

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

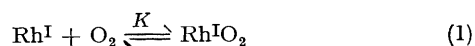
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Summary The cyclo-octene complex $[(C_8H_{14})_2RhCl]_2$ dissolved in dimethylacetamide containing chloride reacts readily with molecular oxygen, hydrogen, carbon monoxide, and some olefins to give species of importance in homogeneous catalytic reactions.

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.

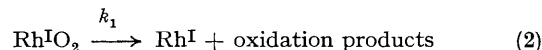
The Rh^I-DMA-Cl⁻ solution (**1**) rapidly absorbs O₂ to a 1:1 ratio at ambient conditions according to equation (1).



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 $g = 2.0485$ 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}-O₂⁻. Previously reported molecular oxygen complexes of the d^8 and d^{10} species, Ir^I, Ni⁰, Pd⁰, and Pt⁰,^{3,4} are all diamagnetic although the magnetic properties of the oxygen complexes of Rh^I⁵⁻⁸ do not appear to have been reported. The oxygen addition appears to be irreversible in the present system.

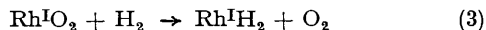
On increasing the temperature to 80°, (**1**) absorbs more oxygen continuously and a catalytic oxidation of the solvent and the cyclo-octene occurs:



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 $-d[O_2]/dt = k_1 K [O_2] [Rh] / (1 + K [O_2])$. Analysis of the kinetic data gives $K = 2.9 \times 10^3 \text{ M}^{-1}$ and $k_1 = 4.2 \times 10^{-4} \text{ sec}^{-1}$ at 80°. Independent spectrophotometric measurements give K ca. $5 \times 10^3 \text{ M}^{-1}$ at room temperature. The oxidation appears to be a free-radical process; hydroperoxides could

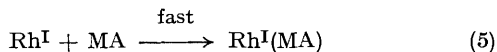
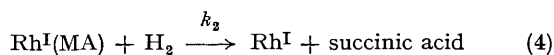
be formed by proton abstraction by the co-ordinated O_2^- . Oxidations through the diamagnetic complexes are thought to involve oxygen atom transfer.^{3,4,9}

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



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 $Rh^I H_2$ decomposes fairly rapidly to metal.

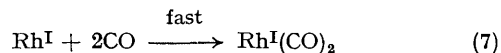
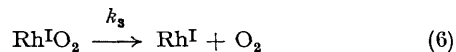
Solution (1) reacts with an olefin such as maleic acid (MA) to give a $Rh^I(MA)$ species. A solution containing this species does not activate oxygen but is oxidized stoichiometrically to Rh^{III} . The $Rh^I(MA)$ solution containing an excess of MA reacts with H_2 (1 atm. ca. 60°) to give a catalytic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



Reaction (4) is thought to involve oxidation addition of the H_2 , followed by two successive single hydrogen atom

transfers.¹⁰ Similar agreement has been found for data for some $RhCl_3(Et_2S)_3$ -catalysed hydrogenations¹¹ and the corresponding 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 $[Rh(CO)_2Cl_2]^-$ anion.¹² A solution of $Rh^I O_2$ 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:



k_3 is $0.6 \times 10^{-3}\text{ sec}^{-1}$ at 80° which combined with the K value gives the rate constant for the forward reaction of equation (1) as ca. $1.7\text{ M}^{-1}\text{ sec}^{-1}$ at this temperature.

Solutions of $Rh^I(CO)_2$ react with O_2 (1 atm.) to produce CO_2 , and a mixture of CO and O_2 is catalytically converted into CO_2 through the $Rh^I(CO)_2$ complex. The nature of this reaction, which could involve carbonate,¹³ peroxy-carbonate,¹⁴ or carbon dioxide¹⁵ complexes, is being studied further.

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