summarised in a catalytic cycle. The kinetic data suggest that a ternary complex involving Co (3MeOsalen), triphenyl-phosphine and molecular oxygen is catalytically acive species but at higher triphenyl-phosphine concentrations the catalyst becomes inactive. The destruction of the catalytic activity could be due to the catalyst becoming coordinated with triphenyl phosphine at both z axis sites of the complex *e.g.* Co $(3MeOsalen)(PPh_3)_2$.

Key Words : Catalytic cycle, Cobalt complexes, Hydrazobenzene, Axial ligands, Reaction mechanisms

Introduction

It has been known since the observation of Pfeiffer and his co-workers[1] in 1933 that Cobalt(II) Schiff's base complexes *e.g. N,N'*-ethylenebis(salicylideneiminato)-cobalt(II), Co(salen), Figure 1, form reversible complexes with oxygen. Tsumaki[2] in 1938 demonstrated that the colour change observed upon exposing Co(salen) to air as due to the reversible oxygenation of complexes, as shown in equations (1) and (2).

Although molecular oxygen reacts reversibly with some metal complexes, there are certain complexes formed

$$Co(salen) + O_2 \rightleftharpoons Co(salen)O_2 \quad (1)$$

$$2Co(salen) + O_2 \rightleftharpoons Co(salen)_2O_2 \quad (2)$$

irreversibly such as $[(Co(NH_3)_5)_2O_2](SCN)_4]$.[3]

A study of synthetic dioxygen complexes is important for understanding the bonding of dioxygen to transition metal complexes and the effect of this bonding upon the reactivity of dioxygen toward other substrates.

There has been considerable recent interest in these compounds because of their relationship to the natural iron-containing oxygen carriers hemoglobin and myoglobin.[3] Hemoglobin and myoglobin consist of an iron-porphyrin complex, the haem group, embedded in the protein which provides one axial ligand, an imidazole group, to the iron. On oxygenation the sixth coordination site of the iron accepts the dioxygen ligand.

Thus the ligand field about the iron in oxyhemoglobin is approximately octahedral.[4] Reversible dioxygen complexes are utilised in living organism for the transport and storage[5] of molecular oxygen. Dioxygen binding also occurs in enzymes which catalyse oxidation processes.[6]

Cobalt(II) Schiff's base complexes are square planner with a low spin d^7 electron configuration. The binding of an axial, fifth ligand leads to a ground state with the unpaired electron in the d_{z2} orbital. This electron configuration is a necessary prerequisite for the binding of dioxygen.[7] Drago and Corden,[8] in their spin-pairing model for the binding of dioxygen, presented evidence that the odd electron in the oxygenated complex is in the dioxygen π^* orbital, but that the extent of electron transfer from cobalt to oxygen is dependent on the nature of the equatorial and axial ligands. In the extreme case of complete electron transfer the complex could be formulated as cobalt(III)-superoxide.

The change in the electronic structure of oxygen from the relatively unreactive triplet ground state to a doublet coordinated species, with a weakened O-O bond bearing fractional negative charge, could be expected to enhance the reactivity of oxygen in radical or nucleophilic reactions.

In recent years the catalytic behavior of dioxygen complexes, Cobalt(II) Schiff base oxygen carrier complexes have been studied by both academics and industrialist.[6] Cobalt(II) Schiff's base complexes with added axial ligands have been shown to catalyse the oxidation by oxygen of secondary alcohols[9] to ketones, and of phenols[10] to quinones.

Cobalt complexes with salen or polyamines and related ligands have been employed as catalysts.[11,12] Savitskii[9] has made a kinetic study of the catalytic oxidation of isopropanol to acetone using initial reaction rates from oxygen consumption, and they have derived the rate law. They have also published a kinetic study of the catalytic oxidation of hydroquinone[13] in presence of Co(salen) in dimethylacetamide (DMA). They identified the main product of the oxidation of hydroquinone as *p*-benzoquinone. Nishinaga[11] indicated that a better model for natural systems is the catalytic double bond oxidation.[3,11] Nishinaga *et al.*[14] have

reported that the oxidation of 2,6-di-*t*-butylphenols by five-coordinate Co(II)Schiff-base complexes, for example cobalt-(II)bis(salicylideneamino)propylamine, has been found to result in the formation of peroxyquinolatocobalt(III) complexes. Drago *et al.*[10,15] began a kinetic investigation to provide insight into both the oxidation of 2,6-dimethylphenol and the deactivation of the catalyst CoSMDPT, cobalt(II)(3-salicylideneaminopropyl)methylamine. They also reported the catalytic oxidation[16] of olefins by molecular oxygen and by using CoSalMDPT, cobalt(II)-bis-(salicylidene-iminopropyl)methylamine. It is interesting to note that the catalyst CoSalMDPT demonstrates some substrate selectivity, oxidising linear olefins but not cyclohexane, and the reaction rate is independent of O_2 pressure.

The structually related bis(dimethylglyoximato)cobalt(II) has been reported to catalyse the oxidation of hydrazobenzene to azobenzene in the presence of triphenylphosphine.[17] Kinetic studies[9,10] have shown that in the oxidation of alcohols and phenols the transition state is a ternary complex of dioxygen, cobalt catalyst (including axial base) and substrate. Thus the reactions resemble an enzyme-catalysed process in which the two substrates, dioxygen and the organic molecule, are brought together by the catalyst.

In this paper we show that the oxidation of hydrabenzene catalysed by Co(3MeOsalen), Figure 1, follows a similar kinetic scheme, providing evidence of saturation of the catalyst by the substrate as an enzyme catalysed reaction. Autoxidation of hydrabenzene was first described in 1901 by Manchot and Herzog.[18] This, and later work[19,20] has shown that the products are *trans*-azobenzene and hydrogen peroxide with the reaction first order in hydrazobenzene and oxygen.

Results and Discussion

Studies of the oxidation of organic substrates catalysed by transition metal complexes have been focussed on three main themes: (1) the discovery of new oxidation catalysts and new catalytic oxidation reactions, (2) the elucidation of mechanisms through kinetic studies, and (3) the tailoring of the catalyst and reaction conditions for maximum catalytic activity.[21] Our work concentrates on the second of these.

Co(II)(3MeOsalen) has been used as a catalyst in the oxdation of hydrazobenzene (H_2AB). Hydrazobenzene is catalytically oxidised to azobenzene (AB) by L·Co(3Me Osalen)·O_2 (L = Ligand) in the polar solvent, methanol. Azobenzene has two isomers (*cis* and *trans*), thus the product of oxidation may provide stereochemical information about the reaction pathway. Hydrazobenzene is readily autoxidised to azobenzene and hydrogen peroxide,[18] and there is a possibility that the hydrogen peroxide produced may also oxidise hydrazobenzene. The rates of the oxidation of hydrazobenzene are measured under O_2 and air saturation at the 315 nm or 437 nm absorption bands of azobenzene.

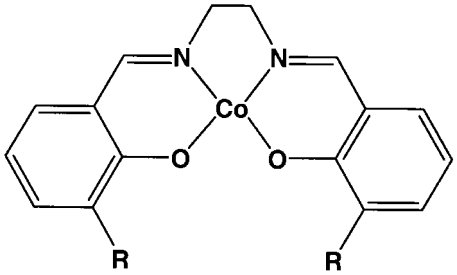


Figure 1. Cobalt(II)-Schiff base complexes, *e.g. N,N'*-ethylenebis (salicylideneiminato)-cobalt(II), Co^{II}(salen), R = H, Co(salen); R = CH_3O, Co(3MeOsalen).

The solvent methanol has a high polarity and the oxidation reaction may be carried out with or without an axial ligand. However, ligands were employed to observe their effect on the catalytic activity.

The results and discussion have been split into two parts : the kinetics of the Co(II)(3MeOsalen) catalysed oxidation of hydrazobenzene, and the reaction mechanism of hydrazobenzene oxidation.

The term autoxidation[22] is applied generally to oxidations which can be effected by free oxygen (*e.g.* by air) at moderate temperatures and may be contrasted with the rapid processes of combustion which require high temperatures. It has long been known that autoxidations are promoted by light[23] and by small quantities of many catalysts.

The autoxidation of hydrazobenzene has already been well studied.[18] Hydrazobenzene is readily autoxidised in ethanol with the formation of azobenzene and hydrogen peroxide.[19] They found that in an alcoholic solution the reaction is practically quantitative, equation (3).

$$C_6H_5NHNHC_6H_5 + O_2 \xrightarrow{EtOH} C_6H_5N{=}NC_6H_5 + H_2O_2 \quad (3)$$

The rate of the autoxidation of hydrazobenzene in methanol was found to be first order in substrate at room temperature.[21] Hinshelwood and Blackadder[24] reported that autoxidation of hydrzobenzene in alkaline solution (44% ethanol) containing oxygen was "a spontaneous reaction of first order with respect to hydrazobenzene". The rate of reaction became independent of oxygen once a concentration about 5% oxygen had been exceeded in the atmosphere to which the solution had been exposed. Savitskii and Nelyubin[13] demonstrated that the rate of O_2 consumption in the oxidation of hydroquinone is independent of oxygen pressure at 1 atmosphere.

When the initial rate R_o is plotted against the hydrazobenzene concentration, the plots are linear, Figure 2. We have demonstrated that autoxidation of hydrazobenzene in anhydrous methanol was found to be first order in O_2 or air, Table 1. The rate constants of the reaction mixture were caclulated to be 3.85×10^{-6} sec^{-1} in the O_2 saturated methanol and 1.98×10^{-6} sec^{-1} in the air saturated methanol. The rates of the autoxidation are used to find the initial rates in the catalysed reaction in Table 2 and 3.

The product azobenzene has two isomers, *cis*- and *trans*-azobenzene.[25] *Trans*-azo-benzene is found to be planar, or at least peri-planar, while the phenyl rings of the *cis*-isomer are

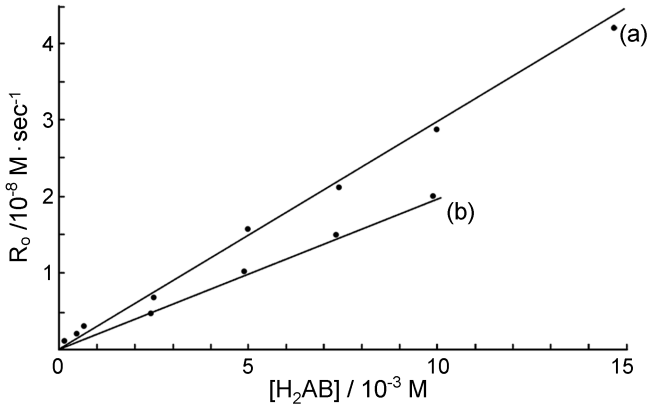


Figure 2. Plots of initial rates R_o against [H_2AB]. O_2 (a) and air (b) saturated methanol at 25.0 °C, λ = 315 nm and 437 nm. The rate constants are k(O_2) = 3.85 × 10^{-6} sec^{-1} and k (air) = 1.98 × 10^{-6} sec^{-1}.

Table 1. Effect of varing hydrazobenzene concentration, [H_2AB] on the autoxidation of hydrazobenzene in O_2 and air saturated methanol at 25.0 °C

NO.	[H_2AB] /10^{-3} M	O_2 saturated methanol		air saturated methanol	
		$(dA/dt)_o$ /10^{-5} sec^{-1}	R_o/10^{-8} sec^{-1}	$(dA/dt)_o$ /10^{-5} sec^{-1}	R_o/10^{-8} sec^{-1}
1	0.102	0.667	0.0469		
2	0.388	2.29	0.161[a]		
3	0.411	3.05	0.215[b]		
4	2.45	10.0	0.704	7.02	0.494
5	4.90	22.6	1.59	14.0	0.986
6	7.35	30.1	2.12	21.1	1.49
7	9.80	41.4	2.91	28.1	1.98
8	14.7	60.0	4.22		

[a]From Table 7. [b]From Table 8, λ = 315 nm (ε$_{315}$ = 1.61 × 10^4 M^{-1}·cm^{-1} (No. 1-3) and λ = 437 nm (ε$_{437}$ = 5.09 × 10^2 M^{-1} cm^{-1} (No. 4-8). Δε^{-1} = 7.04 × 10^{-5} M·cm. R_o = Δε$_{315}^{-1}$·(dA / dt)$_o$.

Table 2. Effect of varing hydrazobenzene concentration, [H_2AB] on the oxidation of hydrazobenzene in O_2 saturated methanol at 25.0 °C

[H_2AB]/ 10^{-3} M	$(dA/dt)_0$/ 10^{-3} sec^{-1}	R_0^a /10^{-7} M·sec^{-1}	R_0^b /10^{-8} M·sec^{-1}	R_0 /10^{-7} M·sec^{-1}	$k_{0\text{-}1}$/10^1 sec	[H_2AB]$^{-1}$/ 10^2 M^{-1}
1.81	3.11	2.19	0.550	2.13	3.49	5.52
3.61	5.29	3.73	1.07	3.62	2.05	2.77
7.22	9.45	6.65	2.15	6.44	1.15	1.39
9.03	12.0	8.47	2.67	8.20	0.906	1.11
10.8	13.0	9.18	3.18	8.86	0.839	0.923
12.6	13.6	9.58	3.71	9.21	0.807	0.791
14.4	14.9	10.5	4.23	10.1	0.734	0.693

R_o^a: initial rate of the reaction mixture, R_o^b: initial rate on the autoxidation of H_2AB (from Figure 2), R_o = R_o^a – R_o^b, k_o^{-1} = [Co(3MeOsalen)]/R_o; [Co (3MeOsalen)] = 7.43 × 10^{-6} M, λ = 315 nm (ε(H_2AB) = 1.89 × 10^3 M^{-1}cm^{-1}, ε(AB) = 1.61 × 10^4 M^{-1}·cm^{-1}), R_o = Δε^{-1} (dA / dt)$_o$; Δε^{-1} = 7.04 × 10^{-5} M·cm.

twisted (by 56°) out of the plane, Figure 3. *Trans*-azobenzene has been calculated (by the self consistent field (SCF) method) to be more stable by 43.5 K·J·mol^{-1} (10.4 Kcal·mol^{-1}) than the *cis*-isomer, which is in good agreement with the

Table 3. Effect of varing hydrazobenzene concentration, [H_2AB] on the oxidation of hydrazobenzene in air saturated methanol at 25.0 °C

[H_2AB]/ 10^{-3}M	$(dA/dt)_0$/ 10^{-3} sec^{-1}	R_{0a} /10^{-7} M·sec^{-1}	R^b_0 /10^{-8} M·sec^{-1}	R_0 /10^{-7} M·sec^{-1}	$k_{0\text{-}1}$/10^1 sec	[H_2AB]$^{-1}$/ 10^2 M^{-1}
1.16	0.619	0.436	0.230	0.413	18.0	8.62
2.32	1.24	0.871	0.470	0.824	9.02	4.31
3.48	1.75	1.23	0.700	1.16	6.41	2.87
4.56	2.30	1.62	0.910	1.53	4.86	2.19
5.70	2.93	2.06	1.15	1.95	3.81	1.75
6.84	3.25	2.29	1.37	2.15	3.46	1.46
7.98	3.85	2.71	1.60	2.55	2.91	1.25
9.12	4.33	3.05	1.83	2.87	2.59	1.09
10.3	4.93	3.47	2.05	3.26	2.28	0.975

R_o^a: initial rate of the reaction mixture, R_o^b: initial rate on the autoxidation of H_2AB (from Figure 2), R_o = R_o^a – R_o^b, k_o^{-1} = [Co(3MeOsalen)]/R_o; [Co (3MeOsalen)] = 7.43 × 10^{-6} M, λ = 315 nm (ε(H_2AB) = 1.89 × 10^3 M^{-1}·cm^{-1}, ε(AB) = 1.61 × 10^4 M^{-1}·cm^{-1}), R_o = Δε^{-1} (dA / dt)$_o$; Δε^{-1} = 7.04 × 10^{-5} M·cm.

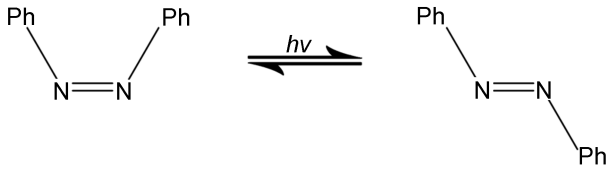


Figure 3. *Cis*- and *trans*-azobenzene (Ph : phenyl).

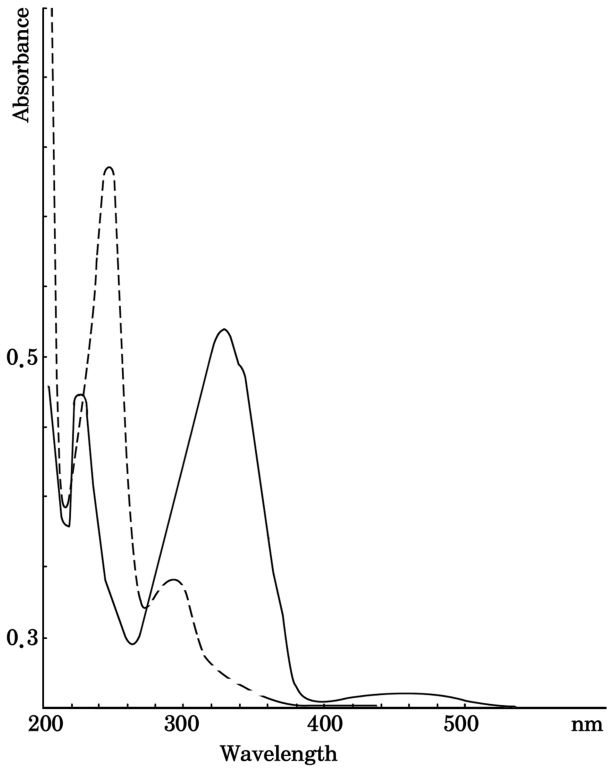


Figure 4. Absorption spectra of hydrazobenzene, broken curve, concentration 3.45 × 10^{-2} M and *trans*-azobenzene (solid curve, 2.75 × 10^{-3} M). Methanol, 25 °C.

experimental value of 41.8 K·J·mol^{-1} (10 Kcal·mol^{-1}).

Absorption spectra of hydrazobenzene (H_2AB) and *trans*-

Table 4. Absorption maxima of hydrazobenzene, *trans*-azobenzene, and *cis*-azobenzene. Methanol, 25.0 °C

Hydrazobenzene (H_2AB)		*Trans*-azobenzene (*trans*-AB)		*Cis*-azobenzene (*cis*-AB)	
λ_{max} (nm)	ε (10^3 $M^{-1}\cdot cm^{-1}$)	λ_{max} (nm)	ε (10^3 $M^{-1}\cdot cm^{-1}$)	λ_{max} (nm)	ε (10^3 $M^{-1}\cdot cm^{-1}$)
245	21.8	227	13.1	240	> 8.61
289	5.23	315	16.1	298	> 6.42
(315	1.89)	(437	0.509)	425	> 1.36

Table 5. Further addition of hydrazobenzene to the reaction mixture

Time (hour)	Absorbance	Time (hour)	Absorbance
0	0.132	0 (49.8 hrs.)	0.620
0.183	0.223	0.117	0.625
0.417	0.290	0.217	0.626
0.767	0.337	0.517	0.636
1.58	0.339	1.48	0.670
2.67	0.445	2.48	0.696
4.17	0.478	3.57	0.719
6.67	0.496	6.15	0.772
18.5	0.509	22.4	0.809
21.7	0.524	28.2	0.822
24.2	0.523	35.1	0.825
30.5	0.536		
49.8	0.538		

At time = 49.8 hrs., a further addition of hydrazobenzene (0.4606 g to 50 mL solution) (5.00×10^{-2} M) to the reaction mixture. O_2 saturated methanol, 25.0 °C, λ = 437 nm, [Co(3MeOsalen)] = 5.24×10^{-4} M, [H_2AB] = 1.01×10^{-1} M.

azobenzene (AB) in methanol was recorded over the rage of 600-200 nm, Figure 4. There are two bands observed at 245 nm and 289 nm. Extinction coefficients for these and of *cis*-azobenzene are given in Table 4.

Some *cis*-azobenzene was produced from *trans*-azobenzene (8.16×10^{-3} M) in methanol at 25.0 °C by irradiating it for about three hours at 315 nm in the cell compartment of a Farrand spectrofluorometer with 20 nm slits. Each isomer of azobenzene has three bands. Two of the bands in *trans*-azobenzene was shifted to shorter wavelengths in the *cis* isomer, Table 4. The absorption spectrum of the isomers in methanol is similar to that of *trans*-azobenzene in ethanol. The extinction coefficients in Table 4 are exact as conversion to the *cis* isomer has not reached 100%. During irradiation there was a large change in the absorbance of the bands at 315 nm and 437 nm in the first half hour, the rate of which decreased rapidly until after 21/2 hours, after which there was no further change in the absorbance. If during the course of the oxidation of hydrazobenzene in methanol, *cis*-azobenzene were formed as an intermediate, a band at 425 nm (literature 433 nm in ethanol)[26] should have been formed before the formation of the band at 437 nm due to *trans*-azobenzene.

The oxidation of hydrazobenzene (1.01×10^{-1} M) catalysed by Co(3MeOsalen) (5.24×10^{-4} M) produced *trans*-azobenzene as witnessed by a band at 437 nm in methanol at

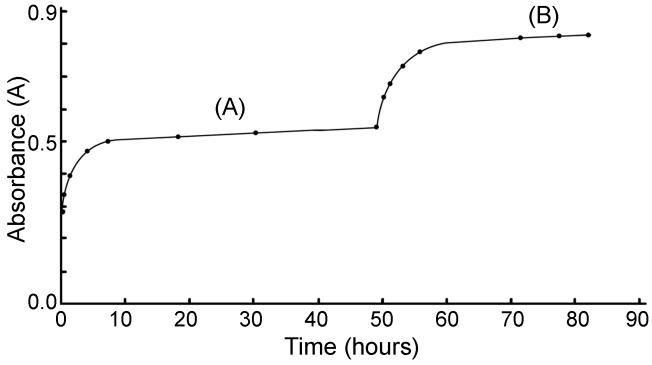


Figure 5. Plot of absorbance, A, against time. O_2 saturated methanol, 25.0 °C, λ = 437 nm. [Co(3MeOsalen)] = 5.24×10^{-4} M. (A): [H_2AB] = 1.01×10^{-1} M (initially); (B): [H_2AB] = 0.500×10^{-1} M (0.4606 g to 50 mL solution) (a further addtion at *ca*. 50 hrs.).

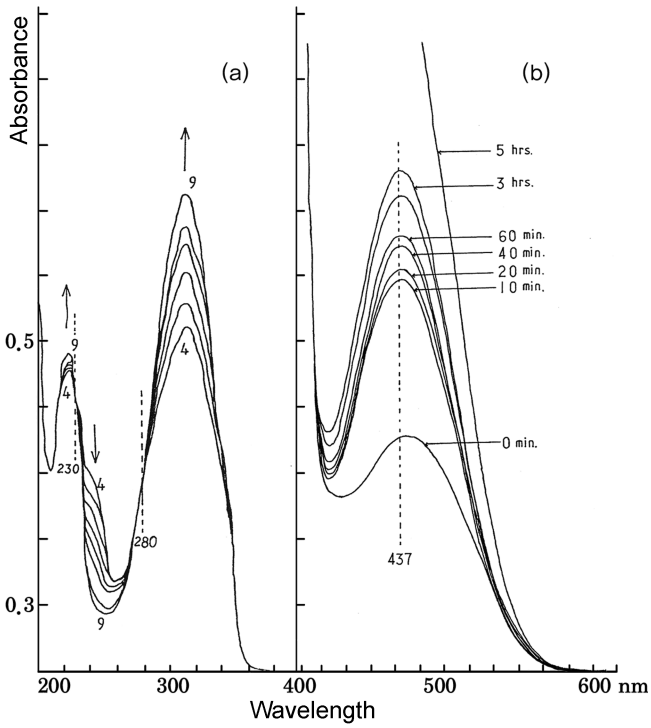


Figure 6. Changes in absorption spectra during reaction. O_2 saturated in methanol, 1 atm, 25 °C. [Co(3MeOsalen)] = 5.20×10^{-6} M, [$H_2AB]_o$ = 3.33×10^{-5} M. No. 4 (20 min.), No. 9 (3 hrs.).

25.0 °C. After most of the substrate was oxidised to azobenzene (in *ca*. 50 hours), a further addition of hydrazobenzene (0.4606 g/50 mL methanol, 5.00×10^{-2} M) into the reaction mixture was made, Table 5. The absorbance at 437 nm again began to increase, and at a similar rate as before, showing that the catalyst remained active, Figure 5. The spectral changes during the reaction are indicated in Figure 5.

Figure 6 shows the time dependence of the changes in the absorption spectrum during the oxidation of hydrazobenzene (3.33×10^{-5} M) with Co(3MeOsalen) (5.20×10^{-6} M) under oxygen at 25.0 °C. The band at 254 nm decreases with time in Figure 6a, due to the oxidation of hydrazobenzene, while

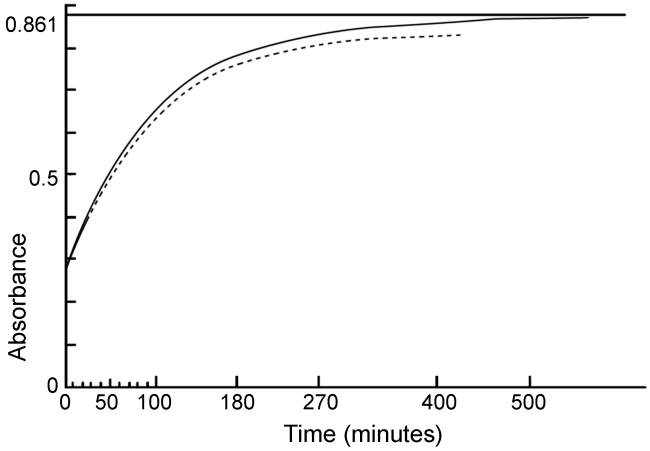


Figure 7. Plot of absorbance A (at 315 nm) against time, O_2 saturated in methanol, 1 atm, 25 °C. [Co(3MeOsalen)] = 5.67×10^{-6} M, $[H_2AB]_o = 3.26 \times 10^{-3}$ M. Solid curve, experi-mental; broken curve, calculated for pseudo-first order kinetics as described in the text.

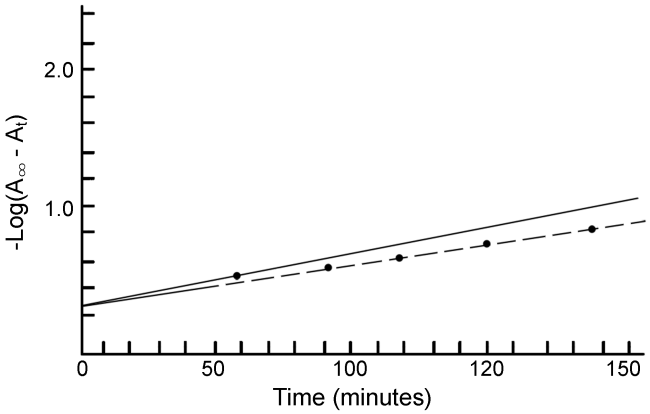


Figure 8. Plot of $-\log(A_\infty - A_t)$ against time, O_2 saturated methanol, 25.0 °C, λ = 315 nm. [Co(3MeOsalen)] = 5.67×10^{-6} M, $[H_2AB]$ = 3.26×10^{-5} M. A_∞ = 0.861. Solid curve: observed value; Dotted line: 1st order kinetics calculated (rate constant k = 3.33×10^{-4} sec^{-1}).

bands at 315 nm and 437 nm (see Figure 4), increase due to the formation of *trans*-azobenzene in Figures 6-a, b. During the oxidation reaction of hydrazobenzene, *trans*-azobenzene was exclusively produced, as indicated by the absorption spectra. The *cis*-isomer, which would have absorption maxima at 298 nm and 425 nm, was not detected, Figure 6. There is an isosbestic point at 280 nm, and in particular is no new band at 281 nm. Hence the reaction product is *trans*-azobenzene, with negligible production of *cis*-isomer.

Kinetic measurements were made at 315 mn, Figure 7. A typical curve of absorbance A versus time t is shown in Figure 7. Plots of $-\log(A_\infty - A)$ against time were found to be curved after approximately one half-life, 60 minutes, indicating deviation from pseudo first order kinetics. Figure 7 and 8 include a pseudo-first order curve calculated to fit the earlier part of the data. Comparison with th experimental data, Table 6, shows that the reaction appears to go faster as reaction proceeds than would be expected for a simple first order reaction. This could be due to the oxidation of hydrazobenzene by the

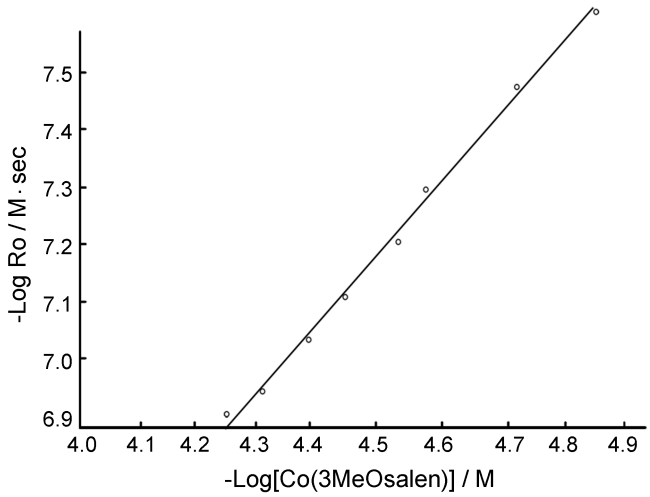


Figure 9. Plot of $-\log R_o$ against $\log[Co(3MeOsalen)]_T$. O_2 saturated methanol, 1 atm, 25 °C, λ = 315 nm. The line is drawn with slope 1.00. $[Co(3MeOsalen)]_T = 1.47 \times 10^{-5}$ M – 5.57×10^{-5} M. $[H_2AB]_o$ = 4.11×10^{-4} M.

Table 6. $\log(A_\infty - A_t)$ values compared with first order kinetics

Time/min	Absorbance (observed)	$-\log(A_\infty - At)$	Absorbance (Calculated)	−log (1st order)
0	0.306	0.256	0.306	0.256
10	0.349	0.291	0.349	0.291
20	0.395	0.332	0.395	0.332
30	0.438	0.374	0.438	0.374
60	0.549	0.506	0.537	0.489
90	0.633	0.642	0.615	0.609
120	0.696	0.783	0.675	0.730
150	0.744	0.932	0.717	0.842
180	0.776	1.07	0.752	0.963
2106	0.861			

O_2 saturated methanol, 25.0 °C, λ = 315 nm. A_∞ = 0.861, [Co(3Me Osalen)] = 5.67×10^{-6} M, $[H_2AB] = 3.26 \times 10^{-5}$ M.

hydrogen peroxide produced.[18] We have demonstrated that hydrogen peroxide (8.29×10^{-3} M) reacted with hydrazobenzene (3.88×10^{-4} M) employing the initial rate method, Table 7. The maximum possible rate for the oxidation of hydrazobenzene by hydrogen peroxide in the catalysed reaction would be when half the hydrazobenzene had been oxidised, equation (3). Assuming that the initial rate R_o is linear (first order) in hydrazobenzene and hydrogen peroxide concentration, the initial rate at $[H_2AB] = [H_2O_2] = 1.63 \times 10^{-5}$ M will be 9.33×10^{-14} M sec^{-1} which is given by

$$R_o = \frac{1.13 \times 10^{-9}\ M\ sec^{-1}}{8.29 \times 10^{-3}\ M\ (H_2O_2)} \times 1.63 \times 10^{-5}\ M\ (H_2O_2) \times \frac{1.63 \times 10^{-5}\ M\ (H_2AB)}{3.88 \times 10^{-4}\ M\ (H_2AB)}$$

which is obtained, Table 7. This is much less than the initial rate observed (2.74×10^{-9} M·sec^{-1}) in the catalysed reaction, Table 7.

To avoid this complication, initial rates R_o, equation (4)

Table 7. Effect of varing H_2O_2 concentration on the oxidation of hydrazobenzene in O_2 saturated methanol at 25.0 °C

$[H_2O_2]/10^{-2}$ M	$(dA/dt)_o/10^{-4}$ sec^{-1}	$R_o/10^{-9}$ M sec^{-1}
0	0.229	1.61
0.829	0.389	2.74
4.15	1.04	7.32
5.80	1.44	10.1
8.29	2.06	14.5

λ = 315 nm ($\varepsilon(H_2AB)$ = 1.89×10^3 $M^{-1}cm^{-1}$, ε (AB) = 1.61×10^4 $M^{-1}cm^{-1}$, $[H_2AB]_o = 3.88 \times 10^{-4}$ M, $\Delta\varepsilon^{-1} = 7.04 \times 10^{-5}$ M·cm, $R_o = \Delta\varepsilon^{-1}(dA/dt)_o$

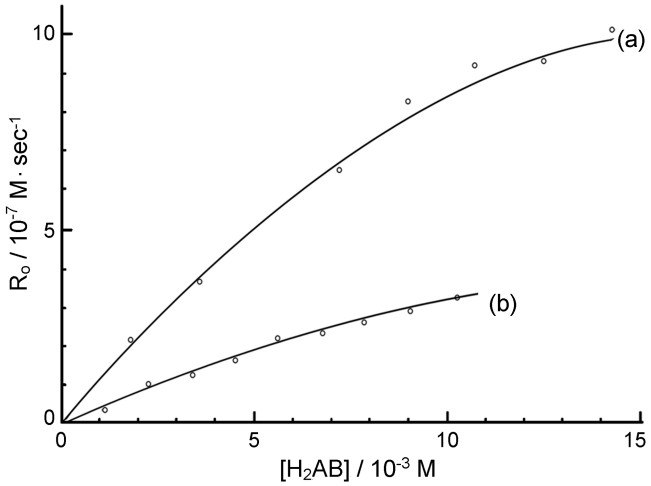


Figure 10. Plots of initial rate R_o against $[H_2AB]$. Curve (a) O_2 saturated, Curve (b) air saturated, methanol, 1 atm, 25 °C, λ = 315 nm and 437 nm. $[Co]_T = 7.43 \times 10^{-6}$ M.

were calculated from slopes of tangents at t = 0:

$$R_o = 1^{-1} \cdot (\Delta\varepsilon)^{-1} \cdot (dA/dt)_0 \quad (4)$$

which is derived from A = εel where l is the path length and $\Delta\varepsilon^{-1} = 7.04 \times 10^{-5}$ M^{-1}·cm obtained from intercept with log R_o against $\log(dA/dt)_o$.

The log of the initial rate is plotted against the log of the Co(3MeOsalen) concentration, Figure 9. The slope of this plot is 1.00, Table 8, which shows that the reaction is first order in catalyst, equation (5). The dependence of rate on total cobalt concentration $[C_O]_T$ is linear, over the range

$$R_0 \propto [Co(II)] \quad (5)$$

$[C_O]_T = (1.5–5.6) \times 10^{-5}$ M, Figure 9.

Table 8. Effect of varing [Co(3MeOsalen)] concentration on the oxidation of hydrazobenzene in O_2 saturated methanol at 25.0 °C

$[C_O$(3MeOsalen)] $/10^{-5}$ M	$(dA/dt)_0$ $/10^{-4}$ sec^{-1}	$R_0/10^{-8}$ M·sec^{-1}	$-\log R_0$/ M·sec^{-1}	$-\log[C_O$(3MeO salen)]/M
0	0.305	0.215	8.67	–
1.47	4.00	2.82	7.55	4.83
2.05	5.53	3.89	7.41	4.69
2.64	7.44	5.24	7.28	4.58
3.22	9.50	6.69	7.17	4.49
3.81	11.5	8.09	7.09	4.42
4.39	13.5	9.50	7.02	4.36
4.98	15.7	11.1	6.95	4.30
5.57	17.2	12.1	6.92	4.25

λ = 315 nm ($\varepsilon(H_2AB)$ = 1.89×10^3 $M^{-1}\cdot cm^{-1}$, ε (AB) = 1.61×10^4 $M^{-1}\cdot cm^{-1}$). $[H_2AB] = 4.11 \times 10^{-4}$ M, R_o(initial rate) = $\Delta\varepsilon^{-1}\cdot(dA/dt)_o$, $\Delta\varepsilon^{-1}$ = 7.04×10^{-5} M·cm.

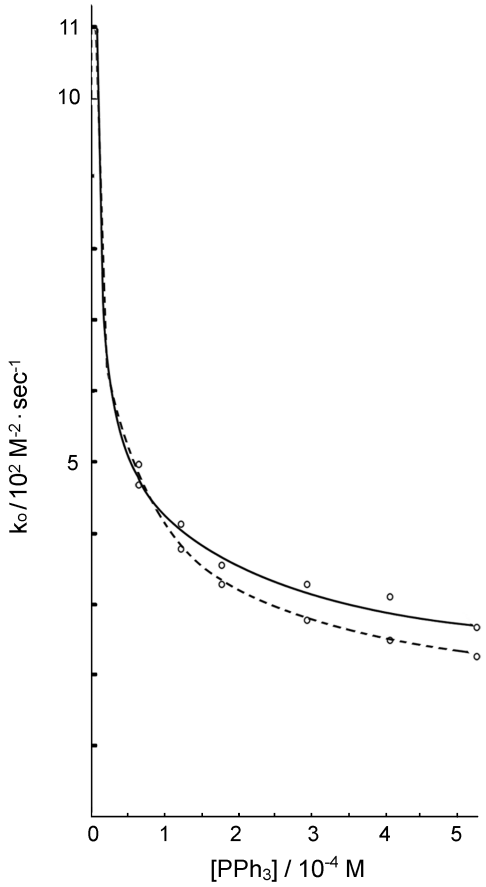


Figure 11. Plots of k against $[PPh_3]$. O_2 saturated methanol, 25.0 °C, λ = 315 nm. $[Co(3MeOsalen)] = 4.78 \times 10^{-5}$ M, $[H_2AB] = 1.95 \times 10^{-4}$ M, Solid curve: experimental value; dotted curve: theoretical value.

The hydrazobenzene dependence is non-linear, suggesting an equilibrium saturation effect, Figure 10. The oxygen dependence, based on measurements at two concentrations, is also non-linear as discussed below. The initial rate of the oxidation reaction of hydrazobenzene in an O_2 saturated solution is faster than that in air by about three times, for example in the region $[H_2AB] = 10 \times 10^{-3}$ M, Table 2 and 3. The data, Figure 10, show that the initial reaction rates are linear in hydrazobenzene concentration at low concentrations, especially for the reaction in air, as expected for a first order reaction. However, as the hydrazobenzene concentration increases the reaction order in substrate appears to decrease, until above 10^{-2} M hydrazobenzene in oxygen the reaction becomes independent of substrate concentration. This is similar to the behaviour observed in enzyme systems where it would indicate saturation of the catalyst with substrate as the Michaelis-Menten equation.

The reaction was followed with Co(3MeOsalen) ($7.43 \times$

10^{-5} M) and the appropriate ligands: triphenylphosphine (1.91×10^{-2} M), ethylisonicotinate (3.57×10^{-2} M), Table 9. As the ligand triphenylphosphine (1.91×10^{-2} M) was added to the reaction mixture, Table 10, the initial rate was decreased. It was also observed that the colour of the catalytic system changed from red to green. The destruction of catalytic system Co(3MeOsalen)(O_2) could be due to the catalyst becoming coordinated with triphenylphosphine in both Z axis sites of the catalyst. There was a little change in rate when ethylisonicotinate (3.57×10^{-2} M) was added to the reaction mixture, Table 9. However, when a strong σ-donor ligand, pyridine (2.00×10^{-3} M), was added to the reaction mixture of hydrazobenzene, the reaction rate was increased. These ligands could affect dioxygen binding to the catalytic system Co(3Me Osalen)(O_2) as triphenylphosphine is usually considered to have not only σ-donor but also π-acceptor properties,[27] ethylisonicotinate is a σ-donor,[13] and pyridine a strong σ-donor ligand.

Triphenylphosphine is an interesting ligand as it decreases the rate of the oxidation of hydrazobenzene in methanol. The initial rates, R_o, of the oxidation of hydrazobenzene with the ligand triphenylphosphine(PPh_3) were measured, Table 10. As the triphenylphosphine concentrations increased, the initial rates were found to decrease. When the initial rates were plotted against the triphenylphosphine concentration, a curve was formed and theoretical values of the initial rates as a dotted curve, Figure 11. The theoretical values of the rates, Table 11, were calculated from equation (6):

$$\text{Rate} = k = \frac{k_1 + k_2K_1[\text{P}]}{1 + K_1[\text{P}] + K_1K_2[\text{P}]^2} \quad (6)$$

where $k = (R_0 - k_0[S][O_2]) / [S][O_2][C]_T$
R_0 = initial rate
k_0 = rate constant for autoxiation
$[C]_T$ = total concentration of the catalyst Co(3Me Osalen)
$[S] = [H_2AB]$
$[P] = [PPh_3]$
k_1 = rate constant for the oxidation without PPh_3
k_2 = rate constant for the oxidation with PPh_3
K_1 = equilibrium constant in equation (7)
K_2 = equilibrium constant in equation (8)

Table 9. Ligand effect on the oxidation of hydrazobenzene in O_2 saturated methanol at 25.0 °C

$[H_2AB]$ / 10^{-3} M	$(dA/dt)_0$ / 10^{-3} sec^{-1}			R_0 / 10^{-7} M sec^{-1}		
	MeOH	EIN	PPh_3	MeOH	EIN	PPh_3
1.70	4.50	4.50	1.20	3.17	3.17	0.845
3.70	7.40	7.40	2.50	5.21	5.21	1.76
7.30	13.2	12.7	3.40	9.29	8.94	2.39
10.0	18.6	16.8	3.70	13.1	11.8	2.60
14.6	20.8	21.5	4.10	14.6	15.1	2.89

λ = 315 nm (ε(H_2AB) = 1.89×10^3 $M^{-1}cm^{-1}$), (ε(AB) = 1.61×10^4 $M^{-1}cm^{-1}$), λ = 437 nm (ε = 5.09×10^2 $M^{-1}cm^{-1}$), [Co(3MeOsalen)] = 7.43×10^{-5} M, Ethylisonicotinate = [EIN] = 3.57×10^{-2} M, $R_o = \Delta\varepsilon^{-1}{}_{315}(dA/dt)_o$, $\Delta\varepsilon^{-1}{}_{315} = 7.43 \times 10^{-5}$ M·cm. Triphenylphosphine = [PPh_3] = 1.91×10^{-2} M.

Table 10. Effect of varing triphenylphosphine concentration [PPh_3] on the oxidation of hydrazobenzene [H_2AB] in O_2 saturated methanol at 25.0 °C

$[PPh_3]$ / 10^{-4} M	$(dA/dt)_0$ / 10^{-4} sec^{-1}	R_0 / 10^{-8} $M{\cdot}sec^{-1}$	R_0' / 10^{-8} $M{\cdot}sec^{-1}$	k / 10^2 $M^{-2}{\cdot}sec^{-1}$	$(k-k_1)10^2$ $M^{-2}{\cdot}sec^{-1}$	$[P]/(k-k_1)/10^{-7}$ $M^3{\cdot}sec$	$k^{-1}/10^{-3}$ $M^2{\cdot}sec$
0	14.2	9.99	9.99	11.0	0	–	0.909
0.529	6.25	4.40	4.32	4.80	−6.20	0.853	2.19
1.09	5.54	3.90	3.82	4.25	−6.75	1.61	2.36
1.60	4.83	3.40	3.32	3.69	−7.31	2.19	2.71
2.70	4.47	3.15	3.07	3.41	−7.59	3.56	2.93
3.77	4.26	3.00	2.92	3.24	−7.76	4.86	3.09
4.88	3.76	2.65	2.57	2.86	−8.14	5.99	3.49

$k = (R_o - k_o[S][O_2][C]_T = 1.11 \times 10^{10}$ ($R_o - 7.51 \times 10^{-10}$ $M^{-2}{\cdot}sec^{-1}$, $R_o' = R_o - k_o[S][O_2]$, $k_o[S][O_2] = 7.51 \times 10^{-10}$ $M{\cdot}sec^{-1}$ from Figure 2, [S] = [H_2AB] = 1.95×10^{-4} M, $[C]_T$ = [Co(3MeOsalen)] = 4.78×10^{-5} M, $R_o = \Delta\varepsilon^{-1}{}_{315}$ $(dA/dt)_o$; $\varepsilon_{315} = 1.61 \times 10^4$ $M^{-1}{\cdot}cm^{-1}$, λ = 315 nm, $\Delta\varepsilon^{-1}{}_{315} = 7.04 \times 10^{-5}$ Mcm, $k_1 = 1.10 \times 10^3$ $M^{-2}{\cdot}sec^{-1}$, $k_2 = 2.69 \times 10^2$ $M^{-2}{\cdot}sec^{-1}$, [P] = PPh_3, $K_1 = 4.56 \times 10^4$ $dm^3{\cdot}mol^{-1}$, $K_2 = 5.39 \times 10^2$ $dm^3{\cdot}mol^{-1}$.

Table 11. Theoretical values of the rates calculated from equation (6) using the values of k_1, k_2, K_1, and K_2

$[PPh_3]$ / 10^{-4} M	$[P]^2$ / 10^{-8}	$1 + K_1[P]$	$K_1K_2[P]^2$	$(k_1 + k_2K_1[P])/10^3$	$1 + K_1[P] + K_1K_2[P]^2$	k / 10^2
0	0	1	0	1.10	1	11.0
0.529	0.279	3.41	0.0686	1.76	3.48	5.06
1.09	1.19	5.97	0.293	2.45	6.26	3.91
1.60	2.56	8.29	0.629	3.08	8.92	3.45
2.70	7.29	13.3	1.79	4.43	15.1	2.93
3.77	14.2	18.2	3.49	5.75	21.7	2.65
4.88	23.8	23.3	5.85	7.11	29.2	2.43

$k = (k_1 + k_2K_1[P]/(1 + K_1[P] + K_1K_2[P]^2)$, [P] = [$PPh_3$], $k_1 = 1.10 \times 10^3$ $M^{-2}{\cdot}sec^{-1}$, $k_2 = 2.69 \times 10^2$ $M^{-2}{\cdot}sec^{-1}$, $K_1 = 4.56 \times 10^4$ $dm^3{\cdot}mol^{-1}$, $K_2 = 5.39 \times 10^2$ $dm^3{\cdot}mol^{-1}$.

Table 12. Rate and Equilibrium Constants at 25 °C

K_N	$0 \pm 10\ M^{-1}$
k_c	$(2.96 \pm 0.2) \times 10^{-1}\ sec^{-1}$
$\frac{1+K_o[O_2]}{k_c k[O_2]}$	$(2.05 \pm 0.04) \times 10^{-1}$ M·sec ($[O_2] = 1.96 \times 10^{-3}$ M)$_a$
	$(5.75 \pm 0.2) 10^{-2}$ M·sec ($[O_2] = 9.63 \times 10^{-3}$ M)$_b$
K_o	$(5.42 \pm 0.1) \times 10^{1}\ M^{-1}$
K	$(9.33 \pm 0.5) \times 10^{3}\ M^{-2}$
K'_N	$(1.72 \pm 0.09) \times 10^{2}\ M^{-1}$

$K = K_o K_N'$. [a]Sheehan, W. F., "Physical Chemistry", 2nd. ed., Allyn and Bacon (1970), pp. 285. [b]Gjaldbek J. C., Acta Chemica Scandinavica, **6**, 623 (1952), ; Moore (1972).

$$C + P \overset{K_1}{\Leftrightarrow} C{\cdot}P \tag{7}$$

$$C{\cdot}P + P \overset{K_2}{\Leftrightarrow} C{\cdot}P_2 \tag{8}$$

where C and P are catalyst and triphenylphosphine. The equation (6) was derived from rate law.

The constants k_2, K_1, and K_2 were determined by reciprocal plots from equation (6), and k_1 is known to be $1.10 \times 10^3\ M^{-2}sec^{-1}$ when [P] = 0, Table 10.

When [P] is small, equation (6) reduces to equation (9) as $K_1[P] \gg K_1K_2[P]^2$

$$k \cong \frac{k_1 + k_2K_1P}{1 + K_1P}, \text{ where } P = [P]$$

Subtracting k_1 from both sides,

$$\frac{k_1 - k_1}{P} = \frac{k_2K_1 - k_1K_1}{1 + K_1P}$$

$$\frac{P}{k_1 - k_1} = \frac{1}{K_1(k_2 - k_1)} + \frac{P}{k_2 - k_1} \tag{9}$$

$P / (k - k_1)$ is plotted against P from equation (9), Figure 12, K_1 and k_2 were obtained graphically, Table 11. When [P] is large, equation (6) reduces to equation (10) as $k_1 \ll k_2K_1[P]$ and $1 \ll K_1[P]$

$$k \cong \frac{k_2K_1P}{K_1P + K_1K_2P^2} = \frac{k_2}{1 + K_2P}$$

$$\frac{1}{k} = \frac{1}{k_2} + \frac{K_2P}{k_2} \tag{10}$$

$1 / k$ is plotted against P from equation (10), Figure 13, and K_2 was determined graphically, Table 11. As the theoretical values of the initial rates agreed fairly well with experimental observations, Figure 11, it is suggested that the catalyst Co(3MeOsalen) was associated with triphenylphosphine which would be a poorer σ donor ligand compared with methanol molecule and the reaction rate therefore decreased. The large K_1 value ($K_1 = 4.56 \times 10^4\ dm^3{\cdot}mol^{-1}$) means that the equilibrium to Co(3MeOsalen)(PPh_3) was soon achieved and was ready to associated with triphenylphosphine and became Co(3MeOsalen)(PPh_3)$_2$ which is catalytically inactive and the rates were then expected to decrease quickly.

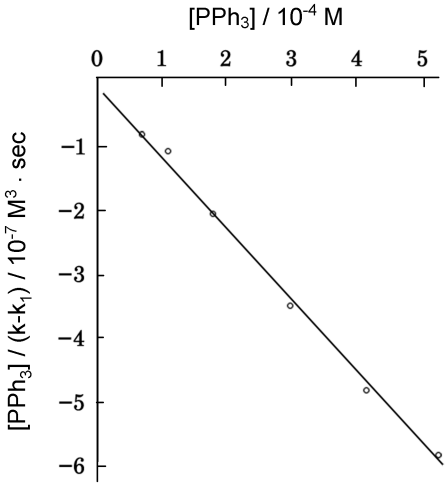


Figure 12. Plot of $[PPh_3] / (k–k_1)$ against $[PPh_3]$, when $[PPh_3]$ is small. O_2 saturated methanol, 25.0 °C, λ = 315 nm, [Co(3MeOsalen)] = 4.78×10^{-5} M, $[H_2AB] = 1.95 \times 10^{-4}$ M, $k_1 = 1.10 \times 10^3\ M^{-2}{\cdot}sec^{-1}$, $k_2 = 2.69 \times 10^2\ M^{-2}{\cdot}sec^{-1}$, $K_1 = 4.56 \times 10^2\ M^4\ dm^3{\cdot}mol^{-1}$.

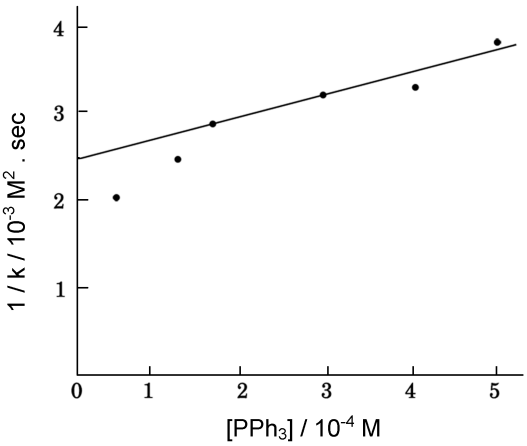
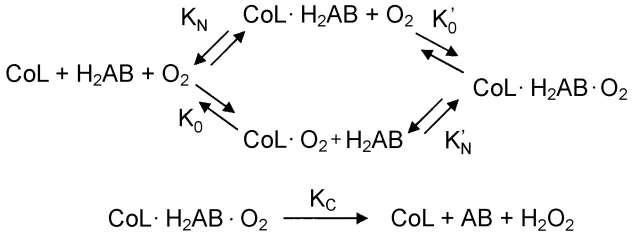


Figure 13. Plot of $1 / k$ against $[PPh_3]$, when $[PPh_3]$ is large. O_2 saturated methanol, 25.0 °C, λ = 315 nm, [Co (3MeOsalen)] = 4.78 $\times 10^{-5}$ M, $[H_2AB] = 1.95 \times 10^{-4}$ M, $K_2 = 5.39 \times 10^2\ dm^3{\cdot}mol^{-1}$.

Discussion

The data suggest the formation of a ternary complex CoL·H_2AB·O_2 (where L = 3MeOsalen), Scheme 1.[28] For completeness, we introducce stepwise equilibria for the formation of this complex, *via* the two binary complexes CoL·H_2AB and CoL·O_2 :



Scheme 1

Under the experimental conditions

$$[O_2] > [H_2AB] > [CoL]$$

the rate of reaction is derived as follows: The rate of formation of the product, azobenzene (AB), is given by equation (11).

$$\frac{d[AB]}{dt} = K_c[CoL \cdot H_2AB \cdot O_2] \quad (11)$$

The equilirium constants K_o, K_N, and K'_N are defined in equations (12)-(14).

$$K_0 = \frac{[CoL \cdot O_2][H_2AB]}{[CoL][H_2AB][O_2]} \quad (12)$$

$$K_N = \frac{[CoL \cdot H_2AB][O_2]}{[CoL][H_2AB][O_2]} \quad (13)$$

$$K_{N'} = \frac{[CoL \cdot H_2AB \cdot O_2]}{[CoL \cdot O_2][H_2AB]} \quad (14)$$

From equation (12) and (14), the value of $[CoL{\cdot}H_2AB.O_2]$ is given by

$$[CoL{\cdot}H_2AB{\cdot}O_2] = K_N'K_o[CoL][O_2][H_2AB] \quad (15)$$

The total concentration of the catayst $[Co]_T$ is given by equation (16)

$$[Co]_T = [CoL] + [CoL{\cdot}O_2] + [CoL{\cdot}H_2AB] + [CoL{\cdot}H_2AB{\cdot}O_2] \quad (16)$$

Substituting the expressions for various catalyst containing species from equation (12), (13), and (14) yields equation (17)

$$[CoL] = \frac{[CoL]_T}{1 + K_0[O_2] + K_N[H_2AB] + K_{N'}K_0[H_2AB][O_2]} \quad (17)$$

Substituting equation (17) into equation (15) gives :

$$[CoL{:}H_2AB{\cdot}O_2] = \frac{K_{N'}K_0[Co]_T[H_2AB][O_2]}{1 + K_0[O_2] + K_N[H_2AB] + K_{N'}K_0[H_2AB][O_2]} \quad (18)$$

The rate of azobenzene formation is derived from equation (11) and (18) :

$$R = \frac{d[AB]}{dt} = \frac{K_cK[Co]_T[H_2AB][O_2]}{1 + K_0[O_2] + K_N[H_2AB] + K[H_2AB][O_2]} \quad (19)$$

, where $K = K_N'K_o$. The constants are best determined by a plot of $1 / k_o$ versus $1 / [H_2AB]$ from equation (20) :

$$\frac{1}{k_o} = \frac{1}{[H_2AB]}\left(\frac{K_0}{k_cK} + \frac{1}{k_cK[O_2]}\right) + \frac{1}{k_c}\left(1 + \frac{K_N}{K[O_2]}\right) \quad (20)$$

where $k_o = R / [Co]_T$ and $K = K_NK'_o = K_oK'_N$. The intercept on the $1 / k_o$ axis is :

$$\frac{1}{k_o} = \frac{1}{k_c}\left(1 + \frac{K_N}{K[O_2]}\right)$$

This is only independent of $[O_2]$ if K_N is zero. The slope of the plot of $1 / k_o$ versus $1/[H_2AB]$ is :

$$\frac{k_o}{k_cK} + \frac{1}{k_cK[O_2]}$$

and it should decrease to a limiting value as the oxygen concentration is increased.

If the kinetic scheme is correct, we expect that plot of the reciprocal of k_o against the reciprocal of the hydrazobenzene concentration at constant $[O_2]$ will be linear in accordance with equation (20). Figure 14 shows that the plots are linear and it is noteworthy that the plots for different O_2 concentrations should intersect at a single point, with $[H_2AB]^{-1} = -K_N$. The intersection point lies within experimental error on the vertical axis. This indicates that the reaction *via* the binary complex cobalt H_2AB ($CoL{\cdot}H_2AB$) does not occur and the value of k_c may be read from the intersection point, while the slopes of the two lines gives K_o and K. Values of rate and equilibrium constants, with estimated limits of error, are shown in Table 12. The kinetic studies show that a ternary complex $CoL{\cdot}H_2AB{\cdot}O_2$ is involved in the rate determining step.

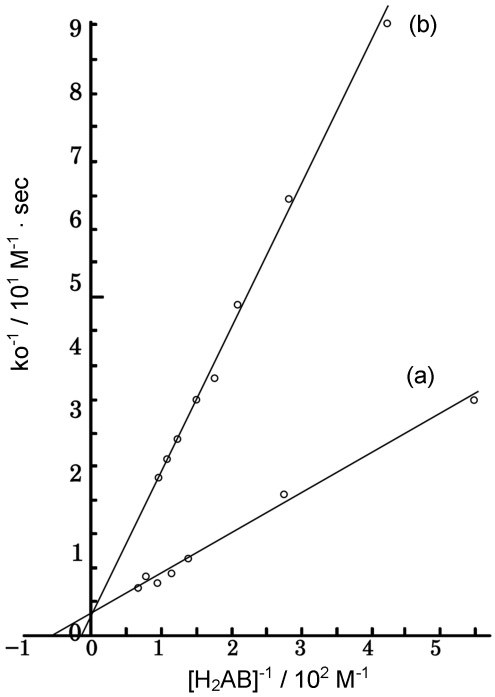
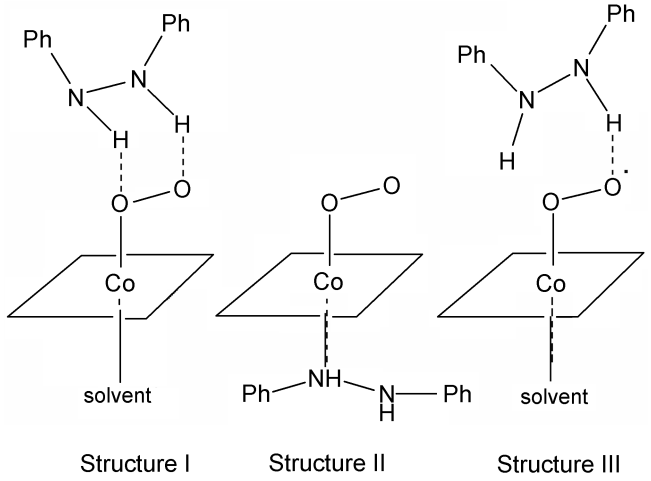


Figure 14. Plots of k_o^{-1} against $[H_2AB]_o$. Curve (a) O_2 saturated, Curve (b) air saturated, Methanol, 1 atm, 25 °C. $[Co]_T = 7.30 \times 10^{-6}$ M.

Possible structures for the ternary complex $CoL{\cdot}H_2AB{\cdot}O_2$ include structure I, structure II, and structure III. To account for the hydrogen abstraction, the structure I with N-H-O bridging seems plausible. However, in a concerted reaction this would be expected to lead to *cis*-azobenzene, which was



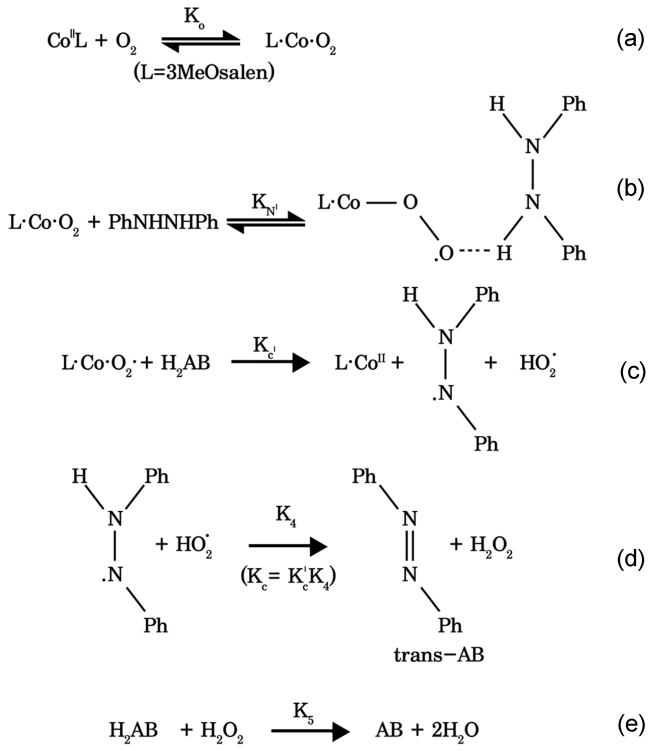


Figure 15. Proposed mechnism for the oxidation of hydrazobenzene by cobalt dioxygen catalyst Co(3MeOsalen)(O_2).[32]

not observed. The isomerisation of *cis*-azobenzene to the *trans* isomer was also followed at 315 nm, and the reaction rate was very slow and was not catalysed by Co(3Me Osalen).

The first order rate constant for the isomerisation was found to be 1.28×10^{-6} sec^{-1} which is much smaller than the rate constant (3.33×10^{-4} sec^{-1}) for the oxidation of hydrazobenzene calculated from Figure 8. Thus *cis*-azobenzene could not have been the initial product. Structure II is not necessarily the effective reaction intermediate. The situation in which an association complex is detected, but some other species of the same composition, but relatively less stable, is the true reaction intermediate, is paralled in

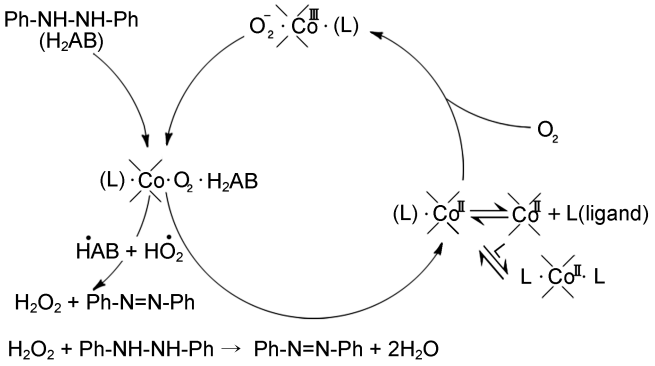


Figure 16. Catalysis cycle for Co(3MeOsalen) catalysed oxidation of hydrazobenzene, [H_2AB] by molecular oxygen.[32]

many other reactions *e.g.* electron transfer by the 'dead-end' mechanism.[29] The most reasonable intermediate is structure III. Drago's group[8] proposed hydrogen bonding to the terminal oxygen of the bound dioxygen molecule because the terminal oxygen has more of the unpaired electron density on it.[30] The upper limit of K_N is estimated as 10^{-1} M^{-1} while $K'_N = K/K_o = 172$ M^{-1}. The difference and be understood if the d_{z2} electron in the complex is partially delocalised onto the O_2 molecule, so that the effective oxidation state of cobalt is intermediate between Co^{II} and Co^{III}.[28]

The proposed mechanism is shown in Figure 15. The polar solvent, methanol, coordinates to the cobalt(II) complex and affects the electron density of the d_{z2} orbital of cobalt, increasing the charge on the dioxygen moiety, equation (a). This cause the abstraction of the hydrogen atom, equation (c). The N-H-O bridging structure III and equation (b) are analogous to that suggested by Savitskii[9] for isopropanol oxidation and by Beckett[31] for the 1-phenylethanol oxidation reaction. After abstraction of the hydrogen atom, radicals $^{\bullet}$HAB and $HO_2^{\bullet}$ (hydroperoxy), may be formed, equation (c), and the catalyst regenerated. The formation of the $HO_2^{\bullet}$ and $^{\bullet}$HAB radicals also agrees with Drago's mechanism[15] for the catalysed oxidation of phenol. If *cis*-HAB$^{\bullet}$ is formed in step (b) it could rearrange rapidly to the *trans* form by rotation about the N-N bond before reacting with $HO_2^{\bullet}$ to produce *trans*-azobenzene and hydrogen peroxide. According to Beckett and Homer's[21] proposal, in a related system, the hydrogen peroxide may affect further oxidation of substrate and produce azobenzene and water. The reactions are summarised in the catalytic cycle, Figure 16.

Experimental Section

H_2(3MeOsalen) was prepared by the method of Diehl *et al.*,[33] 3-methoxysalicylaldehyde (35.5 mmoles) was dissolved in hot absolute ethanol (25 mL) and the solution stirred for 30 minutes ethanol. Yield 72%, mp 162-163 °C, as reported. Elemental analysis based on $C_{18}H_{20}N_2O_4$: calculated C: 65.9, N: 8.5, H: 6.1; found: C 65.6, N: 8.4, H: 6.2.

The catalyst Co^{II}(3MeOsalen), was prepared by the method of Diel *et al.*,[33] as modified by Beckett.[31] The ligand,

H_2(3MeOsalen) (35.5 mmoles) was dissolved in absolute ethanol (300 mL) and cobalt(II) acetate tetrahydrate (35.5 mmoles) was dissolved in hot water under nitrogen and added dropwise to the solution of the ligand. The pink solution changed to dark red. After cooling, a silver gold precipitate was formed. The product was filtered, washed with ethanol (30 mL) and then water (30 mL), and finally dried in vacua at 180 °C for at least two hours. The colour of the product changed from silver gold to violet. Yield 52%. Elemental analysis based on $CoO_4N_2C_{18}H_{15}O_2$: calculated: C: 51.80, H: 4.36, N: 6.71; found: C: 52.15, H: 4.74, N: 6.87.

Hydrazobenzene (Aldrich) was always kept in a dry nitrogen glove bag. Dry nitrogen was produced by passing cylinder nitogen over P_2O_5. Oxygen saturated reaction mixtures were made by bubbling oxygen through the solution for fifteen minuetes.

The rates of the reactions were followed by observing absorbance changes against time in the reaction mixtures at a wavelength of 325 nm or 437 nm in 1 cm cells. The reactions were conducted at a tenfold molar excess or more of hydrazobenzene over the cobalt(II) complex. The absorption spectra were measured on a Pye Unicam SP8-200 spectrophotometer.

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