The principle aim in homogeneously catalyzed oxidations of hydrocarbons is a high degree of product specificity. Unfortunately, most oxidations involve free radical processes which are generally very unspecific. Exceptions are found for cases in which the bond breaking and reforming steps occur primarily at a well defined catalyst center. Over the past decade a new class of homogeneous catalytic oxidations involving non-free radical, non-Wacker type, O₂ oxidation of terminal olefins have been reported [1-5]. These systems are in general quite specific and are indeed proposed to proceed by the coordination of both olefin and dioxygen to the catalyst where they react to form products. The most exceptional case is the Rh(III)/Cu(II) catalyzed O₂ oxidation of 1-alkenes to 2-ketones in ethanol with > 98% specificity [1] (reaction 1).

\[
2\text{CH}_2=\text{CHR} + \text{O}_2 \xrightarrow{\text{Rh(III)}} \text{Cu(II)} \rightarrow 2\text{CH}_3\text{COR} \quad (1)
\]

In this system it has been proposed that an initiation step involving the ethanol reduction of Rh(III) to a Rh(I) catalyst is occurring.

On investigating reaction 1 we made a number of observations which could not be accounted for assuming the catalyst was a rhodium(I) complex. These include a marked enhancement of reaction rates and catalyst stability at greater chloride concentrations, and the observation of induction periods preceding the 1-hexene oxidations when using [Rh(CO)₂Cl]₂ as the catalyst precursor in the absence of Cu(II) (which are not observed using RhCl₃·3H₂O). As a result we chose to investigate the oxidation of [Rh(CO)₂Cl]₂ under conditions typical for the catalytic oxidation of 1-hexene, and found RhCl₃(H₂O)₂ to be formed stoichiometrically (reaction 2). As expected the RhCl₃(H₂O)₂ produced in reaction 2 was an active catalyst for reaction 1, and did not exhibit the induction period found when using [Rh(CO)₂Cl]₂. This, in addition to our ruling out the alcohol reduction of Rh(III) to Rh(I) as proposed earlier [1], indicates the active catalyst for this reaction is a rhodium(III) chloride.
On investigating reaction 2 in detail an unusual mechanism was discovered involving the in situ ethanol reduction of O₂ to HOOH, which subsequently coordinates to [Rh(CO)₂Cl]₂ forming a surprisingly stable hydroperoxorhodium intermediate (I). There are few examples in the literature of hydroperoxo or alkylperoxo complexes of the platinum metals [6-10] (other than those with bio-type or Schiff base ligands). The first evidence for the role of HOOH in reaction 2 was obtained from the rate law determined for this reaction (equation 3), which is independent of the concentration of [Rh(CO)₂Cl]₂. This rules out a mechanism involving as a first step the formation of a hydride complex resulting from the oxidative addition of HCl to [Rh(CO)₂Cl]₂, followed by a reaction with O₂, which has been proposed to occur in several other systems [10,11]. Indeed, equation 3 indicates an intermediate oxidant is being formed from the acid catalyzed reaction between ethanol and O₂ in the initial step(s) of reaction 2. This was confirmed by using aqueous HOOH to directly oxidize [Rh(CO)₂Cl]₂, producing RhCl₃(H₂O)₂ via the same intermediate I. The reduction of O₂ to HOOH by 1° and 2° alcohols has been known for a long time, producing HOOH using AIBN as an initiator [12] and H₂O in the presence of metal oxide catalysts [13] due to their efficient decomposition of HOOH. I has been characterized as H₂[Rh(CO)Cl₂(OOH)] by FT-IR, electronic absorption spectroscopy, and its chemical characteristics. For example, I seems to be capable of both oxidizing CO to CO₂ and 1-alkenes to 2-ketones, and exhibits decomposition characteristics expected for a hydroperoxide complex.

References

5. Ibid. 1975, 2440.


