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Kinetic studies on the oxidation of dichlorotetracarbonyldirhodium(I) by hydrogen peroxide *

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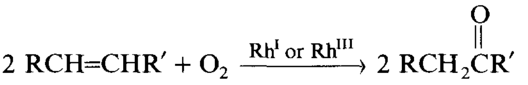
Abstract

Kinetic measurements on the oxidation of dichlorotetracarbonyldirhodium(I) by hydrogen peroxide in ethanol/hydrochloric acid indicate that reaction proceeds through the intermediate "$\{Rh(CO)Cl_3\}$". The reaction rate is first order with respect to the rhodium complex, hydrogen peroxide, and hydrochloric acid, but kinetics are complicated by complex formation between $[Rh(CO)_2Cl_2]^-$ and chloride ions, and between the intermediate and hydrogen peroxide. The reaction is accelerated by decreasing the polarity of the solvent.

Introduction

The autoxidation of alkenes to carbonyl compounds is catalysed by rhodium compounds, eq. 1, and mechanistic aspects of these reactions have been extensively



$$2\ RCH{=}CHR' + O_2 \xrightarrow{Rh^I \text{ or } Rh^{III}} 2\ RCH_2\overset{\overset{O}{\|}}{C}R' \qquad (1)$$

studied [1–12]. If $[\{Rh(CO)_2Cl\}_2]$ is used as catalyst, the rhodium(I) complex is oxidised to rhodium(III), which is thought to be the main catalytically active species. Stanko et al. [13] studied the oxidation of $[\{Rh(CO)_2Cl\}_2]$ by dioxygen in aqueous hydrochloric acid, and proposed that the oxidation could be represented by eq. 2. A kinetic study showed that the rate of reaction was first order in

$$[Rh(CO)_2Cl_2]^- + 2\ H^+ + 3\ Cl^- + O_2 \rightarrow [Rh(CO)Cl_5]^{2-} + CO_2 + H_2O \qquad (2)$$

$[Rh(CO)_2Cl_2]^-$, and that production of carbon dioxide was almost stoicheiometric.

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* Dedicated to Professor Colin Eaborn, a splendid teacher and a friend, in recognition of his outstanding contribution to organometallic chemistry.

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They suggested that reaction proceeded through a rhodium(III) intermediate, $[Rh^{III}(CO)(CO_3)Cl_3]^{2-}$, containing a coordinated carbonate ligand. This then reacted with acid to give carbon dioxide, and the rhodium(III) coordinated with two more chloride ligands.

Nyberg, Pribich and Drago [10] have proposed that in autoxidation catalysed by $[\{Rh(CO)_2Cl\}_2]$, the reduction of dioxygen to hydrogen peroxide by solvent (an alcohol) (eq. 3) is a key feature of the mechanism. The hydrogen peroxide then

$$CH_3CHR(OH) + O_2 \rightarrow CH_3C(O)R + H_2O_2 \tag{3}$$

both oxidises the rhodium(I) to rhodium(III), and also oxidises the alkene, eq. 4 and 5. As part of their study of alkene oxidation, Nyberg et al. [10] investigated

$$Rh^{I} \xrightarrow{H_2O_2} Rh^{III} \tag{4}$$

$$CH_2{=}CHR + H_2O_2 \xrightarrow{Rh^{III}} CH_3CRO + H_2O \tag{5}$$

the oxidation of $[\{Rh(CO)_2Cl\}_2]$ by dioxygen. They used acidified ethanol as solvent, and proposed that the overall reaction is as shown in eq. 6. Further, they

$$[\{Rh(CO)_2Cl\}_2] + 4\,HCl + 2\,O_2 + 4\,EtOH \rightarrow$$
$$2\,[RhCl_3(H_2O)_2(EtOH)] + 2\,CH_3CHO + 4\,CO \tag{6}$$

suggested that hydrogen peroxide is produced by reaction 3 and this is then responsible for oxidation of $[\{Rh(CO)_2Cl\}_2]$ according to eq. 7. They showed that

$$[\{Rh(CO)_2Cl\}_2] + 4\,HCl + 2\,H_2O_2 \xrightarrow[EtOH]{H_2O} 2\,[RhCl_3(H_2O)_2(EtOH)] + 4\,CO \tag{7}$$

changes in UV and IR spectra occurring during reaction were the same whether dioxygen or hydrogen peroxide were used as oxidants. They proposed that reaction proceeded via an intermediate, X, which they identified as $[Rh^{I}(CO)Cl_2(OOH)]^{2-}$ on the basis of (a) no evidence for coordinated hydride in the IR spectrum, and (b) presence of a single CO ligand according to the IR spectrum. They were unable to see the expected band from coordinated hydroperoxide in the 800–900 cm^{-1} region of the spectrum, but the formation and disappearance of the intermediate X could be seen as a band at 2102 cm^{-1} in the IR spectrum and a peak at 385 nm in the UV spectrum of reacting solutions. Kinetic measurements showed that oxidation by hydrogen peroxide was first order in both rhodium complex and hydrogen peroxide. They suggested that carbon dioxide was only formed in the absence of hydrochloric acid (eq. 8) [10].

$$[\{Rh(CO)_2Cl\}_2] + H_2O_2 \rightarrow 2\,CO_2 + 2\,Rh^{I} \tag{8}$$

In order to try to understand more fully the rôle of intermediates in alkene oxidations, we have further studied the oxidation of rhodium(I) by hydrogen peroxide.

Experimental

Reagents

$[\{Rh(CO)_2Cl\}_2]$. This was prepared from rhodium(III) chloride trihydrate (commercial grade, Johnson–Matthey Chemicals Ltd.) by the method of Mc-

Cleverty and Wilkinson [14], and purified by vacuum sublimation (60 °C, 0.1 mmHg).

Ethanol. Absolute ethanol (James Burroughs FAD) was used without purification after GLC analysis had shown that it contained no detectable impurities other than a constant 0.05% w/w water. Hydrogen peroxide (100 vol., Fisons) and hydrochloric acid (AnalaR, BDH) were diluted with absolute ethanol so that a minimum of water was added with the reagents.

Measurements

Kinetic measurements were made using a Unicam SP8000 spectrophotometer fitted with a thermostatted cell holder, in which the cell temperature was controlled to ± 0.1 °C. The temperature was checked before and after each kinetic run. Appropriate solutions were thermostatted in 1 cm cells, and reaction initiated by addition of hydrogen peroxide (5 μl). IR studies on solutions in ethanol were made using a PE 580B spectrometer with a cell of 0.5 mm pathlength fitted with germanium windows [15]. Spectra are complicated by interference fringes which cause regular undulations in the absorbance; a microcomputer was used with the spectrometer [16] to record the fringe pattern and subtract it from the spectra of samples.

Isolation of a derivative of the intermediate

An excess of caesium chloride was added to a solution containing hydrochloric acid (0.022 mol dm^{-3}), $[\{Rh(CO)_2Cl\}_2]$ (2.2×10^{-3} mol dm^{-3}), and hydrogen peroxide (0.020 mol dm^{-3}) which had been allowed to react for 15 min at room temperature: a pale pink precipitate formed. Its IR spectrum showed peaks at 2110(vs), 2030(sh), 520(s) and 315(m) cm^{-1}. This agrees well with the reported spectrum of $Cs_2[Rh(CO)Cl_5]$ [17–20]. $Cs_2[Rh(CO)Cl_5]$ can also be isolated by addition of caesium chloride to a solution of rhodium(III) chloride in hydrochloric acid in the presence of carbon monoxide. The shoulder at 2030 cm^{-1} was not reported in the spectrum of $Cs_2[Rh(CO)Cl_5]$, and perhaps is caused by a trace of impurity. A UV spectrum of this complex was not easy to record, as it was only sparingly soluble in ethanol. Results indicate UV absorption peaks at 300, 385, and 485 nm, in agreement with changes in the UV spectra observed during reaction.

Results and discussion

IR spectra. A solution of $[\{Rh(CO)_2Cl\}_2]$ has two IR bands in the carbonyl region at 2085.5 and 2010.1 cm^{-1}. The anion $[Rh(CO)_2Cl_2]^-$ is formed on addition of hydrochloric acid (eq. 9), and the two peaks shift to 2072.5 and 1997 cm^{-1}: similar bands are shown by an ethanol solution of $[NBu_4][Rh(CO)_2Cl_2]$. Addition of hydrogen peroxide causes the slow formation of two new IR peaks at 2014 and 2337 cm^{-1}. The intensity of the 2104 cm^{-1} peak increases as the peaks at 2072 and 1997 cm^{-1} decrease. The intensity of the 2104 cm^{-1} peak reaches a maximum, and then decays again, so that at the end of reaction it has vanished. The 2337 cm^{-1} peak is caused by carbon dioxide (by comparison with the spectrum of a solution of carbon dioxide in ethanol), and varied in intensity from one reaction mixture to another.

$$2\ HCl + \left[\{Rh(CO)_2Cl\}_2\right] \rightarrow 2\ H^+ + 2\ \left[Rh(CO)_2Cl_2\right]^- \qquad (9)$$

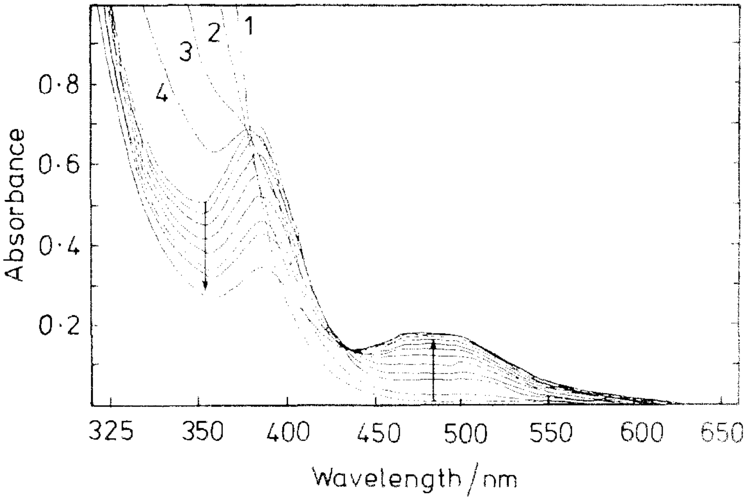

Fig. 1. Changes in the UV-VIS spectra during reaction of [{Rh(CO)$_2$Cl}$_2$] (0.0011 mol dm^{-3}) with hydrogen peroxide (0.01 mol dm^{-3}) in ethanol containing hydrochloric acid (0.022 mol dm^{-3}) at 40.0 °C. Scans were recorded at 2 minutes intervals, arrows show increasing time. The digits alongside scans indicate the scan number.

Similar changes in IR spectra are observed when hydrogen peroxide is mixed with a solution of [NBu$_4$][Rh(CO)$_2$Cl$_2$] in ethanol containing hydrochloric acid.

UV spectra. The UV spectrum of [{Rh(CO)$_2$Cl}$_2$] in ethanol in the presence of hydrochloric acid (more than three moles of hydrochloric acid per mole of rhodium complex) is the same as that of a solution of [NBu$_4$][Rh(CO)$_2$Cl$_2$] in acid-free ethanol. On addition of hydrogen peroxide, two peaks at 385 and 485 nm are formed. The 485 nm peak grows continuously to reach a final maximum value, while the 385 nm peak shows a similar pattern of growth and decay to the 2104 cm^{-1} IR band (Fig. 1). After reaction the spectrum is similar to that of a solution of rhodium(III) chloride in ethanol. If behaviour in ethanol is similar to that in water, the ion [RhCl$_4$]$^-$ will not form at the concentrations of chloride used (0.022 mol dm^{-3}), as the equilibrium constant for its formation is too small [21]. In the presence of either perchloric acid, or lithium chloride, but in the absence of hydrochloric acid, the 385 nm peak does not occur. It does not occur either when [NBu$_4$][Rh(CO)$_2$Cl$_2$] is treated with hydrogen peroxide, or when [NBu$_4$][Rh(CO)$_2$Cl$_2$] is treated with hydrogen peroxide and either perchloric acid or lithium chloride separately. It does, however, form when a mixture of these reagents are used, or when hydrochloric acid is present. This indicates that any intermediate must contain more than two chloride ions per mole of rhodium.

Stoicheiometry of the reaction between [{Rh(CO)$_2$C and hydrogen peroxide. The hydrogen peroxide remaining after treating [{Rh(C $_2$Cl}$_2$] with an excess was measured by titration. As some 20 h reaction time was involved, some hydrogen peroxide could have decomposed by disproportionation according to eq. 10, especially in the presence of a transition-metal salt. The extent of any disproportionation

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2 \qquad (10)$$

was estimated by measuring the amount of disproportionation of hydrogen peroxide in the presence of rhodium(III) chloride. The titration results gave a stoicheiometry of 1.8 moles hydrogen peroxide per mole of rhodium, after allowance for rhodium-catalyzed disproportionation. Carbon dioxide was detected as a reaction product (confirmed by mass spectrometry). Accordingly, the reaction stoicheiometry can be written as eq. 11.

$$[\{Rh(CO)_2Cl\}_2] + 4\ HCl + 4\ H_2O_2 \rightarrow 2\ RhCl_3 + 2\ CO + 2\ CO_2 + 6\ H_2O \qquad (11)$$

Identification of the reaction intermediate (X). Nyberg et al. [10], have proposed that the intermediate, X, is the complex ion $[Rh^I(CO)Cl_2(OOH)]^{2-}$, although they had no IR evidence for a peroxo group. When carbon monoxide is added to a solution of rhodium(III) chloride in methanol containing hydrochloric acid, a strong absorption at 2110 cm^{-1} is seen in an IR spectrum of the solution [17]. This is caused by "$\{Rh(CO)Cl_3\}$", and addition of caesium chloride gives a precipitate of $Cs_2[Rh(CO)Cl_5]$. The complex that we have isolated here (see experimental) shows no IR evidence for peroxo ligands. It does not form from $[Rh(CO)_2Cl_2]^-$ unless both hydrogen ions and chloride ions are present. Its IR spectrum suggests that it is $Cs_2[Rh(CO)Cl_5]$ [17–20]. This means that the reaction intermediate X is probably the species "$\{Rh(CO)Cl_3\}$". In the fairly dilute hydrochloric acid solutions used in the kinetic experiments, it is unlikely that either $[Rh(CO)Cl_4]^-$ or $[Rh(CO)Cl_5]^{2-}$ will form.

Kinetics of the reaction between [$\{Rh(CO)_2Cl\}_2$] and hydrogen peroxide.

Order with respect to $[Rh(CO)_2Cl_2]^-$. The kinetics of the reaction have been studied by monitoring the changes in UV absorbance at 385 and 485 nm with time. At both 385 and 485 nm, the initial rate of absorbance change is linearly proportional to the concentration of $[Rh(CO)_2Cl_2]^-$ if hydrochloric acid and hydrogen peroxide are in a constant excess (Table 1).

Order with respect to hydrochloric acid. When the concentrations of hydrogen peroxide and $[\{Rh(CO)_2Cl\}_2]$ are both kept constant, that of the hydrogen peroxide being in excess over $[\{Rh(CO)_2Cl\}_2]$, and the concentration of hydrochloric acid varied, the initial rate of absorbance changes are as shown in Fig. 2. At low concentrations of hydrochloric acid (up to about three times the concentration of rhodium complex), a secondary reaction dominates. This could be the 'side reaction' noticed by Nyberg et al. At higher concentrations of hydrochloric acid there is a first-order dependence on the concentration of hydrochloric acid, but as the concentration increases the rate becomes lower than that expected for first-order

Table 1

Variation of initial rate of oxidation with concentration of $[\{Rh(CO)_2Cl\}_2]$ [a] at 40.0 °C

$[\{Rh(CO)_2Cl\}_2]$ (10^{-3} mol dm^{-3})	Initial rate (10^{-3} min^{-1}) (385 nm)	Initial rate (10^{-3} min^{-1}) (485 nm)
0.64	38.0	1.29
1.10	67.0	1.95
1.84	122	3.80
3.30	224	7.00

[a] $[H_2O_2]_0$ 0.015 mol dm^{-3}, $[HCl]_0$ 0.022 mol dm^{-3}.

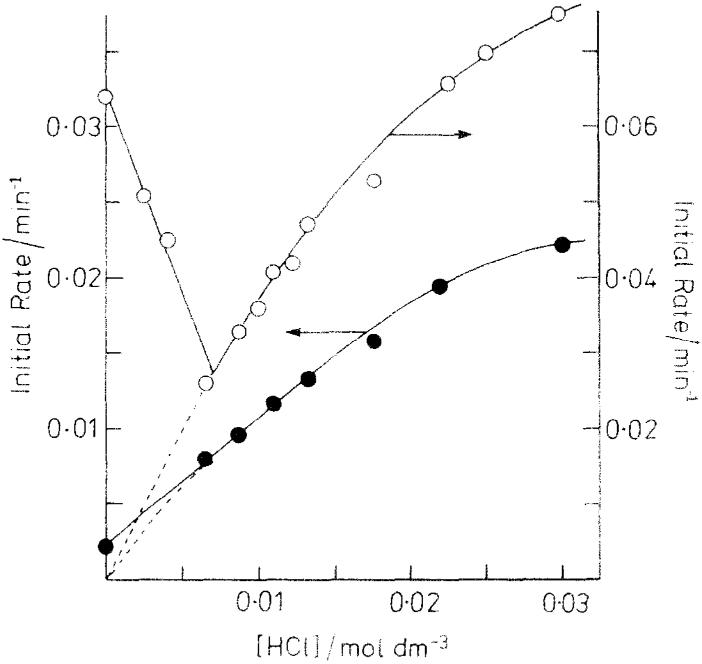

Fig. 2. Variation of initial rate of reaction of 40.0 °C with concentration of hydrochloric acid. ○ data at 385 nm, ● data at 485 nm. $[\{Rh(CO)_2Cl\}_2]$ 0.0011 mol dm^{-3}, $[H_2O_2] = 0.0148$ mol dm^{-3}.

dependence. The shape of this curve suggests that a complex is being formed between hydrochloric acid and $[Rh(CO)_2Cl_2]^-$ (eq. 12).

$$[Rh(CO)_2Cl_2]^- + Cl^- \overset{K_4}{\rightleftharpoons} [Rh(CO)_2Cl_3]^{2-} \tag{12}$$

The reaction rate depends on the concentration of the complex ion $[Rh(CO)_2Cl_3]^{2-}$ and the usual (see Appendix (i)) plot of 1/rate against $1/[Cl^-]$ should be linear with an intercept on the abscissa of $-K_{Cl}$. Figure 3 shows these plots. From these graphs, K_{Cl} is 28.7 dm^3 mol^{-1}.

Order with respect to hydrogen peroxide. Figure 4 shows the effect upon the initial rate of absorbance changes of varying the concentration of hydrogen peroxide, but keeping the concentration of hydrochloric acid and $[\{Rh(CO)_2Cl\}_2]$ constant, that of the hydrochloric acid being in excess over that of $[\{Rh(CO)_2Cl\}_2]$. It can be seen that the rates fall away from first-order dependence at high concentrations of hydrogen peroxide in a way analogous to that seen when the hydrochloric acid concentration was varied. However, the fall away is greater at 385 nm than at 485, and if this behaviour is due to a complex formation between reagents (e.g. eq. 13), then the value of K_P (from plots of 1/rate against 1/

$$[Rh(CO)_2Cl_2]^- + H_2O \overset{K_P}{\rightleftharpoons} [Rh(CO)_2Cl_2(H_2O_2)]^- \tag{13}$$

$[H_2O_2]$) is 27 dm^3 mol^{-1} (from measurements at 385 nm) or 9.5 dm^3 mol^{-1} (from measurements at 485 nm). Of course K_P should not vary with the wavelength, and

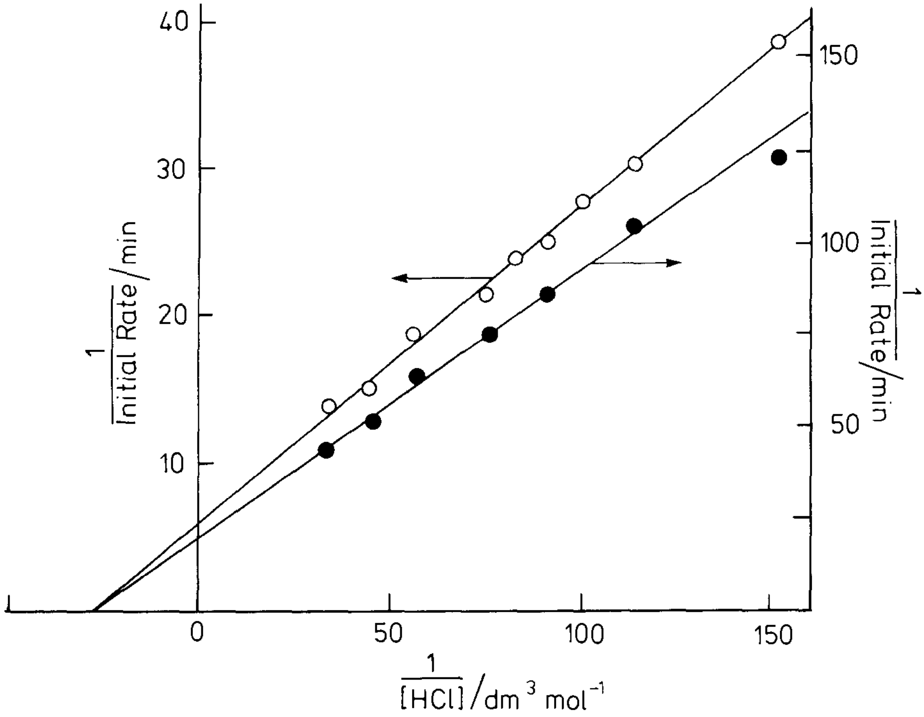

Fig. 3. Plots of 1/(initial rate) against 1/[HCl]. ○ data at 385 nm, ● data at 485 nm. Conditions are the same as those given for Fig. 2.

the formation of a complex between reagents and hydrogen peroxide cannot be the cause of the falling away of rate at high concentrations of hydrogen peroxide. A more likely explanation is that the species X, whose absorbance is being measured at 385 and 485 nm, complexes with hydrogen peroxide, eq. 14 and 15. In the following, it is assumed that the concentration of hydrogen peroxide is high enough so that the concentration of free hydrogen peroxide can be equated to the concentration of hydrogen peroxide added.

$$X + H_2O_2 \overset{K_P}{\rightleftharpoons} X:H_2O_2 \tag{14}$$

$$K_P = \frac{[X:H_2O_2]}{[X][H_2O_2]} \tag{15}$$

The initial absorbance, A_λ, will depend on the molar absorptivities, ϵ_λ, of both X and $X:H_2O_2$ at wavelength λ (eq. 16).

$$A_\lambda = [X]\epsilon_{X,\lambda} + [X:H_2O_2]\epsilon_{X:H_2O_2,\lambda} \tag{16}$$

Substituting for $[X:H_2O_2]$ from eq. 15, eq. 17 is obtained.

$$A_\lambda = [X]\left(\epsilon_{X,\lambda} + K_P[H_2O_2]\epsilon_{X:H_2O_2,\lambda}\right) \tag{17}$$

If the molar absorptivity of $[X:H_2O_2]$ is $\phi_\lambda\epsilon_{X,\lambda}$, eq. 18 can be written.

$$A_\lambda = [X]\epsilon_{X,\lambda}(1 + K_P[H_2O_2]\phi_\lambda) \tag{18}$$

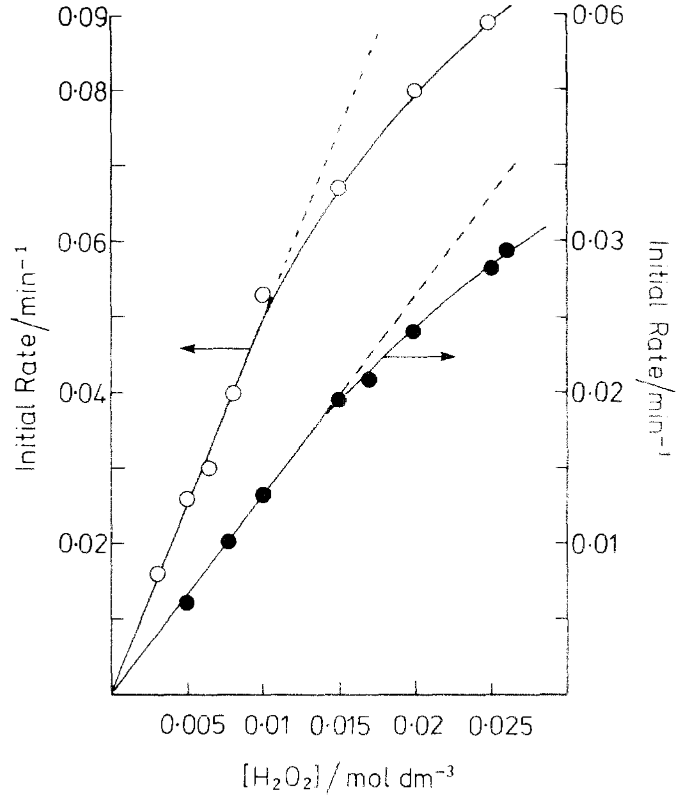

Fig. 4. Variation of initial rate of reaction at 40.0 ° C with concentration of hydrogen peroxide. ○ data at 385 nm, ● data at 485 nm. [$\{Rh(CO)_2Cl\}_2$] 0.0011 mol dm^{-3}. [HCl] 0.022 mol dm^{-3}.

The rate of change of absorbance is then given by eq. 19.

$$\frac{dA_\lambda}{dt} = \frac{d[X]}{dt}\epsilon_{X,\lambda}(1 + K_P[H_2O_2]\phi_\lambda) \tag{19}$$

and the initial rate of reaction, ν_0, is given by eq. 20.

$$\nu_0 = \frac{d[X]}{dt} + \frac{d[X:H_2O_2]}{dt} \tag{20}$$

Substituting for [$X:H_2O_2$] from eq. 15 gives eq. 22.

$$\nu_0 = \frac{d[X]}{dt} + \frac{d[X]}{dt}K_P[H_2O_2] \tag{21}$$

$$= \frac{d[X]}{dt}(1 + K_P[H_2O]) \tag{22}$$

Combining eq. 22 and 19 gives eq. 23.

$$\frac{dA_\lambda}{dt} = \frac{\nu_0\epsilon_{X,\lambda}(1 + K_P[H_2O_2]\phi_\lambda)}{1 + K_P[H_2O_2]} \tag{23}$$

If $\phi_\lambda = 0$, then the initial rate as assessed by dA_λ/dt will reduce by $1/(1 +$

$K_P[H_2O_2]$). If $\phi_\lambda = 1$, the initial rate will be unaffected by $[H_2O_2]$. As it is likely that ϕ_{385} and ϕ_{485} are not the same, the behaviour of initial rate with change of concentration of hydrogen peroxide as measured at the two wavelengths will not be the same.

Equation 23 may be simplified to eq. 24 if $K_P[H_2O_2] \ll 1$ (see Appendix (ii)).

$$\frac{dA_\lambda}{dt} = \frac{\nu_0 \epsilon_{X,\lambda}}{1 + K_P[H_2O_2](1 - \phi_\lambda)} \tag{24}$$

The initial rate will fall away as the concentration of hydrogen peroxide increases, and a plot of ν_0^{-1} against $[H_2O_2]^{-1}$ will give an intercept on the abscissa of $-K_P(1 - \phi_\lambda)$. As ϕ_λ will vary with wavelength this intercept will not stay constant. This is in full agreement with the behaviour observed.

Mechanism. A mechanism for the reaction of $[Rh(CO)_2Cl_2]^-$ with hydrogen peroxide in the presence of hydrochloric acid, which takes into account all the features just discussed, is given in eq. 25–28.

$$[Rh(CO)_2Cl_2]^- + Cl^- \underset{\text{fast}}{\overset{K_{Cl}}{\rightleftharpoons}} [Rh(CO)_2Cl_3]^{2-} \tag{25}$$

$$[Rh(CO)_2Cl_3]^{2-} + 2\,H_2O_2 \xrightarrow[k_{int}]{2H^+} \text{“}\underset{(X)}{\{Rh(CO)Cl_3\}}\text{”} + CO_2 + 3\,H_2O \tag{26}$$

$$\text{“}\{Rh(CO)Cl_3\}\text{”} + H_2O_2 \underset{\text{fast}}{\overset{k_P}{\rightleftharpoons}} [Rh(CO)Cl_3(H_2O_2)] \tag{27}$$

$$\text{“}\{Rh(CO)Cl_3\}\text{”} \xrightarrow{k_{prod}} \text{“}RhCl_3\text{”} + CO \tag{28}$$

Equation 25 shows the rapid complexing of $[Rh(CO)_2Cl_2]^-$ by chloride to form $[Rh(CO)_2Cl_3]^{2-}$. This reacts with hydrogen peroxide to form the intermediate X, “$\{Rh(CO)Cl_3\}$” (eq. 26). This step must be more complex than given here. Hydrogen ions and two moles of hydrogen peroxide are necessary, and both oxidation of rhodium(I) to rhodium(III) and oxidation of a carbonyl ligand to carbon dioxide take place. The kinetics give no clue as to the nature of this process. The intermediate rapidly complexes with a second molecule of hydrogen peroxide (eq. 27). Finally X slowly loses carbon monoxide to give the observed products, (eq. 28). This scheme gives an initial rate of formation of the intermediate, X, shown in eq. 29 and, if this is measured by absorbance changes where both X

$$\frac{d[X]}{dt} = \frac{k_{int}K_{Cl}[Rh(CO)_2Cl_2^-][Cl^-][H_2O_2]}{1 + K_{Cl}[Cl^-]} \tag{29}$$

and $[Rh(CO)Cl_3(H_2O_2)]$ absorb, the rate of absorbance change is given by eq. 30.

$$\frac{dA_\lambda}{dt} = \frac{k_{int}K_{Cl}\epsilon_{X,\lambda}[Rh(CO)_2Cl_2^-][Cl^-][H_2O_2](1 + K_P[H_2O_2]\phi_\lambda)}{(1 + K_{Cl}[Cl^-])(1 + K_P[H_2O_2])} \tag{30}$$

This is in full agreement with the kinetics observed. Absorbances were measured as reaction proceeded, and an attempt made to fit the above reaction scheme to them using the fitting program FACSIMILE [22]. As there are unknown molar absorptivities for many of the species involved, no unique set of fitted parameters could be

Table 2

Variation of rate of reaction with solvent at 40.0 °C [a]

Solvent	$K^\star$ (dm^3 mol^{-1})		k' (dm^3 mol^{-1} m^{-1})		$\frac{k'(\text{solvent})}{k'\ \text{EtOH}}$		Dielectric constant
	385 nm	485 nm	385 nm	485 nm	385 nm	485 nm	
Ethanol	27.4	9.6	6.16	1.42	1	1	24.5
Methanol	105	43.5	16.3	2.88	2.6	2.0	32.7
Propanol	127	59.8	19.7	4.59	3.2	3.2	20.3
2-Propanol	63.1	37.8	13.2	3.25	2.1	2.3	19.9
Butanol	129	48.9	22.7	5.33	3.7	3.7	17.5
t-Butanol	138	12.0	28.6	6.6	4.6	4.6	12.5
2-Butoxyethanol	198	13.4	40.6	7.8	6.6	5.5	9.3

[a] $[\{Rh(CO)_2Cl\}_2]$ 0.0011 mol dm^{-3}, [HCl] 0.022 mol dm^{-3}; 0.003 mol dm^{-3} < $[H_2O_2]$ < 0.025 mol dm^{-3}.

obtained, by the fitting exercise showed that the above mechanism can satisfactorily account for the absorbance changes during reaction.

Variation of reaction rate with solvent. The initial reaction rate was measured in a number of alcoholic solvents. For each, the concentration of hydrochloric acid and $[\{Rh(CO)_2Cl\}_2]$ was kept constant (the hydrochloric acid in ten-fold excess over the complex), and initial rates were measured at a number of concentrations of hydrogen peroxide. In each case the general shape of the curve of rate against concentration of hydrogen peroxide was like that illustrated in Fig. 4. To get comparative data, the initial rate was fitted to the function shown in eq. 31.

$$\text{initial rate} = k'[H_2O_2]/(1 + K^\star[H_2O_2]) \qquad (31)$$

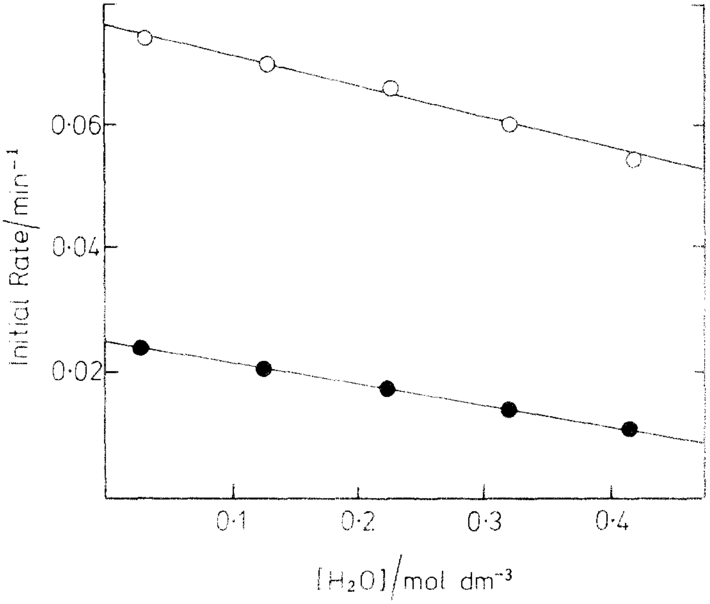

Fig. 5. Effect of water concentration on initial rates of oxidation at 40.0 °C. ○ data at 385 nm, ● data at 485 nm. $[\{Rh(CO)_2Cl\}_2]$ 0.0011 mol dm^{-3}, $[H_2O_2]$ 0.019 mol dm^{-3}, [HCl] 0.022 mol dm^{-3}

Table 3

Variation of initial rates of oxidation with temperature [a]

Temperature (° C)	Initial rate (10^{-3} min^{-1}) (385 nm)	Initial rate (10^{-3} min^{-1}) (485 nm)
26.0	1.05	2.75
35.3	1,94	5.10
40.0	2.60	6.30
45.0	3.72	9.20
50.0	4.90	11.46
54.0	6.88	13.50
57.0	8.20	16.80

[a] $[\{Rh(CO)_2Cl\}_2] = 0.0011$ mol dm^{-3}, $[H_2O_2] = 0.0050$ mol dm^{-3}, $[HCl] = 0.022$ mol dm^{-3}.

and values of k' and $K^{\star}$ are reported in Table 2. It can be seen clearly that, in general, the reaction rate increases as the polarity of the solvent decreases. These relative rates assume that molar absorptivities of the various species do not change markedly with variation of the solvent. The reason for the anomolous position of methanol is not clear. It could be partly caused by changes in molar absorptivities, but the deviation from the expected position (rate expected to be slower than in ethanol) may involve some other specific factor. Other workers have reported that water has a retarding effect on these oxidations. Figure 5 shows that the formation of the intermediate, X, is retarded by increasing the water content of the solvent. This retarding effect is, of course, in line with that noted for other solvents, where increasing polarity retards the rate. The general retardation of rate with increasing solvent polarity may indicate that charges are dissipated on going from the ground state to the transition state.

Activation parameters. Table 3 shows that rates of reaction increase with temperature. The activation energies calculated are 54.7 kJ mol^{-1} for measurements at 385 nm or 47.2 kJ mol^{-1} for measurements at 485 nm. As temperature increases, the positions of equilibria will change as well as the rate coefficients. Interpretation of the rate data in terms of activation enthalpies and entropies is not possible without careful measurement of K_{Cl} and K_P at each temperature.

Appendix

(i) If a concentration of rhodium dichlorodicarbonyl anion $[Rh(CO)_2Cl_2^-]_0$, is added to an excess of hydrochloric acid with chloride concentration $[Cl^-]$, complex formation may take place in accordance with eq. 12. If the subscript 'e' is used to denote concentrations at equilibrium, eq. A1 and A2 can be written:

$$[Rh(CO)_2Cl_2^-]_0 = [Rh(CO)_2Cl_2^-]_e + [Rh(CO)_2Cl_3^{2-}]_e \qquad (A1)$$

$$K_{Cl} = \frac{[Rh(CO)_2Cl_3^{2-}]_e}{[Rh(CO)_2Cl_2^-]_e[Cl^-]} \qquad (A2)$$

From these two equations, the concentration of $[Rh(CO)_2Cl_3]^{2-}$ at equilibrium can be calculated (eq. A3):

$$[Rh(CO)_2Cl_3^{2-}]_e = K_{Cl}[Rh(CO)_2Cl_2^-]_0[Cl^-]/(1 + K_{Cl}[Cl^-]) \qquad (A3)$$

If the observed rate of reaction, ν_0, is proportional to the concentration of the complex $[Rh(CO)_2Cl_3]^{2-}$ at equilibrium, eq. A4 is obtained.

$$\nu_0 = \frac{k\,K_{Cl}[Rh(CO)_2Cl_2^-]_0[Cl^-]}{1 + K_{Cl}[Cl^-]} \tag{A4}$$

Taking reciprocals gives eq. A5:

$$\frac{1}{\nu_0} = \frac{1}{k\,K_{Cl}[Rh(CO)_2Cl_2^-]_0} \cdot \frac{1}{[Cl^-]} + \frac{1}{k[Rh(CO)_2Cl_2^-]_0} \tag{A5}$$

A plot of ν_0^{-1} against $[Cl^-]^{-1}$ will give a straight line with an intercept on the abscissa of $-K_{Cl}$.

(ii) Equation 23 can be written as A6:

$$\frac{dA_\lambda}{dt} = \frac{\nu_0\epsilon_{X,\lambda}}{(1 + K_P[H_2O_2])(1 + K_P[H_2O_2]\phi_\lambda)^{-1}} \tag{A6}$$

If $K_P[H_2O_2]\phi_\lambda \ll 1$, the second term in the denominator can be approximated by the first term of the binomial expansion, giving eq. A7:

$$\frac{dA_\lambda}{dt} = \frac{\nu_0\epsilon_{X,\lambda}}{(1 + K_P[H_2O_2])(1 - K_P[H_2O_2]\phi_\lambda)} \tag{A7}$$

Expanding the denominator, and ignoring the term $K_P^2[H_2O_2]^2\phi_\lambda$, gives eq. 24.

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