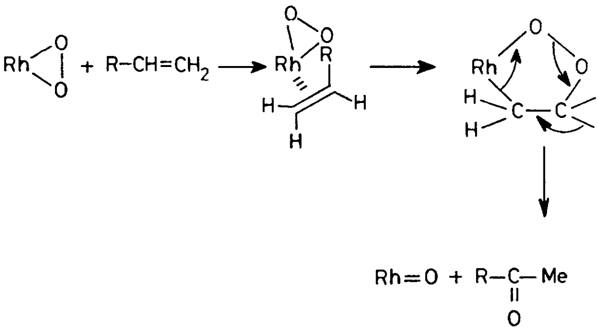
Activation and Transfer of Molecular Oxygen. Oxidation of Terminal Olefins to Methyl Ketones by Rhodium Dioxygen Complexes

By FRANÇOISE IGERSHEIM and HUBERT MIMOUN*
(*Oxidation Laboratory, Institut Français du Pétrole*, 92502 *Rueil-Malmaison, France*)

Summary Direct oxygen transfer from rhodium–dioxygen complexes to terminal olefins yields methyl ketones with high selectivity.

ALTHOUGH dioxygen–metal complexes can be considered as potential oxidising agents, there are still no examples in which direct transfer of oxygen from these complexes to olefins has been observed.[1] However, such a transfer may occur in the $[RhCl(PPh_3)_3]$ catalysed co-oxygenation of terminal olefins to methyl ketones and triphenylphosphine to triphenylphosphine oxide.[2] A study on the rhodium–copper catalysed oxidation of terminal olefins to methylketones[3] has led us to propose the path in reaction (1).

In order to confirm the validity of such a mechanism, we have studied the reactivity of $[Rh(AsPh_3)_4O_2]^+A^-$-$[A^- = ClO_4^-$ (Ia), PF_6^- (Ib)] towards terminal olefins.[4] At ambient temperature and under deoxygenated argon and anhydrous conditions, (Ia) reacted with excess of oct-1-ene in methylene chloride to give a mixture of octan-2-one and triphenylarsine oxide (TPAsO) in, respectively, 40 and 60% yields (based on rhodium) after 4 h.†

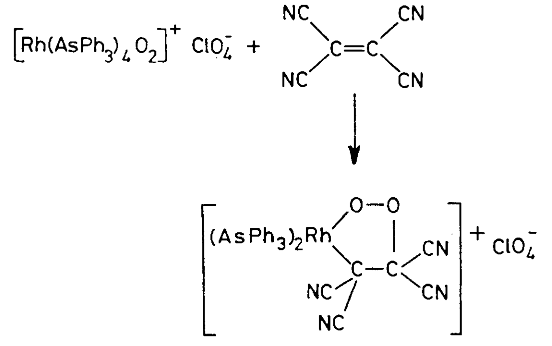


(1)

In the absence of a solvent, *i.e.*, under heterogeneous conditions, the major product was octan-2-one (85% yield) with only traces of TPAsO. Hexan-2-one and pentan-2-one were obtained, in similar yields and under the same conditions, from hex-1-ene and pent-1-ene, respectively. Internal olefins, such as cyclohexene and oct-2-ene were inactive. Octa-1,7-diene yielded only oct-1-en-7-one, suggesting that both oxygen atoms bound to the metal do not react simultaneously with two moles of olefins.

The i.r. spectrum of a 70% ^{18}O complex (Ib), labelled on both oxygen atoms,‡ which was prepared according to the method of Haines,[4] exhibited the characteristic isotopic shift at 840 cm^{-1} for the O–O stretching vibration (-50 cm^{-1}) and 510 cm^{-1} for the Rh–O stretching vibrations (-30 cm^{-1}).[5] Reaction of oct-1-ene with this ^{18}O labelled complex yielded 70% ^{18}O enriched octan-2-one, illustrating exclusive incorporation of co-ordinated oxygen into the ketone.

Further, reaction of (Ia) with tetracyanoethylene (TCNE) in methylene chloride, followed by addition of excess of diethyl ether, yielded a yellow complex which analysed as $[Rh(AsPh_3)_2O_2(TCNE)]ClO_4$ and which exhibited i.r. absorptions at 2150 and 2210 cm^{-1}, $\nu(C\equiv N)$, together with the disappearance of the rhodium–dioxygen vibrations. These i.r. characteristics are similar to those of the known equivalent peroxometallocyclic palladium complex $[(PPh_3)_2Pd(O_2\text{–}TCNE)]$.[6] This therefore suggests the formation of the cyclic peroxo complex (II), according to reaction (2).



(II) (2)

These results further support the scheme in reaction (1), which is similar in several aspects to the mechanism proposed by us for the epoxidation of olefins by peroxomolybdenum complexes.[7] Since the oxidation takes place in the presence of only the anhydrous dioxygen complex (Ia) or (Ib) and dry oct-1-ene, the possibility of a Wacker-type oxidation under these conditions seems rather improbable.[8]

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† Octan-2-one was estimated by g.l.c. analysis with *m*-xylene as internal calibrant; TPAsO was estimated from the intensity of the characteristic i.r. vibration at 1080 cm^{-1}.

‡ The amount of ^{18}O contained in the rhodium dioxygen complex (Ib) was determined by the relative intensities of the i.r. bands at 540 and 510 cm^{-1}, the shifted O–O stretching vibration appearing only as a shoulder in the PF_6 absorption at 840 cm^{-1}.

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