Autocatalytic Reduction of a Bis(dimethylglyoxime) Complex of Rhodium(III) in Alkaline Aqueous Ethanol

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The compound $[Rh^{III}(DH)(DH_2)Cl_2]$ (DH_2 = dimethylglyoxime) is reduced in alkaline aqueous ethanol under an inert atmosphere to a rhodium(I) complex. A detailed kinetic study of this reaction has been carried out and the rate equation governing the reaction shown to be of the form $d[Rh^I]/dt = k[Rh^{III}][Rh^I]$. The observed rate constant varies with the inverse fourth power of the hydroxide-ion concentration, but is independent of the concentration of added chloride ion. The variation of rate with temperature is also reported. A mechanism is postulated to account for the experimental results.

ALTHOUGH bis(dimethylglyoximato)cobalt complexes have been extensively studied,[1,2] the analogous rhodium complexes have received relatively little attention. Recently these systems have become a topic of interest to several workers[3-5] and compounds are known which contain rhodium in the oxidation states I, II, and III. In all known cases the two dimethylglyoxime anions lie in an essentially planar arrangement around each rhodium atom, whether the complex is dimeric rhodium(II),[6] or monomeric rhodium(III).[4,7] Very little information concerning kinetic or mechanistic studies of these complexes is available, although data on complexes containing other ligands are available.

The compound $H[Rh(DH)_2Cl_2]$ (A; DH_2 = dimethylglyoxime), more correctly formulated as $[Rh(DH)(DH_2)Cl_2]$ {although $H_3O^+[Rh(DH)_2Cl_2]^-$ is believed to be formed in water}, in suspension[3] or neutral solution {containing the ion $[Rh(DH)_2Cl_2]^-$},[3,8] is reduced by the tetrahydroborate ion to rhodium(I). In solutions containing more than 0·1M-sodium hydroxide, it is reported[3] that reduction occurs without the addition of tetrahydroborate ions. Whilst our observations are in agreement with this report, we find that reaction proceeds as soon as sufficient base is present to neutralize the hydroxonium ion formed upon solution of (A) in water.

Although reducing agents such as ethanol and hydrazine[4,9] catalyse substitution reactions in rhodium(III) complexes, catalysis is best achieved by using rhodium(I) complexes rather than other reducing agents or hydride producing agents.[10,11] Chloro-bridged dimers have been postulated in such reactions, the dimer being derived from a rhodium(III) and a rhodium(I) complex. Thus $[H_2ORh(py)_4\text{-}Cl\text{-}Rh(py)_4OH_2]^-$ is believed[9] to occur in the ethanol catalysed conversion of $K_2[Rh(H_2O)Cl_5]$ into *trans*-$[Rh(py)_4Cl_2]Cl$ and an analogous species is postulated[12] in the conversion of *trans*-$[Rh(en)_2Cl_2]^+$ into *trans*-$[Rh(en)_2(N_2H_4)Cl]^{2+}$. In this paper, and the following one, similar mechanisms are postulated. The present reactions differ in that catalysis of reduction of rhodium(III) complexes to rhodium(I) occurs rather than that of a substitution reaction.

RESULTS AND DISCUSSION

When compound (A) in ethanolic solution is warmed to 60 °C under an atmosphere of hydrogen or nitrogen, and sodium hydroxide solution then added such that the

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final solution is 25% ethanol by volume and 0·5M-hydroxide, the solution becomes dark blue within a few minutes and exhibits visible absorption peaks at 458 and 575 nm. The measured final optical density at these wavelengths varies linearly with the total rhodium concentration and the ratio of the two optical density values stays constant, within experimental error, as the rhodium and hydroxide-ion concentrations are varied (Tables 1 and 2). Thus it seems that one product is responsible for both visible absorption peaks.

TABLE 1

Effect of total rhodium concentration on the ratio of optical densities at 458 and 575 nm. $[OH^-] = 0\cdot309$M, 60·0 °C, in ethanol (25%)–water under hydrogen at 1 atm

$10^3[Rh^{III}]_T$/M	O.D.(457)/O.D.(575)
1·125	10·7
0·900	10·5
0·675	11·8
0·450	10·4

TABLE 2

Effect of hydroxide-ion concentration on the ratio of optical densities. $[Rh^{III}]_T = 2\cdot98 \times 10^{-3}$M, 60·0 °C, in ethanol (25%)–water under nitrogen at 1 atm, $I = 1\cdot50$M ($NaNO_3$)

$[OH^-]$/M	O.D.(457)/O.D.(575)
0·0562	10·4
0·179	10·5
0·317	10·5
0·393	9·8
0·526	10·4
0·787	9·1
0·972	9·4

Using a higher concentration of the rhodium(III) reagent than is practicable for kinetic experiments, and a two-fold excess of sodium hydroxide, a dark blue-black oxygen-sensitive solid can be isolated from experiments in warm aqueous ethanol under an inert atmosphere. An apparently identical product is obtained when compound (A) is reduced by sodium tetrahydroborate in aqueous methanol at a low temperature. Analysis of the product obtained from the reduction of $[Rh(DH)(DH)_2)Cl_2]$ shows that chloride ion is present only as an impurity, and suggests the formula $[Rh(DH)(DH_2)],3H_2O$. We have been unable to prepare a sample which is absolutely free from chloride. This material shows broad i.r. absorptions at 3400, 2400, and 1650 cm^{-1}, and its solution in alkaline aqueous ethanol obeys Beer's law with visible maxima at 458 (ε 7060) and 575 nm (ε 670 l mol^{-1} cm^{-1}). During the reduction of compound (A) in alkaline aqueous ethanol, transient red streaks are observed within the solution before the colour changes to blue.

We interpret these observations as follows. In aqueous ethanol containing an excess of base, the compound $[RH(DH)(DH_2)Cl_2]$ is soluble yielding the ion $[Rh(DH)_2Cl_2]^-$ which is subsequently reduced to a rhodium(I) complex, probably $[Rh(DH)_2]^-$, in solution. A dimeric rhodium(II) species may occur as an intermediate, causing the transient red colour observed during reaction; the dimeric compound $[Rh(DH_2)(PPh_3)]_2$ is red.[5] The overall reaction does not occur unless the medium contains ethanol and sufficient base to neutralize the H_3O^+ formed when compound (A) dissolves; the greater the concentration of base, once this limit has been exceeded, the more slowly the reaction occurs.

Detailed kinetic studies of this reaction were carried out as follows. Aqueous ethanolic solutions of $[Rh(DH)(DH_2)Cl_2]$ and aqueous solutions of sodium hydroxide and sodium nitrate (as the inert electrolyte) were separately thermostatted under an inert atmosphere of hydrogen or nitrogen. The reaction was initiated at a known time by running one solution into the other in a thermostatted vessel under the inert atmosphere, followed by vigorous shaking. Samples were abstracted at known times and the course of the reaction followed by determining the optical density at one of the absorption maxima of the rhodium(I) product. The several variables were altered over as wide a range as the limitations of our technique allowed.

When the experimental conditions were chosen to give slow rates of reaction, *i.e.* at low temperatures or high hydroxide-ion concentrations, induction periods were observed; in the case of faster rates of reaction such periods were not seen. This may be due to the presence of small amounts of impurities in the starting complex. In all cases the form of the concentration against time curve was typical of an autocatalytic process and showed a maximum rate of reaction at 50% completion. This suggests that the dominant term in the rate law is as in equation (1). The integrated form of this equation is (2),

$$d[Rh^I]/dt = k_{obs}[Rh^{III}][Rh^I] \qquad (1)$$

$$k_{obs}\,t = \frac{1}{[Rh^{III}]_T}\log\frac{[Rh^I]}{[Rh^{III}]_T - [Rh^I]} + \text{constant} \qquad (2)$$

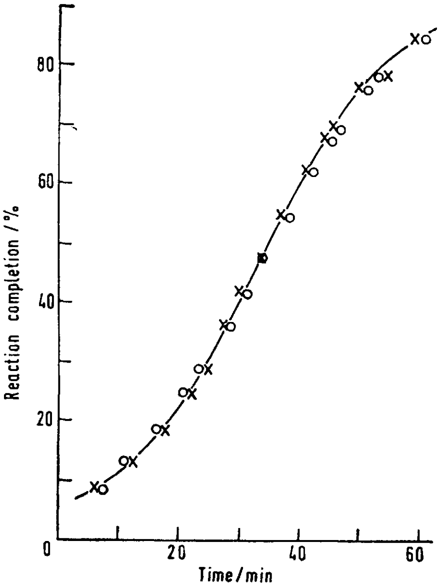
where $[Rh^{III}]_T$ represents the total rhodium concentration and $[Rh^I]$ the concentration of the rhodium(I) product. Using a least-squares computer program, the experimental data were fitted to equation (2) by finding the best values of k_{obs} and the integration constant. A typical result is shown in the Figure, which shows a good fit to *ca.* 90% completion. The reaction profile and the calculated values for the observed rate constants are identical whichever of the visible absorption maxima is used. The calculated value of the rate constant also remains constant as the total rhodium concentration is varied between $9\cdot94 \times 10^{-4}$ and $6\cdot01 \times 10^{-3}$M. In the temperature range 35—70 °C the rate constant increases with temperature (Table 3), the value for the parameter equivalent to an activation energy being $8\cdot8 \pm 0\cdot3$ kcal mol^{-1}.

TABLE 3

Variation of the observed rate constant with temperature, in ethanol (25%)–water, under hydrogen at 1 atm. $[Rh^{II}]_T = 2\cdot98 \times 10^{-3}$M, $[OH^-] = 0\cdot623$M, $I = 1\cdot50$M ($NaNO_3$)

t/°C	k_{obs}/l mol^{-1} min^{-1}
34·5	25·2
44·3	41·1
49·4	46·5
64·6	96·6
69·3	110·8

When the effect of hydroxide-ion concentration in examined, it is apparent that no reaction occurs until the ratio of sodium hydroxide to compound (A) exceeds 1 : 1; when the ratio lies between 1 : 1 and 2 : 1, a slow reaction occurs at 50 °C in ethanol (25%) yielding a brown precipitate. Reaction mixtures containing a two-fold excess of sodium hydroxide react very rapidly, first forming a dark purple solution, and then a dark precipitate and a green solution. These observations are similar to those made by Gillard and Wilkinson [8] who reported that tetrahydroborate ion reduction of an aqueous solution of $\mathrm{Na[Rh(DH)_2Cl_2]}$ gave a diamagnetic green solution, which showed a single high-field ^{1}H n.m.r. signal (τ 26·4) and ultimately produced metallic rhodium and a brown solution. The precipitate described here is certainly not metallic rhodium, but rather a rhodium(I) complex containing two dimethylglyoxime units (see above). When a five-fold excess of hydroxide ion is present, no precipitation occurs. The rate of reaction varies markedly with the hydroxide-ion concentration, and it proved impossible to study a wide range of concentrations, owing to limitations of the sampling technique. In the range $0{\cdot}393\mathrm{M} \leqslant [\mathrm{OH^-}] \leqslant 0{\cdot}901\mathrm{M}$, the observed rate constant shows an inverse fourth power dependence on the hydroxide-ion concentration (Table 4).



Typical plot of the concentration of the rhodium(I) product against time. (×), Experimental points; (○), the calculated fit based on equation (2)

The observed rate constant is independent of the concentration of chloride ion up to 1·25M, at constant ionic strength (Table 5). The addition of free dimethylglyoxime markedly slows the reaction. It proved impossible to obtain results under concentration conditions where the free dimethylglyoxime concentration can be regarded as constant; at much lower concentrations the reproducibility of runs was poor and no quantitative data are therefore provided.

Since the rate of reaction is the same under either nitrogen or hydrogen, while the blue product solution is oxidised by either oxygen or hydrogen peroxide, the active reductant in this system is believed to be ethanol, the ethanol being oxidised to acetaldehyde, which then polymerizes in the alkaline medium employed. This deduction is in agreement with the observation that no reaction occurs in a completely aqueous alkaline medium. However, we have been unable to obtain direct evidence of the oxidation of ethanol.

TABLE 4

Variation of the observed rate constant with hydroxide-ion concentration, in ethanol (25%)–water, under hydrogen at 1 atm. $[\mathrm{Rh^{III}}]_\mathrm{T} = 2{\cdot}98 \times 10^{-3}\mathrm{M}$, $I = 1{\cdot}50\mathrm{M}$ ($\mathrm{NaNO_3}$), 50·0 °C

$[\mathrm{OH^-}]$/M	$k_{\mathrm{obs}}{}^a$/l mol^{-1} min^{-1}
0·901	15·3
0·787	16·8
0·750	22·0
0·713	25·1
0·668	31·8
0·622	44·2
0·526	76·5
0·393	111·5

[a] Mean value of duplicate experiments showing discrepancies below 10%.

TABLE 5

Effect of chloride-ion concentration on the rate of reaction at 50 °C, in ethanol (25%)–water, under 1 atm hydrogen. $[\mathrm{Rh^{III}}]_\mathrm{T} = 2{\cdot}98 \times 10^{-3}\mathrm{M}$, $[\mathrm{OH^-}] = 0{\cdot}623\mathrm{M}$, $I = 1{\cdot}50\mathrm{M}$ ($\mathrm{NaNO_3}$)

$[\mathrm{Cl^-}]$/M	k_{obs}/l mol^{-1} min^{-1}
0	47·8
0·30	45·4
0·45	50·3
0·60	43·2
0·75	38·9
0·90	45·5
1·25	39·7

From our kinetic observations, we deduce that the reaction sequence is as follows, where equation (6) represents the result of several steps following equation (5).

$$[\mathrm{Rh^{III}(DH)_2Cl_2}]^- + 2\mathrm{OH}^- \overset{K_1}{\rightleftharpoons} [\mathrm{Rh^{III}(D)_2Cl_2}]^{3-} + 2\mathrm{H_2O} \tag{3}$$

$$[\mathrm{Rh^{I}(DH)_2}]^- + 2\mathrm{OH}^- \overset{K_2}{\rightleftharpoons} [\mathrm{Rh^{I}(D)_2}]^{3-} + 2\mathrm{H_2O} \tag{4}$$

$$[\mathrm{Rh^{III}(DH)_2Cl_2}]^- + [\mathrm{Rh^{I}(DH)_2}]^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [\mathrm{Cl(DH)_2Rh{-}Cl{-}Rh(DH)_2}]^{2-} \tag{5}$$

$$[\mathrm{Cl(DH)_2Rh{-}Cl{-}Rh(DH)_2}]^{2-} + \mathrm{EtOH} \xrightarrow{k_4} 2[\mathrm{Rh^{I}(DH)_2}]^- + 2\mathrm{Cl}^- + \mathrm{MeCHO} + 2\mathrm{H}^+ \tag{6}$$

In alkaline solution, the two weakly [4] hydrogen-bonded protons of the rhodium(III) complex are likely to be lost, as in equation (3). If the deprotonation is essentially complete, then the concentration of $[\mathrm{Rh^{III}(DH)_2Cl_2}]^-$ is given by equation (7).

$$[\mathrm{Rh^{III}(DH)_2Cl_2}]^- = [\mathrm{Rh^{III}}]_\mathrm{T}[\mathrm{H_2O}]^2/K_1[\mathrm{OH^-}]^2 \tag{7}$$

Similar reasoning leads to a similar equation for rhodium(I).

$$[\mathrm{Rh^I(DH)_2}]^- = [\mathrm{Rh^I}]_\mathrm{T}[\mathrm{H_2O}]^2/K_2[\mathrm{OH^-}]^2 \qquad (8)$$

If the steady-state hypothesis can be applied to the postulated dimer $[\mathrm{Cl(DH)_2Rh{-}Cl{-}Rh(DH)_2}]^{2-}$, equations (3)—(6) yield the rate equation (9) where $k_\mathrm{obs} =$

$$\mathrm{d}[\mathrm{Rh^I}]/\mathrm{d}t = k_\mathrm{obs}\,[\mathrm{Rh^{III}}]_\mathrm{T}[\mathrm{Rh^I}]_\mathrm{T}[\mathrm{OH^-}]^{-4} \qquad (9)$$

$k_3k_4[\mathrm{EtOH}][\mathrm{H_2O}]^4/K_1K_2(k_{-3} + k_4[\mathrm{EtOH}])$. Because the reaction is independent of chloride ion, a chloro-bridged dimer has been postulated, rather than a dimer containing a metal–metal bond.[6] This experimental observation also implies that the loss of the terminal chlorine in the proposed dimer is either irreversible, or occurs after a fast irreversible reaction.

The effect of added dimethylglyoxime can not be determined with certainty, due to our lack of reliable kinetic data. However, we feel that the marked retardation produced by this ligand is probably due to the blocking of an otherwise available co-ordination site on rhodium(I).

EXPERIMENTAL

Kinetic studies were carried out by measuring the optical densities of samples, extracted from the main reaction vessel, using a Unicam SP 500 spectrophotometer with a thermostatted cell compartment. The reaction vessel consisted of a small vessel (capacity 40 cm³) mounted above a larger vessel (capacity 300 cm³). Liquid was added from the upper to the lower vessel, thus initiating reaction, by opening a connecting tap. Both vessels had outer jackets through which thermostat water was rapidly pumped. The upper portions of the vessels were connected together, and to a gas reservoir and manometer to enable separate reagents to be thermostatted under identical atmospheres. Samples were removed *via* a tap at the bottom of the lower vessel and transferred directly to the spectrophotometer. To minimise any contact with air, this tap was surrounded by a flexible Polythene skirt under which a continuous flow of nitrogen or hydrogen was maintained. When samples were not being taken, the whole assembly was vigorously shaken mechanically, this being the most satisfactory way of ensuring uniformity within the reaction mixture.

Between successive runs, the apparatus was thoroughly cleaned using a succession of washing materials, including aqua regia, to ensure that rhodium(I) species, or rhodium metal, were not held on the surfaces and could not be carried over from one experiment to the next. With the exception of the runs with added dimethylglyoxime, all experiments were shown to be reproducible. To ensure the absence of dissolved oxygen from reagent solutions, flushing cycles using the inert gas were repeated several times, and extended periods for equilibration allowed.

trans-*Dichloro*(*dimethylglyoximato*) (*dimethylglyoxime*)*rhodium*(III).—This complex was prepared by the literature method.[13] Yields were found to be reduced if the solution was strongly acidic (Found: C, 23·9; H, 3·75; N, 13·6; Rh, 24·6. $\mathrm{C_8H_{15}Cl_2N_4O_4Rh}$ requires C, 23·7; H, 3·75; N, 13·8; Rh, 25·4%).

(*Dimethylglyoximato*) (*dimethylglyoxime*)*rhodium*(I) *Trihydrate*.— *trans*-Dichloro(dimethylglyoximato)(dimethylglyoxime)rhodium(III) (0·432 g) dissolved in aqueous ethanol (50%, 180 cm³) was added to 0·0119M-sodium hydroxide solution (180 cm³). The mixture was repeatedly evacuated and flushed with White Spot nitrogen and then maintained under a nitrogen atmosphere, before being stirred and heated almost to boiling point. Red streaks developed in the solution which then became blue-black in a few seconds. The mixture was then cooled in ice and a fine blue-black precipitate was filtered off under vacuum. The precipitate was washed with deaerated, nitrogen-saturated water, and dried at room temperature *in vacuo*. The product decomposes if it is heated to 80 °C under vacuum (Found: C, 25·7; H, 3·45; Cl, 0·25; N, 14·2; Na, 0; Rh, 25·1. $\mathrm{C_8H_{21}N_4O_7Rh}$ requires C, 24·7; H, 5·45; N, 14·4; Rh, 26·5%). We were unable to prepare any sample of this product which was free from chloride-ion contamination. A material which appeared to be identical, as judged by analysis, spectroscopy, and solubility and again containing traces of chloride, was prepared by reducing a cold aqueous methanolic solution of the rhodium(III) complex with sodium tetrahydroborate.[14] Samples prepared by both routes turn red on exposure to air, but not when refluxed in toluene.[14] After washing such a red solid with distilled water in air, and drying *in vacuo*, analytical figures were obtained similar to those of the blue-black product (Found: C, 26·9; H. 4·25; Cl, 0·50; N, 15·3%).

Rhodium trichloride (40·6% rhodium) was provided by Johnson, Matthey Ltd. All other reagents used were of analytical grade. The rhodium content of samples was estimated spectrophotometrically by first destroying the organic ligand with concentrated sulphuric acid, treating the resultant solution with concentrated hydrochloric acid and tin(II) chloride (18%, AnalaR) solution, and then measuring the optical density at 457 nm. A sample of rhodium trichloride of known composition was used as calibrant. An E.E.L. flame photometer Mark II was used to check the sodium content. All other analytical data were provided by the microanalytical department of the University of Aston in Birmingham, or by Alfred Bernhardt of Elbach, Germany.

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