Oxygenation Studies. Part 2.[1] Rhodium(I)-catalysed Autoxidation of Oct-1-ene at Ambient Temperature and Pressure

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Oct-1-ene and triphenylphosphine in benzene solutions are catalytically oxygenated to octan-2-one and triphenylphosphine oxide by dioxygen at ambient temperature and pressure in the presence of the complex $[RhCl(PPh_3)_3]$ (1). Minor quantities of heptanal and other products are also formed. The rate of the reaction is sensitive to the triphenylphosphine concentration and the ratio of the yields of the two principal products is sensitive to trace amounts of acid. An initial process giving 0.5 mol of octan-2-one per mol of catalyst precedes the catalytic reaction. Radical-chain processes have not been detected. The generation of a transient dioxetan at the metal centre is suggested to account for the formation of octan-2-one and heptanal.

We have shown that chlorotris(triphenylphosphine)-rhodium(I) (1), in benzene at ambient temperature and pressure, and, significantly, in the presence of radical-chain inhibitors, will promote oxygenation of terminal olefins to give the corresponding methyl ketones in yields of up to 80% based on the complex.[1] This paper reports the catalytic oxygenation of oct-1-ene with dioxygen under these conditions when excess of PPh_3 is present and describes the general features of this process, which gives octan-2-one as the major organic product.

EXPERIMENTAL

Materials.—Benzene (Hopkins and Williams, AnalaR) was heated under reflux with chromic acid solution for 10 h, washed with aqueous sodium hydroxide, sodium hydrogensulphite solution, and water, and dried over anhydrous sodium sulphate. It was subsequently distilled from sodium wire and fractionally redistilled from lithium tetrahydridoaluminate. Oct-1-ene (Koch–Light, pure grade) was fractionally distilled from $Li[AlH_4]$ and stored over this reagent in the dark. The complex $[RhCl(PPh_3)_3]$ (1) was prepared by the method described by Wilkinson and his co-workers.[2] Triphenylphosphine (Fisons) was recrystallised from ethanol under dinitrogen before use (m.p. 79—80 °C). Quinol (B.D.H., AnalaR) and 4-methyl-2,6-di-t-butylphenol (B.D.H.) were used without further purification.

Apparatus and Procedure.—The reaction vessel was a flat-bottomed straight-sided glass flask which carried a side arm capped by a 'suba-seal' and was connected to a vacuum line. Benzene and benzene–oct-1-ene mixtures (25 cm^3) were thoroughly degassed in a separate vessel on the vacuum line, using a freeze–thaw method, before being distilled *in vacuo* from fresh $Li[AlH_4]$ on to complex (1), PPh_3, and, when appropriate, radical inhibitor in the reaction vessel. The reaction vessel was surrounded by a water-bath maintained at ambient temperature (21—24 °C). The solution, which was equilibrated for 15 min before the reaction was started, was screened from light and was stirred by a Teflon-covered follower. Dioxygen was allowed into the vessel at atmospheric pressure and its uptake in the reaction was followed using a sensitive gas-burette system connected to the vacuum line. The observed uptake was corrected for dioxygen dissolved in the solution by subtracting the uptake measured in a blank run.

Estimation of Organic Products.—Octan-2-one and minor organic products were estimated by removing aliquot portions (2 µl) of solution through the side arm of the reaction vessel and injecting directly onto either 10% polyethylene glycol adipate (9 ft) or 10% dinonyl phthalate (5 ft) columns (diam., 0.25 in) fitted to a Pye series 104 chromatograph operating at 100 °C. An internal calibrant, usually hexan-2-one, was added to the reaction solution towards the end of each run. For extended studies on octan-2-one formation, the reaction vessel was disconnected from the vacuum line after 21 h and the solution, containing calibrant, was set aside in a sealed vessel under dioxygen in the dark.

Preparation of Carbon-14-labelled Triphenylphosphine Oxide (carried out by M. Mitchell).—Chlorodiphenylphosphine (14.05 g) in diethyl ether (10 cm^3) was slowly added to a stirred solution (40 cm^3) of the Grignard reagent formed from ^{14}C-labelled bromobenzene (10 g, activity 1.63 mCi mol^{-1}) and magnesium (1.56 g). The solution was heated under reflux under nitrogen for 2 h before being worked up with water to give ^{14}C-labelled triphenylphosphine (10 g). The product (4.16 g), in carbon tetrachloride (30 cm^3), was oxidised with dinitrogen tetraoxide [3] in carbon tetrachloride at −5 °C to give ^{14}C-labelled triphenylphosphine oxide (2.46 g) which was crystallised from chloroform–light petroleum to a constant activity of 1.60 mCi mol^{-1} (m.p. 154—156.5 °C).

Estimation of Triphenylphosphine Oxide.—In a typical procedure an oxidation involving (1) (2.12×10^{-5} mol), oct-1-ene (7.56×10^{-2} mol), and PPh_3 (1.13×10^{-3} mol) was interrupted after 3.25 h when 26.29×10^{-5} mol of dioxygen had been taken up and 6.95×10^{-5} mol of octan-2-one and 0.51×10^{-5} mol of heptanal had been formed. Carbon-14-labelled-triphenylphosphine oxide (18.6 mg, activity 1.60 mCi mol^{-1}) was added to the solution which was stirred for a few minutes, to ensure complete dissolution, before the solution was evaporated to dryness under reduced pressure. Triphenylphosphine oxide was separated from the catalyst residues by preparative high-pressure liquid chromatography in methanol–water (1 : 1) using a Corasil C_{18} column, and crystallised to a constant activity of 0.213 mCi mol^{-1}, which corresponds to the formation of 121 mg (43.52×10^{-5} mol) of Ph_3PO.

RESULTS AND DISCUSSION

On introducing dioxygen, the initial orange colour of the rhodium(I) solutions used in this study immediately changed to a rich yellow which slowly faded over a period of several hours. No precipitates were formed

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[1] Part 1, C. W. Dudley, G. Read, and P. J. C. Walker, *J.C.S. Dalton*, 1974, 1926.

[2] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. (A)*, 1966, 1711.

[3] J. P. Cox and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1958, **80**, 5441.

in any of the solutions, all of which contained rhodium in the concentration range 7.6×10^{-4}—9.0×10^{-4} mol dm^{-3}.

The results of a typical run are given in Figure 1, which shows the variation of the oxygen uptake and the yield of octan-2-one with time. The rate of oxygen uptake and the rate of ketone formation both decreased fairly rapidly over the first 4 h, but it is apparent that ketone continued to be slowly formed for many days. As expected, such solutions showed no ketone formation in the absence of complex (1). From the oxygen uptake and ketone yields it is clear that the rhodium has a catalytic role and a series of studies was made to determine the importance of various parameters and to gain further insight into the processes involved.

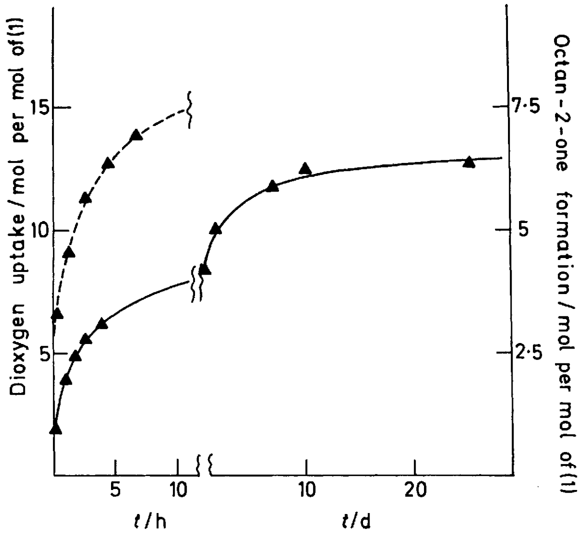

FIGURE 1 Octan-2-one formation (——) and dioxygen uptake (— — —) for [(1)] = 8.8×10^{-4}, [oct-1-ene] = 1.92, and [PPh_3] = 2.9×10^{-2} mol dm^{-3}

When analogous runs were carried out in the presence of 4-methyl-2,6-di-t-butylphenol (3.1×10^{-2} mol dm^{-3}) no changes were observed in the profiles for the oxygen uptake or the ketone formation. Saturation of solutions containing low concentrations of oct-1-ene (0.1 mol dm^{-3}) with quinol also had no effect on the catalytic behaviour, although at higher concentrations of oct-1-ene (1.9 mol dm^{-3}) a 25% reduction in activity was observed. We therefore discount the possibility of the main process being associated with radical-chain reactions similar to those which have been shown to be responsible for the oxygenation of several organic substrates in the presence of rhodium(I) complexes.[4] We also exclude Wacker-type oxygenation processes[5] since there was a small reduction in the ketone yield and correspondingly less dioxygen was taken up when trace amounts of water were intentionally introduced into the system.

The octan-2-one formed in the reaction clearly only accounts for part of the dioxygen uptake. A second major product was found to be Ph_3PO, and in several cases a quantitative measure of the yield of this material was made by dilution analysis using ^{14}C-labelled Ph_3PO. The yields of heptanal, a minor product of the reaction, and compound (A), a second minor product isomeric with octan-2-one on the basis of mass spectral evidence, were estimated by g.l.c. analysis. The total yields of oxygenated products corresponded closely to the total oxygen uptakes.

The profiles of both the dioxygen uptake and the ketone formation were essentially unaffected by reducing the partial pressure of the dioxygen from 760 to 100 mmHg, and variation of the oct-1-ene concentration from 3.8 to 0.02 mol dm^{-3} led to only minor variations in the profiles provided that the ratio [olefin] : [PPh_3] remained above 1.5 : 1. However, the rates of both the oxygen uptake and the ketone formation were markedly affected by the PPh_3 concentration (see Figure 2). Increasing [PPh_3] from 0.01 to 0.25 mol dm^{-3} led to increased rates of oxygen uptake and ketone formation but these were clearly not proportional to [PPh_3]. The results suggest that the rate-determining step is preceded by an equilibrium involving PPh_3; however, the kinetic information that can be obtained from these runs is restricted, for early oxygen uptake rates at high [PPh_3] were limited by the rate of diffusion of oxygen into the solution and in each case the decrease in the rates of

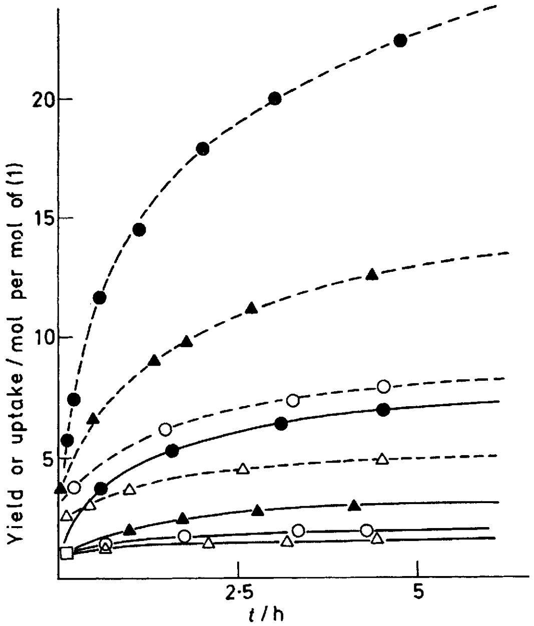

FIGURE 2 Octan-2-one formation (——) and dioxygen uptake (— — —) for [(1)] = 8.8×10^{-4}, [oct-1-ene] = 1.92, and [PPh_3] = 3.3×10^{-3} (△), 9.5×10^{-3} (○), 2.9×10^{-2} (▲), and 2.5×10^{-1} mol dm^{-3} (●)

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[4] V. P. Kurkov, J. Z. Pasky, and J. B. Lavigne, *J. Amer. Chem. Soc.*, 1968, **90**, 4743; J. E. Baldwin and J. C. Swallow, *Angew. Chem. Internat. Edn.*, 1969, **8**, 601; J. Blum, J. Y. Becker, H. Rosenman, and E. D. Bergmann, *J. Chem. Soc.* (*B*), 1969, 1000; L. W. Fine, M. Grayson, and V. H. Suggs, *J. Organometallic Chem.*, 1970, **22**, 219; J. E. Lyons and J. O. Turner, *Tetrahedron Letters*, 1972, 2903; *J. Org. Chem.*, 1972, **37**, 2881; D. R. Paulson, R. Ullman, R. B. Sloane, and G. H. Closs, *J.C.S. Chem. Comm.*, 1974, 186.

[5] P. M. Henry, *J. Amer. Chem. Soc.*, 1972, **94**, 4437 and refs. therein.

oxygen uptake and ketone formation reflect both a decay in the catalytic species and a decrease in [PPh_3].

The studies at lower [PPh_3], which are exemplified by Figure 2, revealed a second feature of these reactions: a rapid initial phase which produces a little less than 1 mol of ketone per mol of catalyst in the first few minutes, regardless of the rates of the subsequent catalytic process. In a further investigation of this phase, dioxygen was allowed to react with complex (1) in the absence of oct-1-ene. A stable yellow solution formed which was degassed twice before dinitrogen-purged oct-1-ene was injected into it, causing the colour to revert rapidly to orange. The reaction produced 0.5 mol of octan-2-one and 0.08 mol of heptanal per mol of the complex within the first minute. No more ketone or aldehyde was produced until normal catalytic behaviour was established by reintroducing dioxygen into the solution. Only 1.1 mol of dioxygen per mol of complex (1) are taken up by such solutions in the absence of terminal olefin.[1] Thus, for the initial phase, the yield of organic product in terms of the oxygen consumed (C : O ratio *) was greater than 0.5 : 1 which is significantly higher than the value of 0.32 : 1 estimated for the catalytic phase. It is also apparent, from the product analysis at the early stages of a large number of runs, that no compound (A) is formed in the initial phase. Therefore, the metal complex species involved in this phase are considered to differ from those involved in the catalytic phase. The initial phase is believed to be associated with all the runs, although it cannot be observed when early rates in the catalytic phase are also fast. For the remainder of this discussion the initial phase is arbitrarily considered to be complete at $t = 5$ min and the oxygen uptake and product yields at this time are subtracted from later values in order to evaluate features of the catalytic phase.

In the catalytic phase the oxygen uptake and ketone formation are directly related. Over a 5 h period both profiles showed a 'near first-order' decay to almost constant rates, but it is clear from extended checks on the ketone production that there were slow further decays over a period of several days which may not be entirely due to the reduction in [PPh_3]. The yield of compound (A) corresponded to 12 ± 2% of the octan-2-one yield over a wide range of olefin and PPh_3 concentrations. In contrast, the amount of heptanal produced in the catalytic phase was sensitive to the [olefin] : [PPh_3] ratio, increasing at the expense of octan-2-one from zero, at a ratio of 1 : 1, to *ca.* 20% of the octan-2-one at a ratio of 140 : 1. The C : O ratio for the period $t = 5 - 300$ min was constant at $0.33 \pm 0.02 : 1$.

Small amounts of acid (1×10^{-3}—3×10^{-3} mol dm^{-3}) had pronounced effects on the catalytic activity (as measured by the total oxygen uptake), the C : O ratio, and the number of products formed. Diphenylphosphinic acid (dppa), in concentrations slightly greater than that of the catalyst, increased the C : O ratio to 0.62 : 1 and completely inhibited the formation of compound (A) and heptanal in the catalytic phase. The influence on the catalytic activity appears to be linked to the olefin concentration, being *ca.* 30% greater than the corresponding run without dppa at [oct-1-ene] = 1.89 mol dm^{-3} but 20% lower than the control run at [oct-1-ene] = 0.10 mol dm^{-3}. The following effects were observed with other acids at [oct-1-ene] = 1.89 mol dm^{-3}. Diphenyldithiophosphinic acid completely inhibited the reaction. The changes with di-(2-ethylhexyl)phosphoric acid were similar to those found for dppa, while toluene-*p*-sulphonic acid hydrate increased the C : O ratio to 0.40 : 1, inhibited the compound (A) and aldehyde formation, and reduced the catalytic activity by *ca.* 50%. Benzoic acid had only a small effect on the C : O ratio. Compound (A) was not formed but the aldehyde yield was not significantly reduced, and in this case also the activity of the catalyst was enhanced.

A brief examination of the effects of changing the solvent showed that the characteristic profiles for oxygen uptake and ketone formation were retained when the solvent was methylene dichloride although the activity of the catalyst was *ca.* 15% lower. When the reaction was carried out in anhydrous methanol considerably less ketone was formed in the initial phase. In the catalytic phase there was a marked reduction in the C : O ratio to 0.10 : 1 and the yield of aldehyde increased to *ca.* 60% of the 2-one yield. There appeared to be no associated oxidation of the solvent.

The absence of any significant influence on the oxygenations by free-radical chain inhibitors indicates that the reactions take place at the co-ordination sphere of the metal, and the similarity between the profiles for octan-2-one formation and the dioxygen uptake points to at least one common intermediate in the catalytic cycles responsible for the formation of octan-2-one and Ph_3PO. In those cases where the mechanism of catalytic oxygenation of PPh_3 by transition-metal complexes has been carefully examined,[6] the oxygenating step is considered to involve the attack by PPh_3 on a peroxo-complex [7] of the metal which also carries a PPh_3 ligand, but the details, in particular of the stereochemical requirement and the distinction between stepwise and concerted electronic shifts, have not been elucidated.

A similar homoco-oxygenation † [Scheme 1, path (*a*)]

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* In calculating C : O ratios we anticipate one of our main conclusions in this paper, that the production of each mol of aldehyde and ketone is associated with the uptake of 1 mol of dioxygen. The C : O ratio for the reaction during a time interval $t_1 - t_2$ is therefore given by:

$$\frac{\sum\limits_{t_1 \text{ to } t_2} \text{(mol of organic product formed)}}{\text{mol of dioxygen taken up } (t_1 \text{ to } t_2)}$$

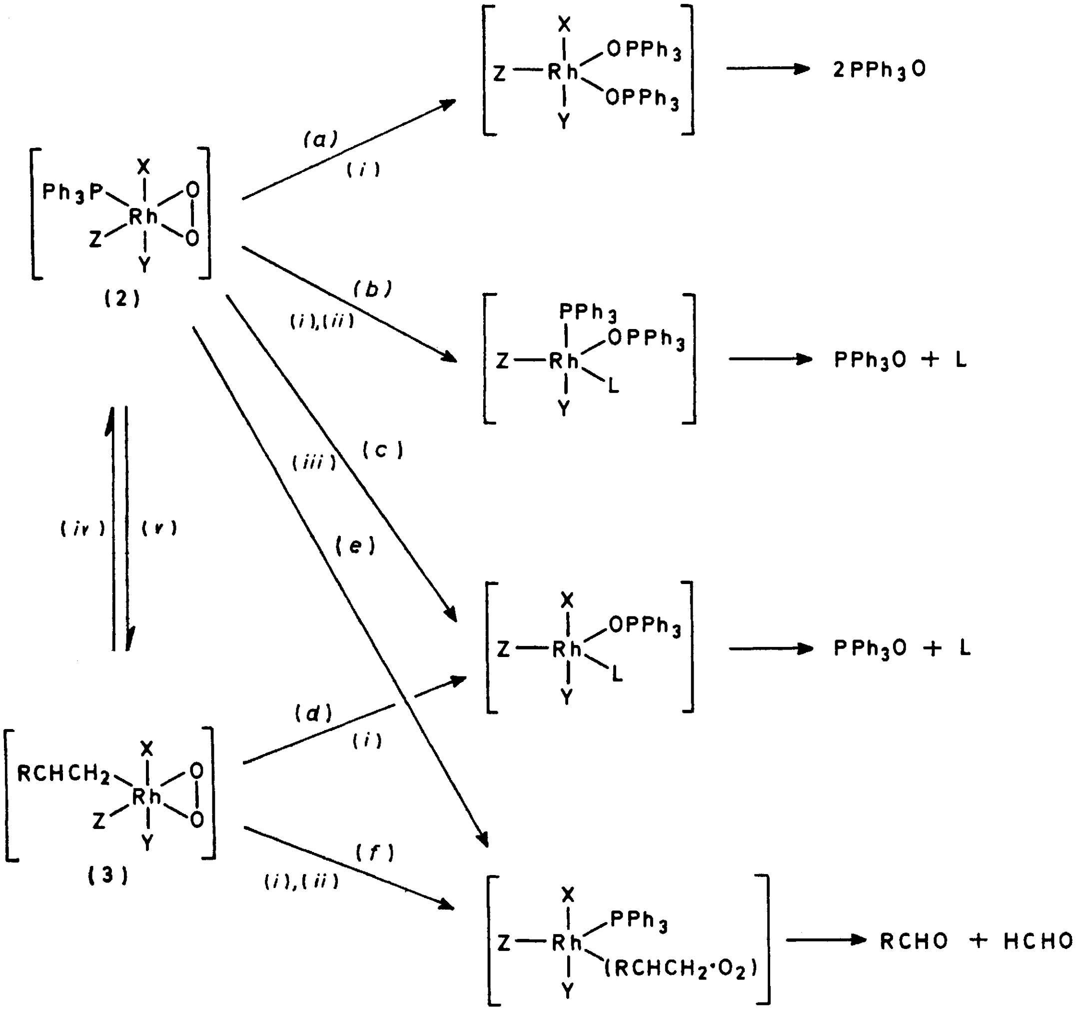
† We adopt the terms homoco-oxygenation and heteroco-oxygenation to describe processes in which two molecules of the same substrate are oxygenated by one molecule of dioxygen and processes in which molecules of two different substrates are oxygenated by one molecule of dioxygen.

[6] J. Halpern and A. L. Pickard, *Inorg. Chem.*, 1970, **9**, 2798; B. W. Graham, K. R. Laing, C. J. O'Connor, and W. R. Roper, *J.C.S. Dalton*, 1972, 1237.

[7] L. Vaska, *Accounts Chem. Res.*, 1976, **9**, 175.

is considered to yield the bulk of the Ph_3PO obtained from the reactions described above when trace amounts of acid are absent. The smaller yield of octan-2-one could conceivably be obtained, together with an equivalent amount of Ph_3PO, by an analogous attack on the same complex, (2), by oct-1-ene [path (*c*)] or attack by PPh_3 on the related complex, (3), [path (*d*)], but if either of these heteroco-oxygenations were competing with the homoco-oxygenation (*a*) the ratio of the Ph_3PO yield to the octan-2-one should be very sensitive to the [oct-1-ene] : [PPh_3] ratio. However, the ratio of the two yields, as reflected by the C : O ratio, does not vary significantly on varying the [oct-1-ene] : [PPh_3] ratio between 0.7 and 204 : 1. Thus paths (*c*) and (*d*) are excluded in favour of (*b*), which requires both oct-1-ene and PPh_3 to be ligands of the peroxo-complex (2). The excess of PPh_3 in solution would be expected to compete with the olefin for the site on (2) occupied by the olefin, unless this site is sterically very hindered. However, the rate of reaction is not significantly affected when the olefin concentration is varied at constant [PPh_3] and it follows that the co-oxygenation steps are unlikely to be rate determining if the intermediate is correctly represented.

Whilst the above discussion applies only to the catalytic phase, it is quite clear that a molecule of olefin must also be associated with the metal complex before any co-oxygenation can take place in the initial phase. After an immediate uptake of 1.1 mol of dioxygen per mol of complex no further uptake of dioxygen is observed even at high [PPh_3] if oct-1-ene is absent. Thus there is no detectable homoco-oxygenation of PPh_3 similar to that reported by Van Vugt *et al.*[8] for solutions of (1) with PPh_3 in benzene at 50 °C and at low dioxygen partial pressures. We conclude that the corresponding active species, which the Dutch workers consider to be the paramagnetic compound [$Rh^{II}Cl(O_2)(PPh_3)_2$], is not formed in significant quantities under our conditions. It seems likely that in our solutions one of the known[9] peroxo-complexes of (1) is



SCHEME 1 Possible co-oxygenation paths (without stereochemical connotations): R = hexyl, L = octan-2-one; (*i*) $+PPh_3$; (*ii*) X = $RCHCH_2$; (*iii*) +X; (*iv*) $-X, +PPh_3$; (*v*) $+X, -PPh_3$

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[8] B. H. Van Vugt, N. J. Koole, W. Drenth, and F. P. J. Kuijpers, *Rec. Trav. chim.*, 1973, **92**, 1321.

[9] M. J. Bennett and P. B. Donaldson, *J. Amer. Chem. Soc.*, 1971, **93**, 3307.

first produced on adding dioxygen but we defer detailed consideration of these and other possible intermediate complexes in both phases of the reaction until further studies have been completed.

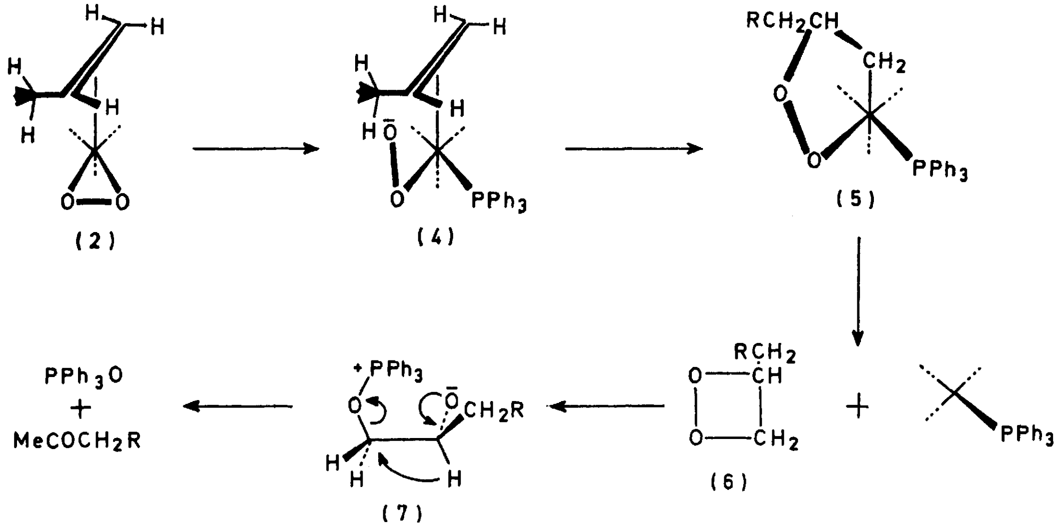
The two major catalytic reactions in the system are therefore regarded as the homoco-oxygenation (1), for

$$2PPh_3 + O_2 \xrightarrow{Rh^I} 2Ph_3PO \qquad (1)$$

which there is ample precedent,[6,10] and the heteroco-oxygenation (2) which appears to be the first *in vitro*

$$PPh_3 + RCH{=}CH_2 + O_2 \xrightarrow{Rh^I} Ph_3PO + RCOMe \qquad (2)$$

example of a low-temperature catalytic conversion of an olefin into a ketone by dioxygen. Comment on the formal similarity between such heteroco-oxygenations and the *in vivo* hydroxylation of aromatic rings by mixed functional oxygenases has already been made.[1] The two co-oxygenations may result from competing processes at one complex, or alternatively the reactions may involve two related complexes, both represented by (2; X = $RCHCH_2$), which react with PPh_3 in different ways. The relative rates of these co-oxygenations are clearly very sensitive to trace amounts of acid, diphenylphosphinic acid in particular, and a direct interaction at the co-ordination sphere of the metal is implicated by the low concentrations required. Whilst no further conclusions can be drawn from the present evidence, a practical consequence of this effect is that octan-2-one, virtually free from other organic by-products, can be obtained under appropriate conditions, *e.g.* [(1)] = 8×10^{-4}, [oct-1-ene] = 1.9, [PPh_3] = 8×10^{-2}, and [dppa] = 1×10^{-3} mol dm^{-3} gives [octan-2-one] = 1.3×10^{-2} mol dm^{-3} in 5 h at 22 °C.



SCHEME 2 Suggested route to octan-2-one: R = pentyl

Milner has shown that rhodium(I) complexes can catalyse the conversion of styrene into acetophenone[11] at 117 °C and promote the conversion of cyclo-octene into a mixture of cyclo-octanone and cyclo-oct-2-en-1-one[12] at 74 °C in the presence of free-radical inhibitors, but in the absence of PPh_3 or an analogous oxygen acceptor. These results are most readily interpreted in terms of homoco-oxygenation of the organic substrates. Styrene is also slowly oxygenated under our conditions but cyclo-octene is unaffected. We discount the possibility of the octan-2-one being formed by a similar homoco-oxygenation for the reasons given above to exclude paths (*b*) and (*d*), but the increase in the heptanal yield with increased oct-1-ene concentration does support the view that two molecules of olefin are required in the co-ordination sphere of the catalyst for aldehyde to be formed. The amount of heptanal produced under the most favourable conditions was relatively small and our results only give a qualitative picture. Furthermore, we do not have direct evidence that the terminal carbon is converted into formaldehyde but we regard this as its most probable fate. If this is the case, the second molecule of olefin may compete with a PPh_3 attacking the peroxo-compound (2), as in path (*e*) or displace a PPh_3 from (2) to give (3) which subsequently reacts with PPh_3 [path (*f*)] to give heptanal.

The detailed picture of the transformations of the oct-1-ene remains obscure, but possibly the fission of the olefinic bond to give heptanal provides one clue to the mechanisms of the reactions. If the co-ordinated

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[10] G. Wilke, H. Schott, and P. Heimbach, *Angew. Chem. Internat. Edn.*, 1967, **6**, 92; S. Otsuka, A. Nakamura, and Y. Tatsumo, *J. Amer. Chem. Soc.*, 1969, **91**, 6994; A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *ibid.*, 1971, **93**, 371; A. L. Balch, *Inorg. Chem.*, 1971, **10**, 276; S. Cenini, A. Fusi, and G. Caparella, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 127; R. Barral, C. Bocard, I. Seree de Roch, and L. Sajus, *Kinetika i Kataliz*, 1973, **14**, 130.

[11] J. Farrar, D. Holland, and D. J. Milner, *J.C.S. Dalton*, 1975, 815.

[12] D. Holland and D. J. Milner, *J.C.S. Dalton*, 1975, 2440.

olefin in the active peroxo-complex (2) adopts the configuration * shown in Scheme 2, the incoming PPh_3 may cause the dioxygen to be displaced from one co-ordination site to give a transition state (4) which contains a unidentate peroxo-ligand.† Nucleophilic attack of the oxygen anion on the π-bonded olefin to produce the metallocyclic intermediate (5) would parallel the hydride attack on co-ordinated olefins which is considered to occur in homogeneous hydrogenation systems [13] and the conversions of peroxobis(triphenylphosphine)platinum-(II) into a range of stable five-membered ring complexes with CO_2, CO, CS_2, and aldehydes and ketones.[14] Octan-2-one formation could result from subsequent attack on (5) by co-ordinated PPh_3; however, a reductive elimination from (5) to give the dioxetan (6) would provide a plausible route to this ketone and the heptanal. A rapid attack on (6) by a suitably positioned PPh_3 would produce the zwitterionic intermediate (7) [15] which is more likely to break down to give octan-2-one and Ph_3PO, by a 1,2-hydride shift, than 1,2-epoxyoctane and Ph_3PO [16] if free rotation about the C(1)–C(2) bond is restricted. With no suitably positioned PPh_3 the metal centre would be expected to act as a catalyst [17] for the decomposition of the dioxetan into heptanal and formaldehyde. More positive identification of the intermediate steps must await the outcome of further investigations but it seems probable that the ketone-forming process will be associated with only one geometric isomer of the active complex.

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* In principal the olefin might adopt one of sixteen configurations with respect to the peroxo-ligand, eight with a facial disposition of the dioxygen and olefinic centres and eight with a meridional disposition. Each may be converted into the transition state (4) but in the majority of cases this would involve considerably greater conformational changes than those shown in the Scheme.

† This unstable co-ordinated dioxygen species would be expected to have strong nucleophilic properties. It should not be confused with the stable co-ordinated superoxide radical ion (see ref. 7).

[13] B. R. James, ' Homogeneous Hydrogenation,' Wiley, New York, 1973, p. 214.

[14] P. J. Hayward, D. M. Blake, G. Wilkinson, and C. J. Nyman, *J. Amer. Chem. Soc.*, 1970, **92**, 5873; R. Ugo, F. Conti, S. Cenini, R. Mason, and G. B. Robertson, *Chem. Comm.*, 1969, 987.

[15] K. R. Kopecky, J. E. Filby, C. Mumford, P. A. Lockwood, and J. Ding, *Canad. J. Chem.*, 1975, **53**, 1103.

[16] P. D. Bartlett, A. L. Baumstark, M. E. Laudis, and C. L. Lerman, *J. Amer. Chem. Soc.*, 1974, **96**, 5267.

[17] P. D. Bartlett, *Chem. Soc. Rev.*, 1976, **5**, 149.