

## Catalytic Di-oxygenation of Cyclo-octa-1,5-diene at a Rhodium Centre

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Cyclo-octa-1,5-diene is di-oxygenated by  $\text{RhCl}(\text{Ph}_3\text{P})_3\text{O}_2$  at room temperature in a regioselective reaction leading to cyclo-octane-1,4-dione; the reaction is catalytic under aerobic conditions.

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It is clearly established that dioxygen rhodium(III) species, such as  $\text{RhCl}(\text{Ph}_3\text{P})_3\text{O}_2$  (**1**) which is readily derived from

$\text{RhCl}(\text{Ph}_3\text{P})_3$  (**2**), can catalyse the oxygenation of alkenes under a range of aerobic conditions.<sup>1-3</sup> However, the  $\text{RhCl}_3\text{-Cu-}$

(ClO<sub>4</sub>)<sub>2</sub> system described by Mimoun,<sup>2</sup> which efficiently converts terminal alkenes into methyl ketones without rapid decay of the catalytic species, represents the only synthetically useful method known at present. Our attempts to understand more fully, and thereby more readily control, these potentially valuable reactions have led to experiments in which we were surprised to find that cyclo-octa-1,5-diene (1,5-cod) can be regioselectively di-oxygenated by molecular oxygen in the presence of (1) or (2).

Cyclo-octane-1,4-dione (3) was slowly produced when dry benzene solutions containing 1,5-cod and Ph<sub>3</sub>P were stirred under an atmosphere of oxygen at 22 °C in the presence of catalytic amounts of (1) or (2) (see Figure 1). A small amount† of the monoketone, cyclo-oct-4-en-1-one (4), was also formed but no cyclo-octane-1,5-dione. The isomeric 1,3-cod was not converted into the diketone under these conditions but the monoketone (4) was oxidised to (3). The rate of this further oxygenation of the monoketone was 30 times slower than the rate of oxidation of 1,5-cod and it follows, in the latter case, that the free monoketone is not an intermediate in the formation of (3). As has been shown for related oxygenations of terminal alkenes,<sup>4</sup> slightly less than 0.5 mol of ketonic product were produced per mol of (1) under anaerobic (non-catalytic) conditions (Figure 1). The competing processes responsible for this low yield appear also to be associated with the decay of the catalyst under aerobic conditions.

When mixtures of <sup>16</sup>O<sub>2</sub> and <sup>18</sup>O<sub>2</sub> (isotopic purity 99%) were used for aerobic oxygenation or when mixtures of RhCl(Ph<sub>3</sub>P)<sub>3</sub>(<sup>16</sup>O<sub>2</sub>) and RhCl(Ph<sub>3</sub>P)<sub>3</sub>(<sup>18</sup>O<sub>2</sub>) were used under anaerobic conditions, [<sup>16</sup>O<sub>1</sub><sup>18</sup>O<sub>1</sub>]cyclo-octane-1,4-dione accounted for less than 2.4% of the diketone produced.‡ Thus it is clear that one molecule of (1) transfers both oxygens to one molecule of 1,5-cod.

As far as we are aware this is the first example of homo-co-oxygenation, stoichiometric or catalysed, at two isolated olefinic centres in one molecule and the first direct evidence for the attack by the peroxide dioxygen of a Group 8B transition metal complex on the double bond of a cycloalkene.

For the catalytic formation of (3), a good linear relationship was found between initial rate/[Rh]<sub>tot</sub> and [1,5-cod]/[Ph<sub>3</sub>P] over the range of concentrations examined. This is consistent with the slow step being the initial co-ordination of 1,5-cod to a vacant site created on complex (1) by dissociation of a phosphine ligand, as shown in Scheme 1. The data led to  $k_1 > 10^{-3} \text{ s}^{-1}$  and  $k_1 k_2 / k_{-1} = 1.2 \times 10^{-5} \text{ s}^{-1}$ . In the absence of cod and at lower [Ph<sub>3</sub>P], there is no evidence (<sup>31</sup>P-n.m.r.) for significant quantities of the dissociated species. Thus  $k_1/k_{-1} < 5 \times 10^{-4} \text{ M}$  ( $k_{-1} > 2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) and  $k_2 > 2.4 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Catalyst decay appears not to compete directly with the slow stage of the reaction. An increase in the rate of decay with the

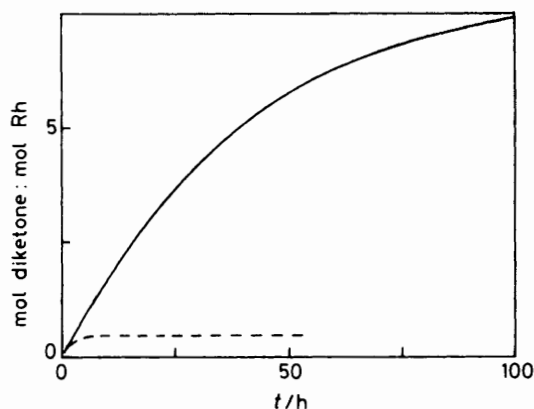
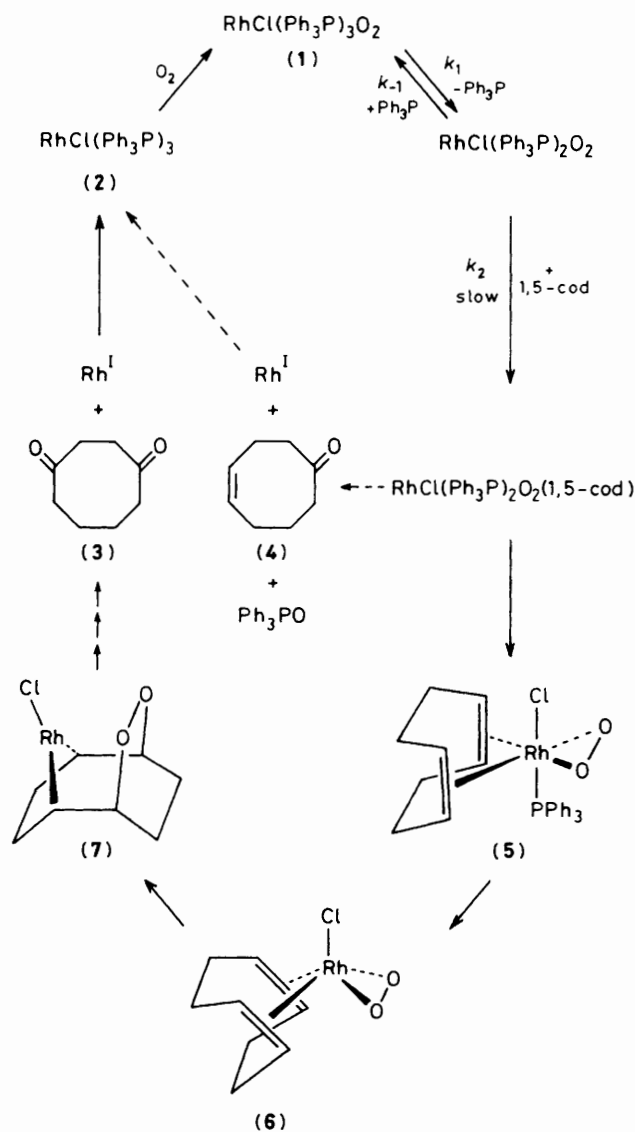


Figure 1. Cyclo-octane-1,4-dione formation at 22.0 °C in benzene containing 1,5-cod ( $1.28 \times 10^{-1} \text{ M}$ ) and Ph<sub>3</sub>P ( $3.0 \times 10^{-2} \text{ M}$ ). For aerobic conditions (—) the partial pressure of O<sub>2</sub> =  $9 \times 10^4 \text{ N m}^{-2}$ , [RhCl(Ph<sub>3</sub>P)<sub>3</sub>] =  $8.3 \times 10^{-4} \text{ M}$ . For anaerobic conditions (---) [RhCl(Ph<sub>3</sub>P)<sub>3</sub>O<sub>2</sub>] =  $8.5 \times 10^{-4} \text{ M}$ .



Scheme 1

† Approximately 0.03 mol of (4) per mol of catalyst were produced within the first hour of oxygenation. Further formation of the monoketone was slow. Under the conditions given in Figure 1, the yield after 80 h was 0.11 mol per mol of catalyst (*i.e.* 1.6% of the diketone yield). At higher temperatures the proportion of monoketone formed was significantly higher.

‡ An atmosphere containing 40% of <sup>16</sup>O<sub>2</sub> and 60% of <sup>18</sup>O<sub>2</sub> gave (3) with composition 44.1% [<sup>16</sup>O<sub>2</sub>]cyclo-octane-1,4-dione and 53.4% [<sup>18</sup>O<sub>2</sub>]cyclo-octane-1,4-dione based on quantitative measurements of the molecular ion. The corresponding composition was 53.0% and 46.1% when, under anaerobic conditions, 48.8% RhCl(Ph<sub>3</sub>P)<sub>3</sub>(<sup>16</sup>O<sub>2</sub>) and 51.2% RhCl(Ph<sub>3</sub>P)<sub>3</sub>(<sup>18</sup>O<sub>2</sub>) was used. In both cases the measured yield of unlabelled, relative to labelled, diketone was proportionally 18% higher. However, since in the anaerobic case, relative rates of ketone formation are not involved, this difference appears to reflect isotopic discrimination in the mass spectral fragmentation of the diketone rather than in any stage of the oxygenation process.

increase in the rate of catalytic oxygenation is observed indicating that it is an alkene complex or derivative which participates in the decay process.

Under analogous conditions to those used for these experiments, terminal alkenes undergo rapid hetero-co-oxygenation to give methyl ketone and  $\text{Ph}_3\text{PO}$ .<sup>1</sup> In this reaction hetero-co-oxygenation, which presumably is involved in the formation of (4), is minimal and we assume that when one alkene group of the 1,5-cod molecule has co-ordinated to the complex, a second phosphine is quickly displaced to give the intermediate (5). However, the manner in which the C–O bonds are formed from such a complex is not obvious. Holland and Milner<sup>5</sup> have suggested direct insertion into the allylic C–H bond, rather than attack at an olefinic centre followed by double bond migration, for the oxygenation of cyclo-octene to cyclo-oct-1-en-3-ol in the presence of  $\text{RhCl}(\text{Ph}_3\text{P})_3$ . Mimoun<sup>2</sup> favours Wacker-type oxygenation of cyclic alkenes to ketones in the  $\text{RhCl}_3\text{--Cu}(\text{ClO}_4)_2$  catalytic system, whilst the important observation by James,<sup>8</sup> that oxygenation of co-ordinated 1,5-cod to give cyclo-oct-4-en-1-one takes place at a hydroperoxide iridium centre, appears to be interpreted in terms of the mechanism proposed by Mimoun<sup>7</sup> to account for the conversion of alkenes into ketones by  $\text{H}_2\text{O}_2$  at a Pd catalyst. Unfortunately, the co-oxygenation reported here is not readily accommodated by any of these propositions. Without supporting evidence, we are reluctant to add to the speculation on this key question in co-oxygenation, but note that loss of the remaining phosphine from (5) could lead to a square based pyramidal intermediate (6) in which the peroxide oxygens are positioned for insertion into the co-ordinated alkene bonds to

give (7), in a reaction analogous to that recently reported by Mawby<sup>8</sup> for co-ordinated electron deficient alkenes. Whilst not being exclusive in these respects, the formation of (7) from (6) would (i) entail the generation of both C–O bonds by the same mechanism, (ii) account for the high degree of regioselectivity, and (iii) avoid the steric restraints imposed by the eight-membered carbocycle which present difficulties for any putative mechanism involving peroxymetallo-cycles.

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