Selective Homogeneous Catalytic Oxidation of Olefins using Oxygen/Hydrogen Mixtures: Oxygen Atom Transfer from an Iridium Hydroperoxide

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An iridium(III) hydride complex in solution catalyses the O_2-co-oxidation of cyclo-octene and H_2 to cyclo-octanone and water, respectively, *via* a hydroperoxide intermediate.

$$X + O_2 + 2e \xrightarrow{2H^+} XO + H_2O;\ (X = \text{substrate}) \qquad (1)$$

$$Me_2SO + O_2 + H_2\ (\text{or } H^- + H^+) \rightarrow Me_2SO_2 + H_2O \qquad (2)$$

The selective O_2-oxidation of olefins to ketones by a single oxygen atom transfer process catalysed by rhodium complexes has been well documented.[1,2] In some systems the second oxygen atom of the O_2 molecule is reduced by a two-equivalent reducing agent, and analogies can then be drawn to the general reaction (1) of monoxygenases such as cytochrome P450.[2–4] The preferred electron donor in the enzyme system is the hydride of NADH, and this coupled with the reported rhodium(III)-catalysed co-oxidation of dimethyl sulphoxide and hydrogen according to equation (2), in which the oxygen-carrier appeared to be a rhodium(III) hydride,[5] led us to test the use of H_2 as co-reductant for monoxygenase-type activity with olefinic substrates. This communication reports the successful catalytic oxidation of cyclo-octene to cyclo-octanone according to equation (3) using dimethylacetamide (DMA) solutions of the 1,5-cyclo-octadiene dimer

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$$C_8H_{14} + O_2 + H_2 \rightarrow C_8H_{14}O + H_2O \qquad (3)$$

$$IrCl(C_8H_{12})(DMA) + HCl \overset{K}{\rightleftharpoons} \underset{(\mathbf{1})}{IrHCl_2(C_8H_{12})(DMA)} \qquad (4)$$

$[IrHCl_2(C_8H_{12})]_2$,[6] or mixtures of the $[IrCl(C_8H_{12})]_2$ dimer[7] with HCl that form the solvated monomeric hydride (**1**) according to equation (4), $K = ca.\ 10^4\ l\ mol^{-1}$ at 20 °C; an iridium(III) hydroperoxide (IrOOH) is a likely intermediate.

Typically, DMA solutions of (**1**) (*ca.* 0.03 M) in the presence of at least a ten-fold excess of cyclo-octene and a five-fold excess of HCl (conveniently added as the DMA adduct) absorb gas from hydrogen/oxygen mixtures at a total pressure of 1 atm and temperatures of 5—30 °C to generate catalytically cyclo-octanone and water as products.‡ The reactions are slow; thus at 5 °C with 350 Torr of each gas, the turnover for cyclo-octanone per iridium is about two per day based on week-long experiments. The amount of water formed is greater than expected from the stoicheiometry of equation (3) because of a competing catalytic hydrogenolysis of the oxygen;[8] at the early stages of reaction the H_2O : cyclo-octanone product ratio was about 40, but this decreased to a steady value of about 10 after one day. *Importantly*, no oxygenation of cyclo-octene occurs at all in the absence of H_2, and the absence of any inhibitory effect of radical inhibitors rules out a free-radical autoxidation reaction. Much higher rates are achieved at 30 °C but the oxygen hydrogenolysis becomes even more dominant.

Evidence for a plausible mechanism comes from the reactivity of (**1**) towards oxygen. At 1 atm pressure and 5 °C, (**1**) in DMA absorbs 1.0 mol of O_2 per iridium, but no free oxygenated organic compound is detected. A suspension of the hydride dimer in CH_2Cl_2 similarly absorbs O_2 to a 1 : 1 ratio to give a deep-red solution that is conveniently monitored by i.r. The ν(Ir–H) band (2260 cm^{-1} in the solid) is replaced by a strong band at 3495 cm^{-1}, considered to be the ν(O–H) of hydroperoxide;[9] this band decreases in intensity and disappears with time as new bands intensify at 3680 and 3605 cm^{-1} [attributed to ν(O–H) of hydroxide], and at 1692 and 1607 cm^{-1} [attributed to the ν(C–O) of free[10] and co-ordinated 4-cyclo-octen-1-one, respectively]. Addition of triphenylphosphine replaces the co-ordinated ketone which is accompanied by a corresponding decrease of the 1607 cm^{-1} band. The data are consistent with reaction (5), written for a monomer, showing oxygen-atom transfer to the diene from an iridium hydroperoxide intermediate. Such metal-catalysed atom transfer to olefins has been postulated but not previously demonstrated,[1,2,9] although transfer from alkylperoxides is well documented; metallocyclic intermediates are likely to be involved.[1,11] Insertion of O_2 into metal hydride bonds is known for some rhodium(III) systems.[12] Reaction of the iridium(I) dimer $[IrCl(C_8H_{12})]_2$ with O_2 is reported to give a hydroxyiridium species with no oxidation of the diene[13] (and we have failed to detect oxygenated diene), which gives indirect evidence for a role of the hydride ligand in reaction (**5**). The cyclo-octenone was detected also in the catalytic cyclo-octene oxygenation described above; presumably removal of the diene by reaction (5) provides vacant or solvated sites for subsequent co-ordination of the monoene. Addition of an excess of cyclo-octadiene to the $[IrHCl_2(C_8H_{12})]_2$ system under H_2/O_2 did not result in catalytic oxidation to the cyclo-octenone. The catalysis requires regeneration of the hydride from the 'Ir(OH)Cl_2' species, and this could involve a net heterolytic splitting of H_2 by such an iridium(III) species, either before or after a protonation step, equation (6). Reaction (5) is more rapid than the catalysis, which indicates that the slow step in the catalysis involves hydride regeneration. The data imply that, compared to a monoene, the more strongly co-ordinating diene inhibits reactions such as (6).

$$IrHCl_2(C_8H_{12}) \xrightarrow{O_2} Ir(OOH)Cl_2(C_8H_{12}) \longrightarrow \text{'}Ir(OH)Cl_2\text{'} + C_8H_{12}O \qquad (5)$$

$$\begin{tikzcd} Ir(OH)Cl_2 + H_2 \arrow[r] \arrow[d, "H^+"'] & IrHCl_2 + H_2O \\ Ir(H_2O)Cl_2 \arrow[ru, "{-H^+,\ H_2}"'] & \end{tikzcd} \qquad (6)$$

Use of H_2/O_2 mixtures richer in H_2 for the cyclo-octene oxidation also produces some cyclo-octane *via* a catalytic hydrogenation process; such hydrogenation involves intermediate alkyls and reaction of these with O_2 to give alkylperoxides (*e.g.*, Ir–O_2R) also could provide a pathway for the oxygenation. However, the experimental evidence for reaction (5) leads us to a working hypothesis invoking reactions (5) and (6) for the net catalysis. Although the reaction discovered is very inefficient, it does prove the potential of using H_2 as the co-reductant in monoxygenase-type catalysis. Although the use of H_2/O_2 mixtures sounds alarming, we have experienced no difficulties under the mild conditions used. Borohydride has been used recently as co-reductant in catalytic oxygenation of olefins using a manganese(III) porphyrin; non free-radical pathways involving a hydroperoxide were again invoked (Mn^{III}–OOH $\longleftrightarrow$ Mn^{IV}=O).[3]§

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‡ Products were identified by g.c. and m.s.; OV-101/chromasorb and Porapak Q were the g.c. column materials for the organic products and water, respectively, using 2-bromomesitylene and methanol as internal standards.

§ *Added in proof:* A report (I. Tabushi and A. Yazaki, *J. Am. Chem. Soc.*, 1981, **103**, 7371) that appeared after submission of this communication describes the use of H_2 with colloidal platinum as the electron donor with the same manganese porphyrin/O_2 system for epoxidation of olefins.