

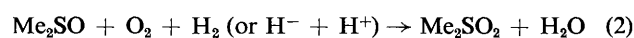
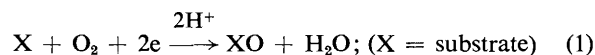
## Selective Homogeneous Catalytic Oxidation of Olefins using Oxygen/Hydrogen Mixtures: Oxygen Atom Transfer from an Iridium Hydroperoxide

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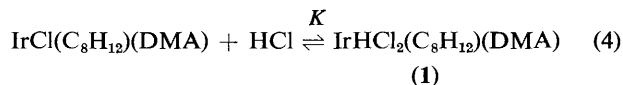
An iridium(III) hydride complex in solution catalyses the O<sub>2</sub>-co-oxidation of cyclo-octene and H<sub>2</sub> to cyclo-octanone and water, respectively, *via* a hydroperoxide intermediate.

The selective O<sub>2</sub>-oxidation of olefins to ketones by a single oxygen atom transfer process catalysed by rhodium complexes has been well documented.<sup>1,2</sup> In some systems the second oxygen atom of the O<sub>2</sub> molecule is reduced by a two-equivalent reducing agent, and analogies can then be drawn to the general reaction (1) of monooxygenases such as cytochrome P450.<sup>2-4</sup> 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,<sup>5</sup> led us to test the use of H<sub>2</sub> as co-reductant for monooxygenase-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

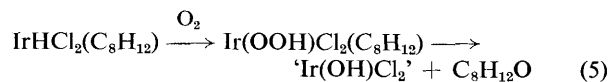
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$[\text{IrHCl}_2(\text{C}_8\text{H}_{12})]_2$ ,<sup>6</sup> or mixtures of the  $[\text{IrCl}(\text{C}_8\text{H}_{12})]_2$  dimer<sup>7</sup> with HCl that form the solvated monomeric hydride (1) according to equation (4),  $K = ca. 10^4 \text{ l mol}^{-1}$  at 20 °C; an iridium(III) hydroperoxide ( $\text{IrOOH}$ ) is a likely intermediate.

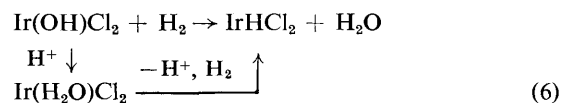
Typically, DMA solutions of (1) (*ca.* 0.03 M) in the presence of at least a ten-fold excess of cyclo-octene and a five-fold excess of HCl (conveniently added as the DMA adduct) absorb gas from hydrogen/oxygen mixtures at a total pressure of 1 atm and temperatures of 5–30 °C to generate catalytically 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 stoichiometry of equation (3) because of a competing catalytic hydrogenolysis of the oxygen;<sup>8</sup> at the early stages of reaction the  $\text{H}_2\text{O}$ : 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  $\text{H}_2$ , 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  $\text{O}_2$  per iridium, but no free oxygenated organic compound is detected. A suspension of the hydride dimer in  $\text{CH}_2\text{Cl}_2$  similarly absorbs  $\text{O}_2$  to a 1:1 ratio to give a deep-red solution that is conveniently monitored by i.r. The  $\nu(\text{Ir-H})$  band ( $2260 \text{ cm}^{-1}$  in the solid) is replaced by a strong band at  $3495 \text{ cm}^{-1}$ , considered to be the  $\nu(\text{O-H})$  of hydroperoxide;<sup>9</sup> this band decreases in intensity and disappears with time as new bands intensify at  $3680$  and  $3605 \text{ cm}^{-1}$  [attributed to  $\nu(\text{O-H})$  of hydroxide], and at  $1692$  and  $1607 \text{ cm}^{-1}$  [attributed to the  $\nu(\text{C-O})$  of free<sup>10</sup> 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  $1607 \text{ cm}^{-1}$  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,<sup>1,2,9</sup> although transfer from alkylperoxides is well documented; metalocyclic intermediates are likely to be involved.<sup>1,11</sup> Insertion of  $\text{O}_2$  into metal hydride



bonds is known for some rhodium(III) systems.<sup>12</sup> Reaction of the iridium(I) dimer  $[\text{IrCl}(\text{C}_8\text{H}_{12})]_2$  with  $\text{O}_2$  is reported to give a hydroxyiridium species with no oxidation of the diene<sup>13</sup> (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  $[\text{IrHCl}_2(\text{C}_8\text{H}_{12})]_2$  system under  $\text{H}_2/\text{O}_2$  did not result in catalytic oxidation to the cyclo-octenone. The catalysis requires regeneration of the hydride from the 'Ir(OH)Cl<sub>2</sub>' species, and this could involve a net heterolytic splitting of  $\text{H}_2$  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).

Use of  $\text{H}_2/\text{O}_2$  mixtures richer in  $\text{H}_2$  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  $\text{O}_2$  to give alkylperoxides (*e.g.*,  $\text{Ir-O}_2\text{R}$ ) 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  $\text{H}_2$  as the co-reductant in monooxygenase-type catalysis. Although the use of  $\text{H}_2/\text{O}_2$  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 ( $\text{Mn}^{\text{III}}\text{-OOH} \longleftrightarrow \text{Mn}^{\text{IV}}\text{-O}$ ).<sup>3§</sup>

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§ *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  $\text{H}_2$  with colloidal platinum as the electron donor with the same manganese porphyrin/ $\text{O}_2$  system for epoxidation of olefins.

† 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.