Oxygenation Studies. Part I. Rhodium(I)-promoted Oxygenation of Terminal Olefins to Methyl Ketones

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Hex-1-ene, hept-1-ene, and oct-1-ene are converted to the corresponding methyl ketones with dioxygen at ambient temperature and pressure in benzene solutions of the complexes [RhH(CO)$(PPh_3)_3$], (I), and [RhCl$(PPh_3)_3$], (II). Small quantities of hexanal and heptanal respectively are also formed from hept-1-ene and oct-1-ene. Higher yields of ketone (70—88% based on the complex) are obtained when [RhCl$(PPh_3)_3$] is used. Radical-chain processes have not been detected and the reactions appear to involve co-oxygenation of co-ordinated PPh_3 and olefin at the metal centre. Evidence for the formation from [RhCl$(PPh_3)_3$] of several complexes which can produce ketones has been obtained. The course of the reaction of the complex [RhCl$(PPh_3)_3$] with dioxygen is sensitive to the concentration of the latter.

OUR interest in the factors responsible for activation of dioxygen by metal ions, *in vivo* and *in vitro*, led us to examine the oxygenating properties of the complexes chlorotris(triphenylphosphine)rhodium(I), (II), and carbonylhydridotris(triphenylphosphine)rhodium(I), (I), in the presence of some simple olefins. Early claims for catalysed oxygenation at elevated temperatures by complex (II) appear not to be justified. Later evidence indicates that the metal complex acts primarily as a catalyst in the breakdown of intermediate hydroperoxides generated by the normal radical-chain process.[1] However, (II) is reported to form dioxygen complexes [2,3] which are potential oxidants, *cf.* [Pt$(O_2)$$(PPh_3)_2$],[4] and there is some evidence for (II), or a product derived from it, being involved in the initiation of a chain reaction.[2] The suggestions that (I) and (II) form olefin intermediates under conditions of hydrogenation [5] and isomerisation [6] significantly influenced our choice of complex.

RESULTS AND DISCUSSION

Oxygenation of the Complexes [RhH(CO)$(PPh_3)_3$] *and* [RhCl$(PPh_3)_3$].—Before discussing reactions of complexes (I) and (II) with dioxygen in benzene solutions containing hex-1-ene, hept-1-ene, and oct-1-ene, it is convenient to consider their reactions in the absence of olefins. The uptake of dioxygen by benzene solutions of complex (I) was 90% complete in 200 min [Figure 1(□)]. No further uptake was detected after 24 h when a value of 2·30 moles of dioxygen per mole of complex was obtained, after correction for solvent saturation. This indicates that in the products as many as five oxygen atoms can interact with each rhodium and associated ligands but, as yet, we have no evidence on which to base a more detailed explanation of these findings.

Solutions of complex (II) absorbed dioxygen more rapidly than those of (I) and in an unexpected manner. At moderate stirring rates, the rate of oxygen uptake corresponded to that of the diffusion of dioxygen into the solution for the major portion of the run [Figure 1(○)]. A final average uptake of 1·74 moles of dioxygen per mole of complex was obtained after 30 min, and an insoluble brown complex (III) slowly precipitated from the solution. Thin-layer chromatography (t.l.c.) showed that at least one soluble metal complex and Ph_3PO were present in the solution. At a rapid stirring rate, diffusion-controlled uptake of dioxygen over a period of 1 min, to 1·1 moles of dioxygen per mole of complex, was observed and then the uptake virtually ceased [Figure 1(△)]. No precipitate formed, but a very slow further uptake of from 0·4 to 0·55 moles of dioxygen per mole of complex was detected when stirring was continued for 20 h. This was accompanied by slow deposition of the precipitate.

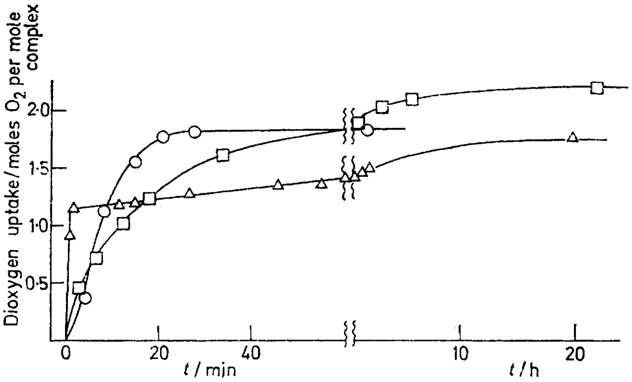

FIGURE 1 Dioxygen uptake in benzene by the complexes: (□), [RhH(CO)$(PPh_3)_3$] at a moderate stirring rate (1 000 rev. min^{-1}); (○), [RhCl$(PPh_3)_3$] at a moderate stirring rate (1 100 rev. min^{-1}); and (△), [RhCl$(PPh_3)_3$] at a rapid stirring rate (3 300 rev. min^{-1})

The precipitated complex, (III), was isolated as a red-brown powder which showed i.r. bands at 1 094,

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[1] V. P. Kurzov, 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; L. W. Fine, M. Grayson, and V. H. Suggs, *J. Organometallic Chem.*, 1970, **22**, 219.

[2] J. Blum, J. Y. Becker, H. Rosenman, and E. D. Bergmann, *J. Chem. Soc.* (*B*), 1969, 1000.

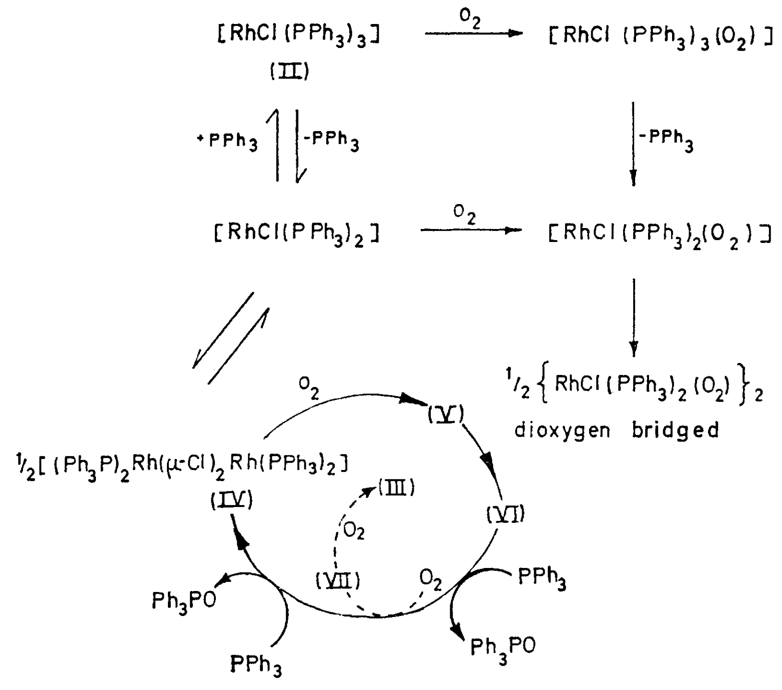
[3] (*a*) M. J. Bennett and P. B. Donaldson, *J. Amer. Chem. Soc.*, 1971, **93**, 3307; (*b*) R. L. Augustine and J. Van Peppen, *Chem. Comm.*, 1970, 497.

[4] P. J. Hayward, D. M. Blake, G. Wilkinson, and C. J. Nyman, *J. Amer. Chem. Soc.*, 1970, **92**, 5873.

[5] C. O'Connor and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 2665; M. Yagupsky and G. Wilkinson, *ibid.*, 1970, 941.

[6] A. S. Hussey and Y. Takeuchi, *J. Amer. Chem. Soc.*, 1969, **91**, 672; *J. Org. Chem.*, 1970, **35**, 643.

1 120 and 1 190, and 850 cm^{-1}, characteristic of triphenylphosphine, triphenylphosphine oxide, and metal peroxide respectively. On heating above 90 °C under a nitrogen atmosphere, the complex decomposed. Bands associated with co-ordinated dioxygen and triphenylphosphine decreased in intensity and eventually disappeared, whilst at the same time the intensity of bands associated with triphenylphosphine oxide increased, indicating that internal oxygenation of triphenylphosphine was involved. Analyses were in good agreement with the formula [RhCl(PPh$_3$)(Ph$_3$PO)O$_3$],C$_6$H$_6$ and on this basis the percentage of rhodium recovered in this form from runs at the moderate stirring rate varied from 20 to 28%. The precipitate obtained when anhydrous methanol was used as solvent analysed for [RhCl(PPh$_3$)(Ph$_3$PO)O$_3$] but in other respects did not differ from the material obtained from benzene.



SCHEME

In several respects the above findings agree with those reported by Augustine and Van Peppen.[3b] However our analyses for the precipitates obtained from benzene and methanol are in excellent agreement with the formula {RhCl(PPh$_3$)(Ph$_3$PO)(O$_2$)}$_2$(O$_2$) rather than the reported {RhCl(PPh$_3$)$_2$(O$_2$)}$_2$O; the spectroscopic evidence for co-ordinated (O$_2$) and Ph$_3$PO is also clear. Since free Ph$_3$PO is a product of this reaction and our observed oxygen uptake corresponds on average to 3·5 atoms of oxygen per atom of rhodium when moderate stirring rates are employed, it follows that some of the rhodium is present in the final solutions as less highly oxygenated species. Consistent with this view is the observation that only part of the rhodium was recovered in the form of the precipitate.

Bennett and Donaldson isolated two products from oxygenation of complex (II) in methylene dichloride.[3a] One was fully characterised as the stable dimeric species {RhCl(PPh$_3$)$_2$(O$_2$)}$_2$ which contains an unusual dioxygen bridge, and the second was tentatively formulated as solvated [RhCl(PPh$_3$)$_3$(O$_2$)]. It seems probable that a major portion of the rhodium is converted to these products under the conditions of our experiment by the paths shown in the Scheme. However, a small portion (*ca.* 10%) of the rhodium will be in the di-μ-chloro-bridged form (IV) before dioxygen is introduced[7] and this complex might also be expected to react rapidly with dioxygen. If the rate with which complex (IV) reacts with dioxygen is markedly faster than that of the two monomeric species, significant quantities of rhodium could associate with dioxygen by this route when the concentration of the latter is very low [rapid formation of (IV) being assumed]. We suggest that these conditions may be met, at least in part, when moderate stirring rates are used, and speculate that the complex formed from dioxygen and (IV), *i.e.* (V), is not stable and decomposes to give (VI). This reaction, which may involve intervention of a solvent molecule or a further molecule of PPh$_3$, is considered to be similar in character to those involved in catalytic co-oxygenation of PPh$_3$ and CO by a variety of transition-metal complexes.[8] Displacement of the two Ph$_3$PO ligands by two PPh$_3$ molecules would

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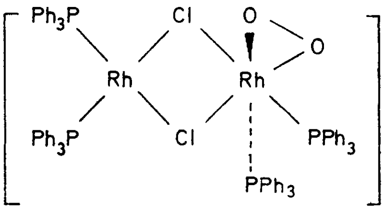
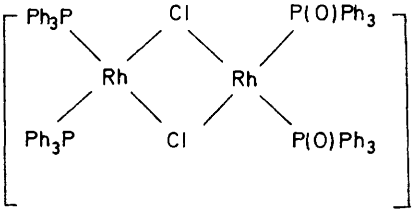
[7] H. Arai and J. Halpern, *Chem. Comm.*, 1971, 1571.

[8] G. Wilke, H. Schott, and P. Heimbach, *Angew. Chem. Internat. Edn.*, 1967, **6**, 92; J. Kiji and J. Furukawa, *Chem. Comm.*, 1970, 977; B. W. Graham, K. R. Laing, C. J. O'Connor, and W. R. Roper, *J.C.S. Dalton*, 1972, 1237; J. P. Birk, J. Halpern, and A. L. Pickard, *J. Amer. Chem., Soc.* 1968, **90**, 4914.

regenerate complex (IV), creating a catalytic cycle in which free PPh_3 is oxygenated. Eventually, at low concentration of PPh_3, species such as $\{RhCl(PPh_3)(Ph_3PO)(O_2)\}_2$, (VII), would form which could slowly react with a further molecule of oxygen to give the precipitate (III). If, under rapid stirring, conditions with an excess of dioxygen are quickly reached, little additional dissociation of complex (II) may occur before it is oxygenated. The very slow further uptake of dioxygen observed after 1·1 moles of dioxygen per mole of complex had been added is then due to the small amount of catalytically active species present. In keeping with this hypothesis is the observation that only 1·1 moles of dioxygen per mole of complex were taken up at moderate stirring rates when the solutions contained excess of PPh_3.



(V)



(VII)

Summary of rhodium(I)-promoted oxygenations

Study *	Olefin	[Olefin] mol l⁻¹	10³ [Complex] mol l⁻¹	Additional O_2 † mole per mole complex	Yield/mole per mole complex: Ketone After 24 h	Ketone 11 days	Aldehyde 24 h
(*a*)	Hex-1-ene	1·56	6·42	0·61	0·59	0·70	
	Hept-1-ene	1·39	6·28	0·68	0·70	0·88	0·10
	Oct-1-ene	1·28	6·42	0·53	0·64	0·75	0·09
(*b*)	Hex-1-ene	1·58	6·40	0·26	0·35	0·39	
	Hept-1-ene ‡	1·42	6·38	0·34	0·48	0·55	0·07
	Oct-1-ene	1·30	6·36	0·26	0·46	0·52	0·07
(*c*)	Hex-1-ene	1·63	6·28	1·00	0·36	0·43	
	Hept-1-ene	1·42	6·21	0·88	0·36	0·42	0·02
	Oct-1-ene	1·33	6·15	0·57	0·32	0·35	0·03

* Conditions: (*a*), $[RhCl(PPh_3)_3]$ with rapid stirring rate; (*b*), $[RhCl(PPh_3)_3]$ with medium stirring rate; and (*c*), $[RhH(CO)(PPh_3)_3]$ with rapid stirring rate. † Based on uptake after 3 h for (*a*) and (*b*) and uptake after 24 h for (*c*). ‡ Figures based on one run only.

Oxygenation of Complexes (I) *and* (II) *in the Presence of Olefins.*—When the above oxygenations were carried out in carefully degassed and purified benzene solutions containing hex-1-ene, hept-1-ene, or oct-1-ene, higher oxygen uptakes were always found, after correction for solvent saturation (see Table). This clearly indicates that the olefins are associated with the reaction between the complexes and dioxygen. With the aid of gas–liquid chromatography (g.l.c.) two derivatives from the olefins were detected when either complex was oxidised in benzene–oct-1-ene or benzene–hept-1-ene solutions. These were subsequently shown to be octan-2-one and heptanal and heptan-2-one and hexanal respectively.* Hexan-2-one was similarly detected as a product from the oxidations in benzene–hex-1-ene, but practical restrictions prevented the detection of any pentanal which may have been formed in this case. In the absence of convenient analytical procedures which would distinguish between, for example, co-ordinated dioxygen and oxygen in Ph_3PO, it was not possible to directly relate the extra dioxygen taken up in the presence of olefin to the yields of oxygenated organic products. We therefore simply report in the Table the moles of product per mole of complex used. The yields of ketone were always more than seven times greater than those of the corresponding aldehyde.

It is clear that, under the conditions of our experiments, terminal olefins are oxygenated to methyl ketones and, although no direct evidence for formaldehyde formation was obtained, the aldehydes also appear to be formed directly from the olefins. We consider therefore that the reactions (1) and (2) are

$$RCH{=}CH_2 + \tfrac{1}{2}O_2 \longrightarrow RC(O)Me \qquad (1)$$

$$RCH{=}CH_2 + O_2 \longrightarrow RCH{=}O + HCH{=}O \qquad (2)$$

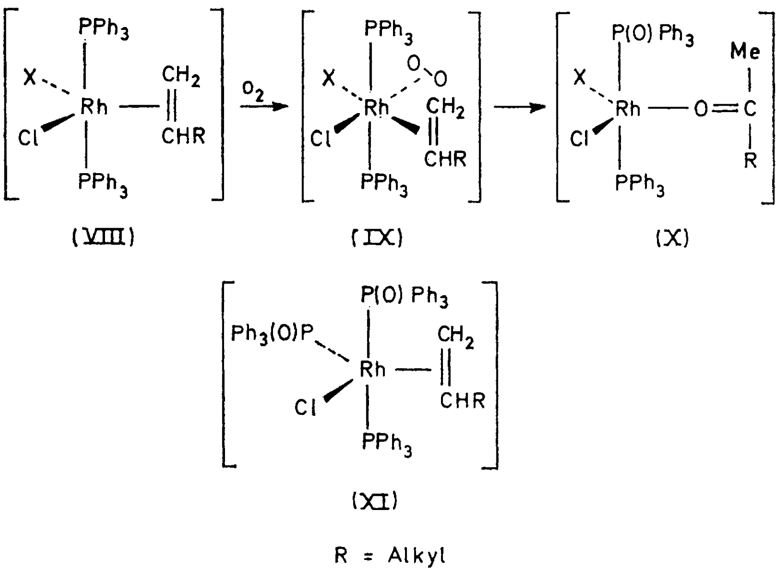
involved. These aldehydes and ketones are not normally produced in Haber–Weiss-type radical-chain reactions but, in view of erroneous conclusions drawn by earlier workers from oxygenations in the presence of complex (II), we sought evidence for radical intermediates in our reactions. Hex-1-en-3-ol, a typical product from autooxidation of hex-1-ene, and 1,2-epoxyhexane, a possible secondary product, were not detected (g.l.c.) in the reaction mixture from benzene–hex-1-ene and dioxygen

* We acknowledge the generous help given by the g.l.c.–m.s. group at University College, Cardiff, in identifying these compounds.

in the presence of complex (II). Indeed, no significant quantities (>3%) of additional oxidation products were found in this or any of the reaction mixtures.* Furthermore, no sustained radical oxidation was induced under our conditions when an initiator (t-butyl hydroperoxide) was introduced into the system. Most significantly, yields of octan-2-one and heptanal were not affected when oct-1-ene was oxygenated with complex (II) in benzene solutions containing hydroquinone ($6{\cdot}5 \times 10^{-2}$ mol l^{-1}) or 4-methyl-2,6-di-t-butylphenol ($3{\cdot}6 \times 10^{-2}$ mol l^{-1}). There is no obvious mechanism for the production of singlet oxygen under these conditions and, in any event, singlet oxygen would not be expected to produce methyl ketones from terminal olefins. We conclude, therefore, that these products are formed by a rhodium(I)-promoted oxygenation.

The results presented in the Table show that for individual olefins most additional dioxygen was taken up in solutions containing complex (I) and the ketone to aldehyde ratio in these solutions was higher than with (II). However, the ketones and aldehydes detected accounted for only a relatively small portion (20—35%) of the additional dioxygen and we concentrated our attention on the oxygenations with complex (II) in which the yields of ketone are higher.

With complex (II), approximately the same amount of the precipitate (III) was obtained as in the reactions discussed above, where olefin was absent, but in other respects these reactions were different. The oxygen uptake was 90% complete in 30 min, regardless of whether rapid or moderate stirring rates were employed, and it was apparent that a significant portion of the rhodium species in solution, after the initial phase, contained co-ordinated ketone or co-ordinated dioxygen and olefin (see below). For this reason, and because the uptake contrasts with that found under rapid-stirring conditions when the olefin was absent, we consider that a major portion of the rhodium complex participates in these oxygenations.



The simplest explanation for the observed results would be oxygen attack on an olefinic species such as (VIII) in which X could be PPh_3, solvent, or, after some reaction has occurred, Ph_3PO. Alternatively it could be the chlorine atom of a chlorine-bridged species. The intermediate (IX) formed by this attack could break down by co-oxygenation to give (X), but when X = PPh_3 a competing process to give (XI) with two Ph_3PO ligands might occur. Some Ph_3PO or ketone would be displaced by free PPh_3 in solution to generate four- or five-co-ordinated species which could react with a further molecule of dioxygen and, in the case of a chlorine-bridged species, form (VII) and subsequently (III). The results at moderate stirring rates, where additional oxygen uptake was only *ca.* half that found when rapid stirring was employed and where the yields of ketone were also lower, are consistent with the initial equilibrium concentrations being altered by a fast reaction between dioxygen and one or more of the species which do not carry an olefinic ligand. The formation of aldehydes appears to be a secondary process which we shall discuss in a later paper in this series.

Ketones continued to be formed in reaction solutions of complexes (I) and (II) after detectable oxygen uptake had ceased (*ca.* 3 h) and, although the rate of formation had become very low by 24 h, ketones were still being slowly produced after several weeks. Figure 2(□) shows a characteristic profile for reaction of complex (II) with oct-1-ene and dioxygen. The rate of ketone formation after 73 days (*ca.* 0·004 mol mol^{-1} day^{-1}) was not significantly lower than that at 12 days and a very slow

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* On standing for several weeks at room temperature, dioxygen-saturated solutions showed a very slow build up of additional products (g.l.c.), consistent with a slow auto-oxidation.

catalytic process is probably involved. This reaction was not inhibited by quinol or 4-methyl-2,6-di-t-butylphenol.

Slow formation of ketone also took place in solutions [oct-1-ene–(II)–benzene] which had been degassed and saturated with dinitrogen after reaction in dioxygen. However, the rate of subsequent ketone formation in these cases was lower and diminished further with time. In a quantitative study [Figure 2(○) and (△)], a solution was degassed after 5 h, saturated with dinitrogen, and divided into two portions. Excess of PPh_3 was added to one portion immediately and a relatively rapid rise in ketone content followed. After 56 days excess of PPh_3 was added to the second portion and a similar relatively rapid increase in ketone content was observed which equalised the ketone contents in the two solutions. Slow formation of ketone after dioxygen had been removed from the reaction solution is clear from plot (○) of Figure 2 and must result from either (*i*) slow release of ketone from a complex or (*ii*) slow oxygenation of olefin by irreversibly bound dioxygen at a complex. Ketone (0·075 mol mol^{-1}) formed when excess of PPh_3 is added to this solution appears to originate from a different complex which, in the absence of PPh_3, does not produce ketone, for virtually the same amount of additional ketone is formed when PPh_3 is added after 56 days as when PPh_3 is added after 5 h. These results strongly suggest that a series of stable or near-stable rhodium complexes, containing either ketone or dioxygen plus olefin, are present in the reaction solution after a few hours. The precipitate (III) was very slightly soluble in benzene–hex-1-ene solutions but no hexan-2-one was formed when a suspension of (III) was stirred in dioxygen-saturated benzene–hex-1-ene for several days.

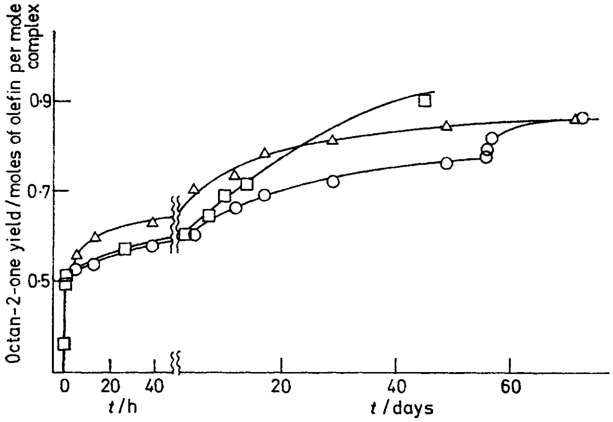

FIGURE 2 Octan-2-one formation in benzene–oct-1-ene solutions with the complex $[RhCl(PPh_3)_3]$: (□), $[RhCl(PPh_3)_3]$ + oct-1-ene + dioxygen; (○), as (□) but with dioxygen replaced by dinitrogen after 5 h and excess of PPh_3 added after 56 days; (△), as (○) but with dioxygen replaced by dinitrogen and excess of PPh_3 added after 5 h

The significance of the oxygenations reported here lies not in the products formed or yields obtained but in the clear demonstration that the process observed involves reactions of dioxygen with organic substrates at ambient temperatures which are quite different from those associated with triplet and singlet oxygen. The patent literature contains several reports of catalytic oxygenation of olefins to ketones and related products by transition-metal complexes in aqueous solutions [9] but these do not distinguish between Wacker-type oxidation,[10] which involves hydration, and oxygenation by dioxygen. Other reports by Takao *et al.* of oxygenation at Ir^I and Rh^I complexes at elevated temperatures under anhydrous conditions [11] may involve reactions similar to those discussed above, but Lyons and Turner [12] have shown that radical-chain processes are involved in closely related reactions.

This metal-ion promoted oxygenation of olefins to methyl ketones is analogous in several respects to *in vivo* hydroxylation of aromatic rings which is catalysed by metalloenzymes of the mixed-functional oxygenase class.[13] In taking up one of the atoms in dioxygen, PPh_3 plays a similar role to the hydrogen donor of the biological system, and the migration of a hydrogen atom from C(2) of the olefin to C(1) of the ketone parallels the N.I.H. shift [14] characteristic of the *in vivo* process. As in the biological system, an epoxide intermediate may be involved, but we were unable to detect any corresponding epoxide in our products and found that free epoxide is not isomerised under the reaction conditions. However this does not mean that a co-ordinated epoxide molecule formed at the metal centre would not rapidly isomerise under our conditions, *cf.* ref. 15.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 357 spectrophotometer using KBr discs. Microanalysis was carried out by Drs. F. and E. Pascher, W. Germany.

Benzene (Hopkins and Williams, AnalaR) was heated under reflux with chromic acid solution for 10 h, washed with aqueous sodium hydroxide, sodium hydrogen sulphite solution, and water, and dried over anhydrous sodium sulphate. It was subsequently distilled from sodium wire and fractionally redistilled from lithium tetrahydridoaluminate. Hex-1-ene, hept-1-ene, and oct-1-ene (Koch–Light, pure grade) were fractionally distilled from lithium tetrahydridoaluminate. Cylinder oxygen (B.O.C.) was used without further treatment. The complexes $[RhCl(PPh_3)_3]$, (II), and $[RhH(CO)(PPh_3)_3]$, (I), were prepared by methods

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[9] U.S.P. 3,384,669 and 3,479,262; Belg. P. 635,407; F.P. 1,507,137.

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[13] I. C. Gunsalus, H. E. Conrad, and P. W. Trudgill, ' Oxidases and Related Redox Systems,' Wiley, New York, 1965, vol. 1, p. 417; O. Hayaishi, Y. Ishimura, T. Nakazawa, and M. Nozaki, ' Biochemie des Sauerstoffs,' Springer-Verlag, Berlin, 1968, p. 196.

[14] G. Guroff, J. W. Daly, D. M. Jerina, J. Renson, B. Witkop, and. S. Udenfriend, *Science*, 1967, **157**, 1524.

[15] B. Rickborn and R. M. Gerkin, *J. Amer. Chem. Soc.*, 1971, **93**, 1693.

described by Wilkinson and his co-workers [16] and Levison and Robinson [17] respectively.

Apparatus and Procedure.—The reaction vessel was a flat-bottomed straight-sided glass flask (40 cm^3) which was connected to a vacuum line. Benzene or benzene–olefin mixtures (*ca.* 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 lithium tetrahydridoaluminate on to the solid rhodium complex in the reaction vessel. After the reaction vessel and its contents had equilibrated at ambient temperature (21—24 °C), the reaction vessel was surrounded by a water-bath maintained at that temperature and light was excluded from the solution. Stirring was effected by a Teflon-covered follower in the reaction vessel. Dioxygen was allowed into the vessel at atmospheric pressure and its uptake by the solution was followed using a sensitive gas-burette system connected to the vacuum line. The dioxygen uptake by the solvent was determined in blank runs and in most cases each reaction was repeated at least once.

G.l.c. Analysis.—G.l.c. measurements were made using a Pye series 104 chromatograph with a flame-ionisation detector. Columns (diameter 0·25 in) of either 10% polyethylene glycol adipate (5 ft) or 10% dinonyl phthalate (9 ft) were used at 100 °C. After oxygen uptake had ceased, standards were added to the reaction mixtures and the mixtures were sampled at intervals for up to 12 days.

The Precipitated Complex (III).—Precipitates from oxidations carried out with complex (II) were removed from the reaction mixtures by filtration, washed repeatedly with pure benzene and hexane, and dried *in vacuo*. I.r. spectra of all solids so obtained were indistinguishable in the region 4 000—400 cm^{-1}. Samples from the reaction of complex (II) with dioxygen in (*a*) benzene–oct-1-ene and (*b*) methanol–oct-1-ene were analysed [Found (*a*): C, 62·5; H, 4·5; P, 7·4; Rh, 12·9. Calc. for $C_{42}H_{36}ClO_4P_2Rh$: C, 62·6; H, 4·5; P, 7·7; Rh, 12·8. Found (*b*): C, 59·45; H, 4·4; Cl, 5·1; P, 8·8; Rh, 14·7. Calc. for $C_{36}H_{30}ClO_4P_2Rh$: C, 59·5; H, 4·2; Cl, 4·9; P, 8·5; Rh, 14·2%].

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