Oxygenation Studies. Part 7.† Catalytic Dioxygenation of Cyclo-octa-1,5-diene at a Rhodium Centre

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Studies on the oxygenation of cyclo-octa-1,5-diene by molecular oxygen using as catalysts $[RhCl(PPh_3)_3(O_2)]$ (**1**), and related dioxygen complexes in the presence of excess PPh_3 are reported. A regioselective homoco-oxygenation of the diene is found to occur with (**1**) to give cyclo-octane-1,4-dione, in competition with some homoco-oxygenation of PPh_3. ^{18}O-Labelling experiments establish that both oxygens in a molecule of (**1**) are transferred to a molecule of the diene and initial rate measurements indicate that the slow step in the catalytic cycle follows displacement of one phosphine ligand in (**1**) by the diene. An overall mechanistic cycle, involving a sequence of five-, seven-, and four-membered metallacyclic intermediates, is suggested.

The use of oxygen for the controlled oxygenation of organic substrates on a laboratory scale is limited to the few reactions of singlet oxygen,[1] even though triplet oxygen features as a common and versatile reagent in biological systems.[2] As part of a study on the oxygenating properties of dioxygen–rhodium species, the stability of $[RhCl(PPh_3)_3(O_2)]$ (**1**) in the presence of the three cyclo-octadienes was examined.[3] The detection of oxygenated products in the case of cyclo-octa-1,5-diene (cod) was of particular interest, because in related studies involving rhodium catalysts this substrate was reported to resist oxygenation[4] and to inhibit oxygenation of monoenes.[5,6] Under conditions similar to those which catalytically convert terminal alkenes and triphenylphosphine into methyl ketones and triphenylphosphine oxide,[7] slow catalytic oxygenation of cod was observed. This paper reports a detailed investigation into this reaction of (**1**) and of related complexes of rhodium and iridium.

Experimental

Microanalyses were carried out using a Carlo-Erba Elemental Analyser model 1102. Infrared spectra were recorded on a Perkin-Elmer 357 grating spectrometer. For mass spectra, samples were chromatographed on a Pye 104 instrument [7 ft (2.1 m),10% Apiezon L column] before being led directly into a Micromass 16 F instrument. N.m.r. spectra were determined with a JEOL PS/PFT machine. A Petric Instrumentation Gas Control Unit was used to maintain constant oxygen pressures and to monitor oxygen uptake.

Benzene was purified as previously described.[7] Cyclo-octa-1,5-diene, cyclo-octa-1,3-diene, and bicyclo[2.2.1]hepta-2,5-diene were purified by fractional distillation from $LiAlH_4$ under nitrogen and stored over $LiAlH_4$ under nitrogen at -10 °C in the dark. Triphenylphosphine was recrystallised from ethanol under nitrogen.

The complexes $[RhCl(PPh_3)_3]$,[8] $[Rh(SCN)(PPh_3)_3(O_2)]$,[9] $[\{RhCl(C_2H_4)\}_2]$,[10] $[\{RhCl(cod)\}_2]$,[11] $[RhCl(PPh_3)(cod)]$,[11] and $[IrCl(PPh_3)_3]$[12] were obtained by previously described procedures. Cyclo-oct-4-en-1-one was prepared by the method described by Crandall *et al.*[13] Cyclo-octane-1,4-dione and cyclo-octane-1,5-dione were synthesized from cyclo-octane-1,4-diol[14] and cyclo-octane-1,5-diol, following the procedure of Crandall *et al.*[13] For the synthesis of 1,2:5,6-diepoxycyclo-octane the method described by Cope *et al.*[15] was followed with minor variations.

$[^{18}O_2]$Oxygen, isotopic purity 99%, was supplied by Prochem.

† For Part 6 see ref. 9.

Chlorodioxygentris(triphenylphosphine)rhodium and Chloro-[$^{18}O_2$]dioxygentris(triphenylphosphine)rhodium.—A stirred solution of $[RhCl(PPh_3)_3]$ (0.52 g, 5.6×10^{-4} mol) and PPh_3 (0.752 g, 2.9×10^{-3} mol) in benzene (15 cm^3), prepared under nitrogen, was treated with a stream of oxygen for 5 min. Ethanol (10 cm^3) was added dropwise to the brown solution which, on concentration under reduced pressure to about half volume, yielded the dioxygen adduct (0.40 g, 4.2×10^{-4} mol), m.p. 113—115 °C (*in vacuo*) after drying under high vacuum (Found: C, 67.4; H, 4.4. $C_{54}H_{45}ClO_2P_3Rh$ requires C, 67.8; H, 4.7%); $\nu = 890$ cm^{-1} (O–O) (KBr).

The $^{18}O_2$ adduct was prepared on a similar scale using a closed system. The solution was stirred under an atmosphere of $^{18}O_2$ for 5 min and the product was isolated as dark brown microcrystals, m.p. 86.7 °C (*in vacuo*); $\nu = 845$ cm^{-1} (^{18}O–^{18}O) (KBr).

Chlorodioxygentris(triphenylarsine)rhodium.—A suspension of $[\{RhCl(C_2H_4)_2\}_2]$ (0.10 g, 2.6×10^{-4} mol) in methanol (15 cm^3) containing $AsPh_3$ (2.50 g, 2.3×10^{-3} mol) was refluxed under a nitrogen atmosphere for 1 h and then in air for 5 min. The brown product was filtered off, washed with diethyl ether, and dried to give the oxygen adduct (0.45 g, 4.13×10^{-4} mol) as a microcrystalline powder, m.p. 178 °C (*in vacuo*) (Found: C, 58.9; H, 4.1. $C_{54}H_{45}As_3ClO_2Rh$ requires C, 59.5; H, 4.2%); $\nu = 890$ cm^{-1} (O–O) (KBr).

Chlorodioxygentris(triphenylphosphine)iridium.—A solution of $[IrCl(PPh_3)_3]$ (0.34 g, 3.37×10^{-4} mol) and PPh_3 (0.54 g, 2.0×10^{-3} mol) in benzene (15 cm^3) was stirred in a stream of oxygen for 10 min at room temperature. Methanol (15 cm^3) was slowly added to the orange-yellow solution and on concentrating (*ca.* 15 cm^3) a pink precipitate was obtained which was filtered off, washed with methanol, and dried under high vacuum to give the oxygen adduct (0.325 g, 3.11×10^{-4} mol), m.p. 124—125 °C (*in vacuo*); $\nu = 852$ cm^{-1} (lit.,[16] 852 cm^{-1}) (O–O) (KBr); $\delta_P(C_6H_6$–$C_6D_6)$, 7.7 (1 P, t, $J_{PP} = 14.0$ Hz, $P_{eq.}$) and 19.0 (2 P, d, $J_{PP} = 14.7$ Hz, $P_{ax.}$).

Catalytic Oxygenation at Room Temperature (Typical Run).—Benzene (25 cm^3), dried ($LiAlH_4$) and degassed, was transferred on a vacuum line to a 50-cm^3 flat-bottomed reaction vessel fitted with a side-arm carrying a 'Suba-seal' septum (B 14) and containing $[RhCl(PPh_3)_3(O_2)]$ (20 mg, 2.11×10^{-5} mol), PPh_3 (0.20 g, 7.63×10^{-4} mol), durene (1,2,4,5-tetramethylbenzene) (internal standard) (3.3 mg, 2.46×10^{-5} mol), and a magnetic follower. When a solution had been obtained, oxygen was introduced into the reaction vessel which was then disconnected

from the vacuum line and sealed with a second 'Suba-seal' (B 19). The cyclo-octa-1,5-diene (0.175 g, 1.62×10^{-3} mol) was introduced through a larger septum and also more oxygen to *effect a small* positive pressure. Further small additions of oxygen were made during the course of the run. The stirred solution was held at 22 ± 1 °C throughout the period of the run.

Samples were withdrawn through the smaller septum at intervals for g.l.c. analysis [9 ft (2.7 m), 3% OV1 column, 110 °C].

Catalytic Oxygenation at 43 °C.—The above procedure was modified for work at 43 °C by introducing the diene into the reaction vessel before the benzene was added and suspending the catalyst in a 'teflon' cup above the solution until the temperature had stabilised. A positive pressure of oxygen (*ca.* 10^5 Pa) was maintained by a Petric Instrumentation Gas Control Unit which also monitored the oxygen uptake.

Catalytic Oxygenation using $^{16}O_2$ *and* $^{18}O_2$ *Mixtures.*—The evacuated reaction vessel containing a magnetic follower and a solution of $[RhCl(PPh_3)_3]$ (21 mg, 2.24×10^{-5} mol), PPh_3 (0.20 g, 7.66×10^{-4} mol), and hydroquinone (10 mg) in dried and degassed benzene (25 cm^3), prepared under anaerobic conditions, was connected to a gas burette system containing $^{16}O_2$ (41.7%), ^{16}O–^{18}O (0.6%), and $^{18}O_2$ (57.7%). The gas mixture, a little above atmospheric pressure, was introduced into the reaction vessel and degassed cyclo-octa-1,5-diene (0.352 g, 3.26×10^{-3} mol) was injected into the solution *via* a 'Suba-seal' capped side-arm. The sealed reaction vessel was stirred in a nitrogen atmosphere for 48 h during which time samples were removed by syringe for analysis.

Stoicheiometric Oxygenation at Room Temperature (*Typical Run*).—A solution of PPh_3 (0.20 g, 7.63×10^{-4} mol), cyclo-octa-1,5-diene (0.352 g, 3.26×10^{-3} mol), and durene (4 mg, 3.0×10^{-5} mol) in benzene (25 cm^3) was prepared under anaerobic conditions in the reaction vessel which also contained a magnetic follower and the catalyst, $[RhCl(PPh_3)_3(O_2)]$ (20 mg, 2.11×10^{-5} mol), supported above the solution in a 'Teflon' cup. The reaction vessel was filled with nitrogen and transferred to an 'Atmosbag' containing a nitrogen atmosphere. The catalyst was released into the solution which was stirred throughout the run. Samples for g.l.c. analyses were withdrawn through a 'Suba-seal' at intervals.

Stoicheiometric Oxygenation using $[RhCl(PPh_3)_3(^{16}O_2)]$ *and* $[RhCl(PPh_3)_3(^{18}O_2)]$.—Oxygenation was carried out in a sealed reaction vessel composed of two interconnected limbs, A and B.

$[RhCl(PPh_3)_3(^{16}O_2)]$ (9.9 mg, 1.07×10^{-5} mol), $[RhCl(PPh_3)_3(^{18}O_2)]$ (10.4 mg, 1.12×10^{-5} mol), and a magnetic follower were placed in limb A which was then sealed at the top. In limb B a solution of PPh_3 (0.20 g, 7.63×10^{-4} mol), cyclo-octa-1,5-diene (0.352 g, 3.26×10^{-3} mol), and hydroquinone (10 mg) in benzene (25 cm^3) was prepared under anaerobic conditions and frozen. The vessel was evacuated to $< 10^{-3}$ mmHg before the top of limb B was sealed. The solution was thawed, transferred *via* the interconnecting arm to the catalyst in A, and stirred at room temperature.

After 24 h the solution in A was frozen and concentrated (to *ca.* 5 cm^3) by subliming benzene back into B. The reaction vessel was transferred to a glove box and opened under an atmosphere of nitrogen. The residual solution in A was transferred to a flask which was sealed with a 'Suba-seal' stopper. Samples were immediately removed by syringe for analysis.

Estimation of Isotopic Abundances in Labelled Cyclo-octane-1,4-dione.—The relative abundances of the components of the molecular-ion signal were obtained by a weighted averaging of from 12 to 15 scans (3 s duration) over the *m/e* range 136—146, taken at regular intervals as the dione passed through the mass spectrometer from the g.l.c. column. The composition of the dione was estimated by an optimised fit for $^{16}O_2$, ^{16}O–^{18}O, and $^{18}O_2$ contributions using the relative abundances of the molecular-ion components in unlabelled cyclo-octane-1,4-dione as standard.

Results and Discussion

Cyclo-octane-1,4-dione, (**2**), was slowly produced when dry benzene solutions containing cod (1.6×10^{-2} mol l^{-1}) and PPh_3 (8×10^{-3} mol l^{-1}) were stirred under an atmosphere of oxygen at 22 °C in the presence of complex (**1**) (8×10^{-4} mol l^{-1}). The yield, which indicated that the reaction was catalytic, was not affected significantly when hydroquinone (3×10^{-3} mol l^{-1}) was present in solution. Small quantities of the monoketone, cyclo-oct-4-en-1-one, (**3**), were also formed. Similar results were obtained when air or oxygen was allowed to enter solutions of $[RhCl(PPh_3)_3]$, PPh_3, and cod that had been prepared under anaerobic conditions. The two ketonic products were identified by directly comparing their g.l.c. characteristics and their mass spectral fragmentation patterns with those of authentic specimens. No isomeric diketone, cyclo-octane-1,5-dione, could be detected and, in the absence of the rhodium complex, no oxygenation took place. Cyclo-octa-1,4-diene and bicyclo-[2.2.1]hepta-2,5-diene were not converted to diketones under the same conditions.

The important question of whether or not both oxygen atoms of a molecule of complex (**1**) were incorporated into ketonic groups could not be answered by simply measuring the diketone formed under strictly anaerobic conditions for the maximum yield did not exceed 46%. A 2.6% yield of the monoketone was also obtained. Although the remainder of the oxygen might have been lost in competing dimeric decay or phosphine co-oxygenation,[9] the participation of two linked heteroco-oxygenations, as implicated in equation (1), could not be ruled out.

$$2\,[RhCl(PPh_3)_3(O_2)] + C_8H_{12} + 2\,PPh_3 \longrightarrow 2\,[RhCl(PPh_3)_3] + C_8H_{12}O_2 + 2\,PPh_3O \quad (1)$$

(**2**)

Studies with $^{18}O_2$-labelled $[RhCl(PPh_3)_3(O_2)]$ provided an unequivocal answer to this question. When mixtures of the labelled and unlabelled complex were used under anaerobic conditions the measure of singly-labelled diketone from crossover reactions was below the 1% accuracy limit of the experiment. Under aerobic conditions, using $[RhCl(PPh_3)_3]$ as catalyst and an atmosphere of $^{16}O_2$ and $^{18}O_2$, the measure of singly-labelled diketone from crossover reactions was also very low (2.3%). Table 1 gives values for both studies. The measure of the relative abundance of the $[^{16}O_2]$diketone to $[^{18}O_2]$diketone in each experiment is approximately 16% higher than would be expected on the basis of the relative abundance in the substrates. This difference probably reflects isotopic discrimination in the mass spectral fragmentation of the diketone rather than kinetic isotope effects within the oxygenation process for, in the anaerobic cases, the relative rates of ketone formation should not be reflected in the product ratios.

The isotopic studies clearly demonstrate that both ketonic oxygens in each molecule of cyclo-octane-1,4-dione originate from one molecule of complex (**1**). The reaction is therefore one of homoco-oxygenation. As far as we are aware this is the first established homoco-oxygenation, stoicheiometric or catalytic, at two isolated olefinic centres in one molecule and probably constitutes the simplest example of olefin homoco-oxygenation. It also provides the first direct evidence for the attack by the

Table 1. The isotopic compositions (%) of cyclo-octane-1,4-dione obtained from anaerobic runs, (a) and (b), using $[RhCl(PPh_3)_3(O_2)]$, and an aerobic run, (c), using $[RhCl(PPh_3)_3]$ as catalyst

Isotopic composition	(a)		(b)		(c)	
	$[RhCl(PPh_3)_3(O_2)]$	Dione	$[RhCl(PPh_3)_3(O_2)]$	Dione	Dioxygen	Dione
$^{16}O_2$	48.8	52.5	49.8	53.0	41.7	43.9
$^{16}O,^{18}O$	0.5	1.4	0.5	1.3	0.6	2.9
$^{18}O_2$	50.7	46.1	49.7	45.7	57.7	53.2

Table 2. A summary of results obtained at various concentrations of PPh_3 and cod using $[RhCl(PPh_3)_3(O_2)]$ in benzene at 22 °C

				After 160 h		
Run	10^4[Catalyst]/mol l^{-1}	10^2[PPh_3]/mol l^{-1}	10^2[cod]/mol l^{-1}	[Monoketone]/[Catalyst]	[Diketone]/[Catalyst]	10^8 Initial rate/mol l^{-1} s^{-1}
1	8.340	0.761	1.631	0.049	2.122	2.06
2	8.532	0.761	3.261	0.0721	3.425	4.53
3	8.291	0.765	6.522	0.108	4.600	8.64
4	8.102	0.747	13.044	0.128	4.810	17.44
5	8.257	1.525	1.613	0.040	2.132	1.00
6	8.240	1.534	3.261	0.046	2.722	1.76
7	8.415	1.528	6.522	0.109	5.623	3.51
8	8.266	1.498	13.044	0.137	6.631	8.24
9	8.241	3.036	1.627	0.046	2.614	0.51
10	8.349	3.042	3.255	0.056	3.785	1.03
11	8.399	3.026	6.509	0.082	5.518	1.90
12	8.292	2.998	13.019	0.127	8.076	4.07

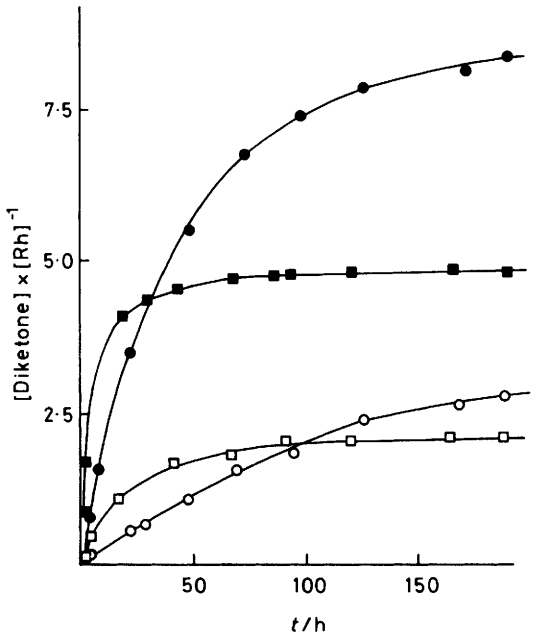


Figure 1. Diketone formation in benzene at 22 °C with $[RhCl(PPh_3)_3(O_2)] = 8.24 \times 10^{-4}$ mol l^{-1}, and $[PPh_3]$ and [cod] respectively $= 3.00 \times 10^{-2}$ and 1.30×10^{-1} mol l^{-1} (●), 0.75×10^{-2} and 1.30×10^{-1} mol l^{-1} (■), 3.04×10^{-2} and 1.63×10^{-2} mol l^{-1} (○), and 0.76×10^{-2} and 1.63×10^{-2} mol l^{-1} (□)

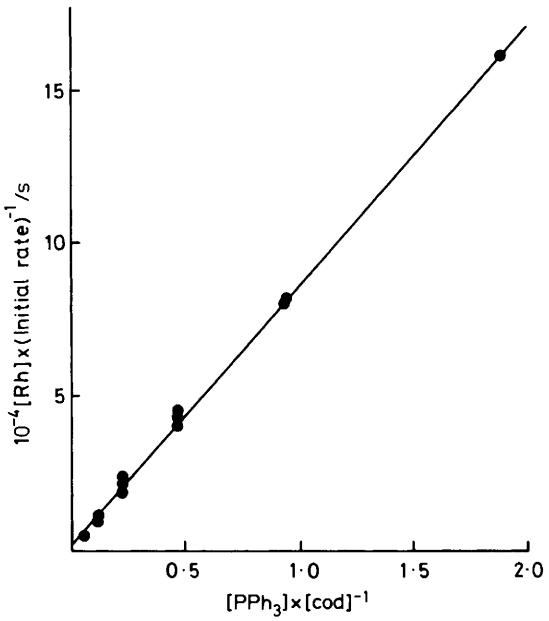


Figure 2. Plot of [Rh] × (initial rate)$^{-1}$ *versus* [PPh_3] × [cod]$^{-1}$

peroxide dioxygen of Group 8 metal complexes on the double bond of a cycloalkene.

Earlier studies with (1) and terminal olefins had shown that the extent of catalyst decay could be limited by changing the concentration of the phosphine and the alkene. Since catalyst decay was marked in this case also, the co-oxygenation was examined at different concentrations of diene and PPh_3. Table 2 summarises the findings and Figure 1 shows the profiles for diketone formation at the limits of the range of concentrations examined. The decrease in the initial rate of diketone formation with increase in [PPh_3] suggests that a pre-equilibrium, involving dissociation of PPh_3, is associated with the rate-controlling process, whilst the increase in rate with increase in diene indicates the direct involvement of the diene in the slow phase of the catalytic cycle. The reaction showed a linear dependence of [catalyst]/(initial rate) on [PPh_3]/[diene], as illustrated in Figure 2, which is in accord with the situations (i) and (ii) shown in Scheme 1.

(i) $[RhCl(PPh_3)_3(O_2)] \underset{\text{fast}}{\overset{K}{\rightleftharpoons}} [RhCl(PPh_3)_2(O_2)] + PPh_3$

$[RhCl(PPh_3)_2(O_2)] + cod \xrightarrow[\text{slow}]{k} [RhCl(PPh_3)_2(O_2)(cod)]$

(ii) $[RhCl(PPh_3)_3(O_2)] + cod \underset{\text{fast}}{\overset{K}{\rightleftharpoons}} [RhCl(PPh_3)_2(O_2)(cod)] + PPh_3$

$[RhCl(PPh_3)_2(O_2)(cod)] \xrightarrow[\text{slow}]{k}$ products

Scheme 1.

In the light of further evidence (see later), the situation (ii) in which the slow process follows the formation of the η^2-diene complex, appears the more likely. The corresponding rate law is given by equation (2) and the data lead to values of 1.14×10^{-5}

$$\frac{[\text{Catalyst}]}{\text{Initial rate}} = \frac{1}{k} + \frac{1}{kK} \cdot \frac{[PPh_3]}{[\text{Diene}]} \qquad (2)$$

s^{-1} for kK and $>1 \times 10^{-3}$ s^{-1} for k from which a value of $<1.2 \times 10^{-2}$ for the pre-equilibrium constant is obtained. It follows that this adverse pre-equilibrium makes a major contribution to the slowness of the observed reaction. The oxygenation is relatively fast once the alkene is co-ordinated to the metal centre.

It was not practicable to measure oxygen uptake for these reactions over the period required for substantial oxygenation at room temperature. However, this could be measured for runs at 43 °C. Significantly more oxygen was taken up than was required for diketone formation (see Figure 3) and it is assumed that, at least at this higher temperature, an approximately equal amount of PPh_3 homoco-oxygenation is also taking place. As is apparent from Figure 1, the more rapid co-oxygenation leads to a faster decay of catalyst. Four mol of diketone per mol of catalyst were produced in 4 h at 43 °C compared with 25 h at 22 °C. However, 94% decay of catalytic activity was observed in the former case compared with only 50% in the latter.

It is difficult to envisage a catalytic cycle for this reaction which does not involve at least one Rh^I complex. It was therefore of interest to examine the catalytic activities of the complexes $[\{RhCl(cod)\}_2]$ and $[RhCl(PPh_3)(cod)]$ which are potential components of the solution when (1) is used catalytically. These two complexes behaved in a virtually identical manner (see Figure 4). At room temperature the rate of diketone formation gradually increased over a 25-h period and after achieving a rate close to the initial rate for the corresponding $[RhCl(PPh_3)_3(O_2)]$ catalysed reaction, proceeded to follow a similar decay. In consequence, at 70 h, the diketone yield was 40% higher than that obtained with $[RhCl(PPh_3)_3(O_2)]$. Corresponding characteristics were observed over a shorter time scale at 43 °C. These findings are consistent with the slow displacement of the cod ligand from $[RhCl(PPh_3)(cod)]$ generating $[RhCl(PPh_3)_3]$ prior to the intervention of oxygen. It follows from the slow displacement of the diene ligand, that attack by oxygen on Rh^I intermediate(s) carrying phosphine ligands in the catalytic cycle is significantly faster than displacement of those ligands by cod. These findings also serve to underline an important general feature of the catalytic co-oxygenation of alkenes, namely, oxygen interaction with the rhodium(I) centre must precede alkene co-ordination.

The oxygenating abilities of two related complexes were compared with that of (1). The triphenylarsine analogue $[RhCl(AsPh_3)_3(O_2)]$, when used in conjunction with $AsPh_3$, produced 0.9 mol of the diketone and 0.03 mol of the monoketone per mol of catalyst in 1 h under aerobic conditions, but very little increase in either product could be detected over a longer period. Although the rate of diketone formation is relatively high, the extent to which rhodium is recycled under these conditions must be small for under strict anaerobic conditions the yield of diketone was only 10% lower. This lack of catalytic activity is attributed to the lower nucleophilic character of $AsPh_3$ compared to that of PPh_3. The diene successfully competes with $AsPh_3$ for Rh^I species and regeneration of the starting complex by oxidative addition of oxygen does not occur. The iridium analogue of (1), $[IrCl(PPh_3)_3(O_2)]$, also failed to show catalytic activity. No

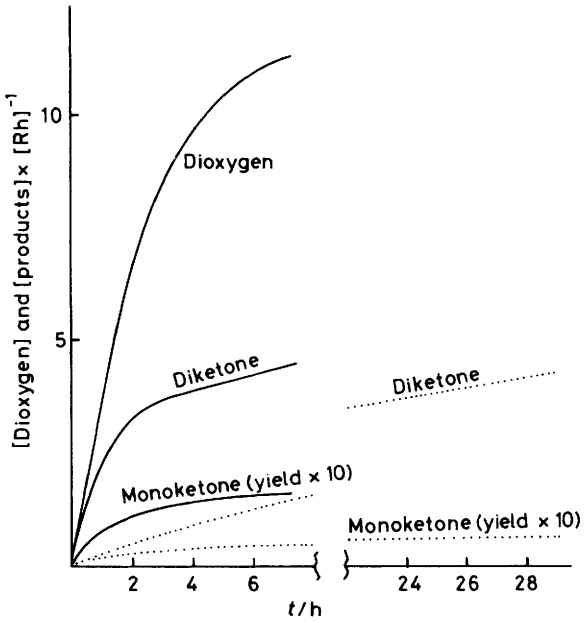


Figure 3. A comparison of the oxygenation of cod in benzene at 43 (—) and 22 °C (·····); $[RhCl(PPh_3)_3(O_2)] = 8.36 \times 10^{-4}$, $[PPh_3] = 3.05 \times 10^{-2}$, and $[cod] = 1.30 \times 10^{-1}$ mol l^{-1}

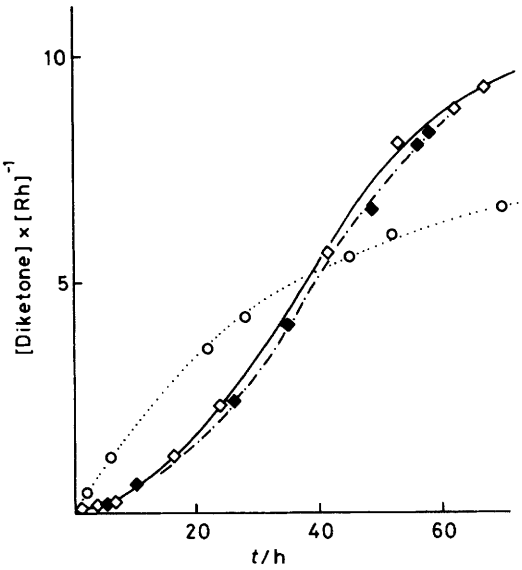
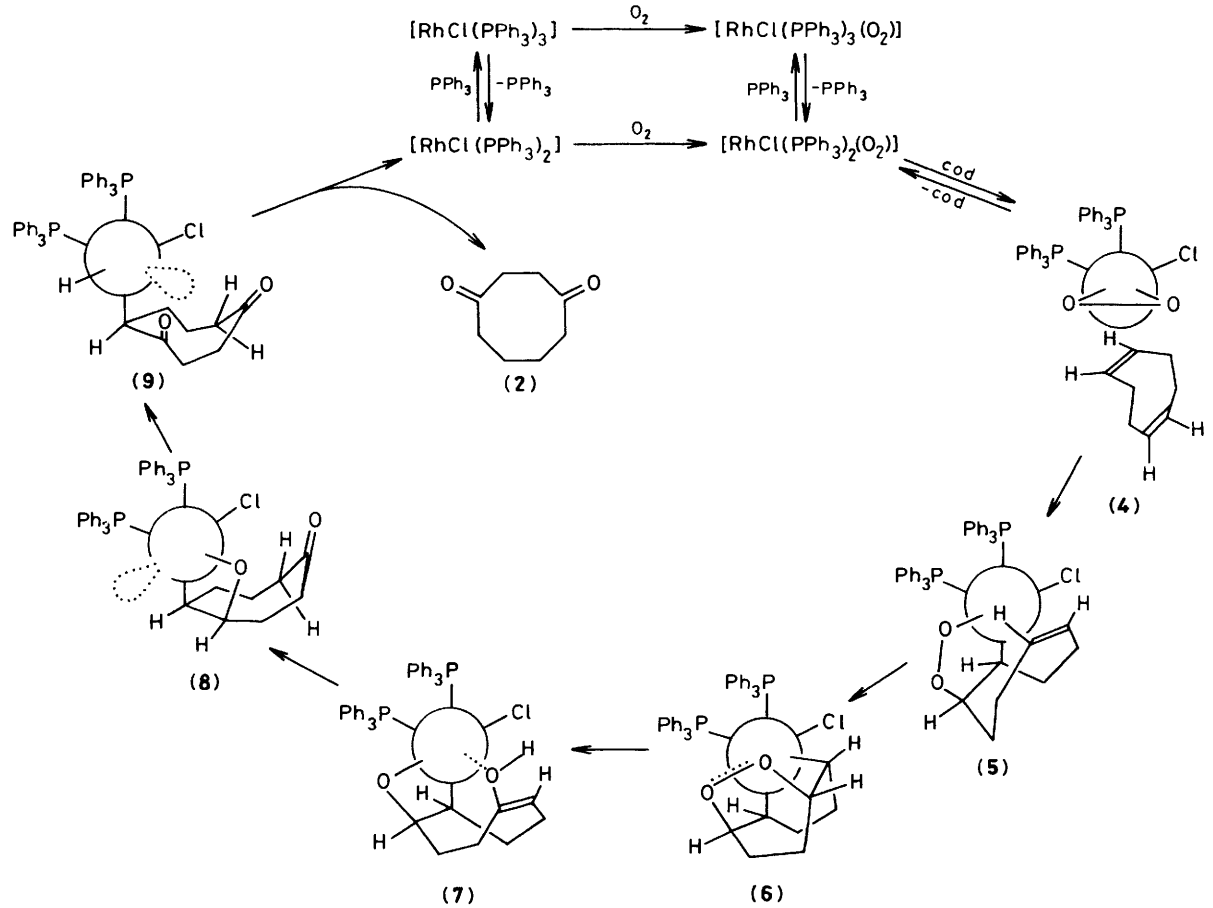


Figure 4. Diketone formation in benzene at 22 °C with $[RhCl(PPh_3)_3(O_2)] = 8.24 \times 10^{-4}$ (○), $[RhCl(PPh_3)(cod)] = 8.80 \times 10^{-4}$ (□), and $[\{RhCl(cod)\}_2] = 4.22 \times 10^{-4}$ mol l^{-1} (■); $[PPh_3] = 3.00 \times 10^{-2}$, and $[cod] = 1.30 \times 10^{-1}$ mol l^{-1}



Scheme 2. Suggested catalytic pathway for the conversion of cod into cyclo-octane-1,4-dione. For clarity only hydrogens which were vinylic in the substrate are shown

diketone could be detected but 0.48 mol of monoketone per mol of catalyst was obtained in 20 h under both anaerobic and aerobic conditions. It seems probable that catalytic activity is absent in this case because the relatively slow attack by oxygen on Ir^{I} phosphine complexes generated in the reaction allows capture by cod to form inert products.

In the case of $[RhCl(PPh_3)_3(O_2)]$ the possibility that the diketone was formed by rapid oxygenation of the free monoketone was discounted when the latter was found to oxygenate 30 times more slowly than the 1,5-diene in the presence of this complex. However, only 1,4-diketone was formed, no 1,5-isomer was obtained, and consideration must be given to the monoketone being a transient intermediate at the metal centre. Superficially the higher relative yield of monoketone at 43 °C (Figure 3) compared to that at room temperature supports this view. However, closer examination of the monoketone production at the lower temperature shows that this does not parallel the diketone production, which would be expected if the monoketone was on the direct pathway to the diketone. *cis,cis*-1,2:5,6-Diepoxycyclo-octane was completely inert under the reaction conditions.

In a previous paper in this series we drew attention to effects which were consistent with the formation of at least two isomeric alkene complexes in the initial stages of oct-1-ene and PPh_3 co-oxygenation.[9] Also in the monoene oxygenation we observed the rapid formation of a small amount of heptanal in the initial stage but under some conditions hardly any of this compound was produced over the remaining period of catalytic activity,[7] a situation very similar to that which we now report for the cyclo-oct-4-en-1-one formation but on a much shorter time-scale. These findings may point to a common feature in the early phase of both these oxygenations. If the cycloalkene adds to a five-co-ordinate intermediate, $[RhX(PPh_3)_2(O_2)]$, to give more than one of the four possible geometric isomers, and if subsequent modification is slow, the immediate concentrations of these species will be kinetically controlled. However, as steady-state conditions develop, partial, if not full, thermodynamic control of the concentrations of each isomeric complex could provide a relative concentration distribution which is markedly different from that initially obtained. We suggest that the initial bursts of monoketone and aldehyde production in the two systems originate from the reactions of alkene complexes initially present in relatively high concentrations, whereas the catalytic pathways associated with the formation of cyclo-octane-1,4-dione and octan-2-one involve alkene complexes whose relative dominance is established thermodynamically. In the diene case it should be noted that the observed rate of monoketone formation never exceeds 10% of that of diketone formation. Therefore it will not significantly distort the data on which the initial rate measurements and subsequent estimates of K and k are based. Equilibria involving more than one alkene complex will however lead to a low value for k, as the concentration of the reacting species will only be a fraction of the total concentration of alkene complexes.

The slow step, following co-ordination of one olefinic centre of the diene, may be either the dissociation of a further phosphine ligand from the rhodium complex or intramolecular attack by the peroxidic ligand. The value for kK, obtained from the kinetic data, is remarkably close to that found for the co-oxygenation of cyclo-octene under analogous conditions.[17] It

therefore seems likely that this step is oxygenative attack on the η^2-cod complex (**4**) as shown in Scheme 2. A stereospecific reaction leading to intermediate (**5**) is envisaged in which there is (*i*) formation of the five-membered peroxymetallacycle, often proposed but yet to be detected in this class of oxygenation, and (*ii*) the rapid intramolecular co-ordination of the second olefinic moiety to the site vacated by the attacking oxygen. The newly co-ordinated alkene moiety is now positioned for nucleophilic attack by the adjacent peroxidic oxygen and such an attack would lead directly to the species (**6**). Models show that the seven-membered metallacycle, so obtained, can readily adopt a conformation which allows an oxygen in the new dialkyl peroxide bridge to remain co-ordinated to the rhodium centre. As with protonated alkyl hydroperoxides,[18] (**6**) is expected to decompose readily by facile hydride migration from the oxygenated centre to give (**7**), which contains a co-ordinated transoid enol and a four-membered oxametallacycle. Related metallacycles have been considered by Milstein and Calabrese[19] as intermediates in the catalytic isomerisation of epoxides by rhodium and iridium complexes and Lenarda *et al.*[20] have prepared stable analogues from low-valent Group 8 complexes and tetracyanoethylene oxide. Collapse of the enol in (**7**) followed by isomerisation leads to intermediate (**8**), which might be expected to break down by a β-hydride shift to give (**9**). Subsequent reductive elimination to release the diketone regenerates a Rh^I species within the catalytic cycle.

We have recently proposed the generation of an oxametallacyclic intermediate, similar to (**7**), to account for the formation of an allylic alcoholic function instead of a ketone group in the related co-oxygenation of cyclo-octene and PPh_3.[17] We suggest that the difference in the reaction reported in this paper is that association of the enol with the co-ordination site, made available by breakdown of the peroxymetallacycle (**6**), prevents the participation of that site in a β-hydride shift of the type proposed in the cyclo-octene case.

It is of interest that a similar oxametallacycle to that proposed above is regarded by Collman[21] as a probable intermediate in the catalytic conversion of alkenes to epoxides by manganese porphyrins when hypochlorite is the oxidant. Evidence for the generation of an intermediate species not involved in the rate-determining step is not easily acquired. The speculative nature of the proposed catalytic cycle must therefore be emphasised. However the basic components appear able to accommodate not only the findings reported here but also many of the results obtained in related co-oxygenations in aprotic solvents. Strict stereochemical requirements for co-oxygenation are implicit in this scheme and this aspect of these reactions will be a focal point of further work.

Co-oxygenation in protic solvents[6,22] probably follows a distinctly different course. Certainly the regioselectivity of the cod homoco-oxygenation and the results of the ^{18}O-labelling studies would appear to exclude, in this case, the mechanism forwarded by Mimoun *et al.*[6] for the homoco-oxygenation of terminal alkenes in protic media.

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