Activation of Molecular Oxygen, Hydrogen, Carbon Monoxide, and Olefins by a Rhodium(I) Complex in Nonaqueous Media

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Summary The cyclo-octene complex $[(C_8H_{14})_2RhCl]_2$ dissolved in dimethylacetamide containing chloride reacts readily with molecular oxygen, hydrogen, carbon monoxide, and some olefins to give species of importance in homogeneous catalytic reactions.

THE cyclo-octene complex,[1] $[(C_8H_{14})_2RhCl]_2$ is practically insoluble in dimethylacetamide (DMA) under vacuum at room temperature but dissolves readily in the presence of 0·5 M-LiCl. The labile octene ligands are detected in solution and the complex is probably present as a monomeric Rh^I species containing only co-ordinated chloride and solvent. Metal production occurs after long periods due to disproportionation.

The Rh^I–DMA–Cl^- solution (**1**) rapidly absorbs O_2 to a 1 : 1 ratio at ambient conditions according to equation (1).

$$\mathrm{Rh^I} + \mathrm{O_2} \overset{K}{\rightleftharpoons} \mathrm{Rh^IO_2} \qquad (1)$$

The solution i.r. spectrum shows a band at 895 cm^{-1} attributable to the O–O stretch.[2] Most significantly, the oxygenated solution shows an e.s.r. signal with $g = 2{\cdot}0485$ at 25°; at liquid-nitrogen temperatures the signal is split into three components whose g values average out to that measured at room temperature. These e.s.r. studies are being continued but the signal is thought to be due to a species such as $Rh^{II}–O_2^-$. Previously reported molecular oxygen complexes of the d^8 and d^{10} species, Ir^I, Ni^0, Pd^0, and Pt^0,[3,4] are all diamagnetic although the magnetic properties of the oxygen complexes of Rh^I [5–8] do not appear to have been reported. The oxygen addition appears to be irreversible in the present system.

On increasing the temperature to 80°, (**1**) absorbs more oxygen continuously and a catalytic oxidation of the solvent and the cyclo-octene occurs:

$$\mathrm{Rh^IO_2} \xrightarrow{k_1} \mathrm{Rh^I} + \text{oxidation products} \qquad (2)$$

The initial linear oxygenation rate is first order in total rhodium and between zero and first order in oxygen. Reactions (1) and (2) give rise to the rate law $-d[O_2]/dt = k_1K[O_2][Rh]/(1 + K[O_2])$. Analysis of the kinetic data gives $K = 2{\cdot}9 \times 10^3\ M^{-1}$ and $k_1 = 4{\cdot}2 \times 10^{-4}\ sec^{-1}$ at 80°. Independent spectrophotometric measurements give K *ca.* $5 \times 10^3\ M^{-1}$ at room temperature. The oxidation appears to be a free-radical process; hydroperoxides could be formed by proton abstraction by the co-ordinated $\mathrm{O_2^-}$. Oxidations through the diamagnetic complexes are thought to involve oxygen atom transfer.[3,4,9]

On exposing a solution of $\mathrm{Rh^{I}O_2}$ to $\mathrm{H_2}$, reaction (3) occurs,

$$\mathrm{Rh^{I}O_2 + H_2 \rightarrow Rh^{I}H_2 + O_2} \qquad (3)$$

The O–O band at 895 cm^{-1} disappears and a hydride stretch at 1980 cm^{-1} appears; there is no net gas absorption or evolution. In the absence of stabilizing ligands, the $\mathrm{Rh^{I}H_2}$ decomposes fairly rapidly to metal.

Solution (**1**) reacts with an olefin such as maleic acid (MA) to give a $\mathrm{Rh^{I}(MA)}$ species. A solution containing this species does not activate oxygen but is oxidized stoicheiometrically to $\mathrm{Rh^{III}}$. The $\mathrm{Rh^{I}(MA)}$ solution containing an excess of MA reacts with $\mathrm{H_2}$ (1 atm. *ca.* 60°) to give a catalytic reduction to succinic acid. The kinetic data (first order in $\mathrm{H_2}$ and Rh, and zero order in olefin) are in excellent agreement with those obtained earlier for a system in which $\mathrm{RhCl_3}$ was used as the starting material,[10] and give strong evidence that $\mathrm{Rh^{I}}$ intermediates are involved in the $\mathrm{Rh^{III}}$ system:

$$\mathrm{Rh^{I}(MA) + H_2} \xrightarrow{k_2} \mathrm{Rh^{I}} + \text{succinic acid} \qquad (4)$$

$$\mathrm{Rh^{I} + MA} \xrightarrow{\text{fast}} \mathrm{Rh^{I}(MA)} \qquad (5)$$

Reaction (4) is thought to involve oxidation addition of the $\mathrm{H_2}$, followed by two successive single hydrogen atom transfers.[10] Similar agreement has been found for data for some $\mathrm{RhCl_3(Et_2S)_3}$-catalysed hydrogenations[11] and the corresponding $\mathrm{Rh^{I}}$–cyclo-octene system in the presence of diethyl sulphide.

Solution (**1**) rapidly absorbs 2 moles of CO per mole of Rh to give solutions containing the $\mathrm{[Rh(CO)_2Cl_2]^-}$ anion.[12] A solution of $\mathrm{Rh^{I}O_2}$ absorbs CO in a first-order manner, the reaction rate being independent of CO pressure. The data show that reactions (6) and (7) are occurring:

$$\mathrm{Rh^{I}O_2} \xrightarrow{k_3} \mathrm{Rh^{I} + O_2} \qquad (6)$$

$$\mathrm{Rh^{I} + 2CO} \xrightarrow{\text{fast}} \mathrm{Rh^{I}(CO)_2} \qquad (7)$$

k_3 is $0{\cdot}6 \times 10^{-3}$ sec^{-1} at 80° which combined with the K value gives the rate constant for the forward reaction of equation (1) as *ca.* $1{\cdot}7$ M^{-1} sec^{-1} at this temperature.

Solutions of $\mathrm{Rh^{I}(CO)_2}$ react with $\mathrm{O_2}$ (1 atm.) to produce $\mathrm{CO_2}$, and a mixture of CO and $\mathrm{O_2}$ is catalytically converted into $\mathrm{CO_2}$ through the $\mathrm{Rh^{I}(CO)_2}$ complex. The nature of this reaction, which could involve carbonate,[13] peroxycarbonate,[14] or carbon dioxide[15] complexes, is being studied further.

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