The Specific Oxidation of [Rh(CO)$_2$Cl]$_2$ by O$_2$
Via the Coordination of in situ Generated HOOH.
Implications for the Rh(III)/Cu(II) Catalyzed O$_2$ Oxidation
of 1-Alkenes to 2-Ketones

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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, O$_2$ 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 O$_2$ oxidation of 1-alkenes to
2-ketones in ethanol with $\geq$ 98% specificity [1] (reaction 1).

$$2CH_2{=}CHR + O_2 \xrightarrow[Cu(II)]{Rh(III)} 2CH_3COR \qquad (1)$$

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)$_2$Cl]$_2$ as the catalyst precursor in
the absence of Cu(II) (which are not observed using RhCl$_3 \cdot$3H$_2$O).
As a result we chose to investigate the oxidation of [Rh(CO)$_2$Cl]$_2$
under conditions typical for the catalytic oxidation of 1-hexene,
and found RhCl$_3$(H$_2$O)$_2$ to be formed stoichiometrically (reaction 2).
As expected the RhCl$_3$(H$_2$O)$_2$ produced in reaction 2 was an active

$$[Rh(CO)_2Cl]_2 + 4HCl + 2O_2 + 2CH_3CH_2OH$$
$$\longrightarrow 2RhCl_3(H_2O)_2 + 4CO + 2CH_3CHO \qquad (2)$$
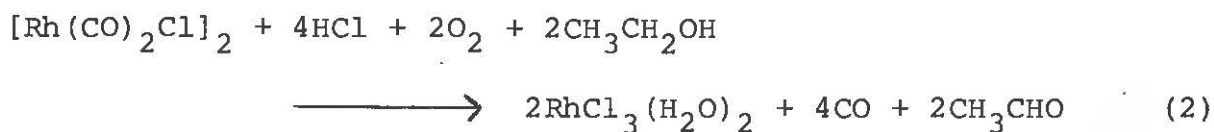
catalyst for reaction 1, and did not exhibit the induction period
found when using [Rh(CO)$_2$Cl]$_2$. This, in addition to our ruling out
the alcohol reduction of Rh(III) to Rh(I) as proposed earlier [1],
indicates the active catalyst for this reaction is a rhodium(III)
chloride.

On investigating reaction 2 in detail an unusual mechanism was discovered involving the in situ ethanol reduction of O_2 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

$$\frac{d[I]}{dt} = k[H^+][O_2] \tag{3}$$

step the formation of a hydride complex resulting from the oxidative addition of HCl to $[Rh(CO)_2Cl]_2$, followed by a reaction with O_2, 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 O_2 in the initial step(s) of reaction 2. This was confirmed by using aqueous HOOH to directly oxidize $[Rh(CO)_2Cl]_2$, producing $RhCl_3(H_2O)_2$ via the same intermediate I. The reduction of O_2 to HOOH by 1° and 2° alcohols has been known for a long time, producing HOOH using AIBN as an initiator [12] and H_2O in the presence of metal oxide catalysts [13] due to their efficient decomposition of HOOH. I has been characterized as $H_2[Rh(CO)Cl_2(OOH)]$ by FT-IR, electronic absorbtion spectroscopy, and its chemical characteristics. For example, I seems to be capable of both oxidizing CO to CO_2 and 1-alkenes to 2-ketones, and exhibits decomposition characteristics expected for a hydroperoxide complex.

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