Liquid-phase Metal-centred Autoxidation of Styrene Catalysed by Rhodium Species

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During the autoxidation of styrene, catalysed by $[\{RhCl(C_2H_4)_2\}_2]$ at 110 °C in the presence of radical inhibitor, acetophenone and benzaldehyde arise by a path avoiding both radical chains and a Wacker cycle. Only about half of the oxygen and styrene consumed appear as measured products, and the nature of the side-reactions is unknown. The various activities of several rhodium(I) complexes suggest that co-ordination of both the styrene and oxygen to the metal is essential for reaction, and the co-ordination of each of these ligands to rhodium has been observed under conditions approaching those of reaction. The initial rate of acetophenone formation accords with the expression:

$$\text{Rate} = \frac{C[\text{styrene}][\text{catalyst}][O_2]}{1 + C'[O_2]}$$

A sequential mechanism is proposed in which an initially formed catalyst–styrene adduct reacts with oxygen. In oxygen-saturated solution, the activation energy is 70 kJ mol^{-1}. The catalyst undergoes rapid oxidative deactivation, but is not regenerated by treatment with hydrogen. Styrenes having methyl or phenyl substituents at the olefinic positions are resistant to oxidation.

THE aerial oxidation of triarylphosphines,[1] carbon monoxide,[2] and isocyanides,[3] catalysed by transition-metal complexes which form adducts with oxygen, appear to involve oxygen-atom transfer within the co-ordination sphere of the metal. The analogous metal-centred oxidation of olefins conceivably could lead to novel and commercially interesting product spectra, but alkene autoxidations promoted by several promising metal species involve free-radical chains.[4] Oxidation of styrene catalysed by iridium, rhodium, and palladium complexes at *ca.* 100 °C is claimed [5-7] to demonstrate metal-centred oxygen activation, but the evidence is not compelling. Moreover, no evidence for co-ordination catalysis was observed [8] with similar species at 75 °C. Results consistent with much of these reports, and indicating metal-centred autoxidation of styrene, are the subject of this paper.

EXPERIMENTAL

Materials.—Koch–Light (puriss) styrene was distilled under nitrogen at 1 mmHg. Tetralin was passed down an alumina column and then distilled through a 1-m Oldershaw column packed with single-turn glass Fenske helices. Di-t-butyl-*p*-cresol was recrystallised from ethanol and dried *in vacuo*.

Preparation of Complexes.—(a) *Di-μ-chloro-bis(styrene)-rhodium*(I). A solution of $RhCl_3 \cdot H_2O$ (3·28 g) in a mixture of water (5·0 ml) and methanol (70 ml) was degassed. Degassed styrene (6·4 ml) was added to the mixture which was then stirred under nitrogen for 16 h. The orange solid which separated was isolated under nitrogen and dried *in vacuo*; yield 2·5 g, decomposed at 150 °C (Found: C, 53·1; H, 4·9; Cl, 11·2; Rh, 27·8. Calc. for $C_{16}H_{16}ClRh$: C, 55·4; H, 4·6; Cl, 10·2; Rh, 29·8%).

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(b) *Cyclopentadienylbis(styrene)rhodium*(I). To $[\{(PhCHCH_2)_2RhCl\}_2]$ (0·83 g) in tetrahydrofuran (5 ml) under nitrogen there was added a four-fold molar excess of sodium cyclopentadienide in tetrahydrofuran (*ca.* 10 ml) to yield a cloudy brownish yellow mixture, which was heated under reflux for 30 min and then stirred at room temperature for 16 h. After removal of the solvent under reduced pressure, the remaining solid was partly dissolved in n-heptane (20 ml) and the residue filtered off. On cooling of the filtrate in liquid nitrogen a yellow solid separated which was isolated and washed at *ca.* −50 °C; yield 0·4 g (Found: C, 65·5; H, 5·2; Rh, 25·7. Calc. for $C_{21}H_{21}Rh$: C, 67·0; H, 5·6; Rh, 27·4%).

Other complexes were prepared by standard procedures and references are given in the text.

Product Analysis.—Products were not isolated but were identified by combined g.l.c. mass spectrometry. Volatile products were analysed on an F11 gas chromatograph fitted with a flame-ionisation detector and using a 2-m column of 5% OVI-silicone on 85—100 mesh diatomite 'CQ.' In initial experiments, dodecane was used as an external standard, but it was found that dodecane was inert under the reaction conditions and this compound was then used as an internal standard present in reaction mixtures to the extent of 1%.

In the absence of metallic species, polystyrene oxide was estimated using its characteristic n.m.r. band at τ 5·9.

Water Determination.—The water content of solutions was measured on a Pye 104 gas chromatograph fitted with a katharometer detector and using a 2-m column of Porapak Q.

General Procedure.—Typically, a mixture (14 ml) of styrene (2·3 g), tetralin (8·6 g), di-t-butyl-*p*-cresol inhibitor (2·42 g), and the metal catalyst (2×10^{-4} g atom of metal) was saturated with oxygen and then heated at 110 °C under an atmosphere of oxygen. Samples were withdrawn at intervals for analysis.

These reaction conditions were used for all experiments reported in the Results section unless stated otherwise.

Variation of Oxygen Concentration.—Nitrogen–oxygen mixtures were passed through the reactants. It was assumed that the dissolved oxygen was proportional to the fraction of oxygen in the gaseous mixture (Henry's Law).

Experiments with Limited Quantities of Oxygen.—The catalyst was weighed into a 2-ml syringe fitted with a Luer lock and needle. The standard, oxygen-saturated reaction mixture (1 ml) was added, air was excluded from the syringe, and the needle was sealed in a rubber bung. The syringe was plunged into a bath at 110 °C and agitated throughout the reaction (stirring of the solution was assisted by the presence of small glass spheres within the syringe). Samples were removed periodically *via* the needle.

Oxygen Absorption.—Solutions were degassed, and oxygen uptake was measured manometrically. Solid complexes were added to solutions at equilibrium with the gas phase.

RESULTS

Radical Chain Autoxidations.—(i) On oxidation of styrene in tetralin, in the absence of both initiator and inhibitor, a 40 min induction period was observed. After 3 h about a quarter of the styrene had been consumed and the product ratio, polyoxide : benzaldehyde : styrene oxide, was 20 : 4 : 1.

(ii) In the presence of cobalt naphthenate (2.5×10^{-4} g atom) or t-butyl perbenzoate as initiator (5×10^{-4} mol), there was no induction period. After 10 min, *ca.* 0·5 mmol of benzaldehyde and *ca.* 0·1 mmol of styrene oxide had been formed.

In none of these radical-chain autoxidations was acetophenone observed, and in each case the formation of volatile products was completely suppressed by addition of di-t-butyl-*p*-cresol inhibitor (2·42 g).

Reactions with Group VIII Metals.—The styrene–tetralin mixture containing inhibitor was treated under the standard conditions, described in the general procedure, for 16 h in the presence of various metal species. The results are shown in Table 1. Yields of products are expressed in moles per g-atom of metal (turnover number).

TABLE 1

Oxidation of styrene under standard conditions in the presence of various complexes

Complex	Ref.	Product (turnover number)	
		Acetophenone	Benzaldehyde
$[IrCl(CO)(Ph_3P)_2]$	9		
$[IrBr(CO)(Ph_3P)_2]$	9		
$[IrI(CO)(Ph_3P)_2]$	9		
$[\{Ir(C_2H_4)_2Cl\}_2]$	10	1	
$[IrCl(Ph_2PCH_2CH_2PPh_2)_2]$	11		
$[IrCl(C_2H_4)_2(Ph_3P)]$		0·8	
$IrCl_3$			
$RhCl_3{\cdot}3H_2O$			
$RhCl_3$			
$[\{Rh(CO)_2Cl\}_2]$	12	12	4
$[Rh(CO)Cl(Ph_3P)_2]$	13	14	3
$[\{RhCl(C_2H_4)_2\}_2]$	14	17	4
$[RhCl(Ph_3P)_3]$	15	5	2
$[\{RhCl(PhCHCH_2)_2\}_2]$		8	2
$[\{RhCl(cod)\}_2]$	16		
$[Rh(C_2H_4)_2(C_5H_5)]$	17	0·4	
$[Rh(PhCHCH_2)_2(C_5H_5)]$		0·5	
$[Pd(OAc)_2]$		2	0·1
$[Pt(Ph_3P)_2]$	18		
$[RuCl_2(Ph_3P)_3]$	19		2

Reactions with $[\{RhCl(C_2H_4)_2\}_2]$

(i) *Effects of Inhibitor and of Initiator.*—The yields of acetophenone and benzaldehyde responded very differently to the presence of di-t-butyl-*p*-cresol and of t-butyl perbenzoate as is shown in Figures 1 and 2. In these experiments, the volume of each reaction mixture was initially made up to 14 ml by the addition of tetralin in excess of 8·6 g where necessary.

(ii) *Effect of Added Acetophenone.*—Addition of acetophenone (1 mmol) to an oxidation mixture did not alter the rate at which acetophenone and benzaldehyde were formed. Similarly, acetophenone was unchanged by treatment at 110 °C in tetralin with $[\{RhCl(C_2H_4)_2\}_2]$ for 2 h.

(iii) *Effect of Added Styrene Oxide.*—Addition of styrene

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oxide (1 mmol) to an oxidation mixture did not alter the yield of acetophenone. When styrene oxide was heated for 14 h at 110 °C in tetralin in the presence of [$\{RhCl(C_2H_4)_2\}_2$], all the styrene oxide was consumed to yield benzaldehyde (*ca.* 17%), but no acetophenone was observed.

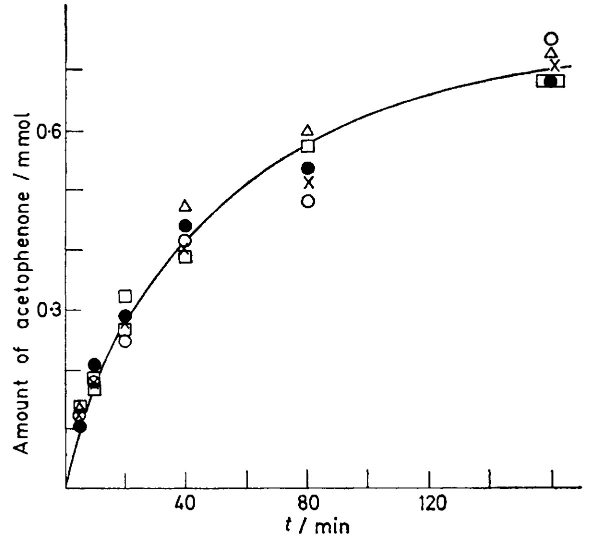

FIGURE 1 Influence of inhibitor on acetophenone formation: ○, no inhibitor; ●, 0·024 g inhibitor; △, 0·24 g inhibitor; □, 2·42 g inhibitor; ×, no inhibitor, 0·1 g t-butyl perbenzoate

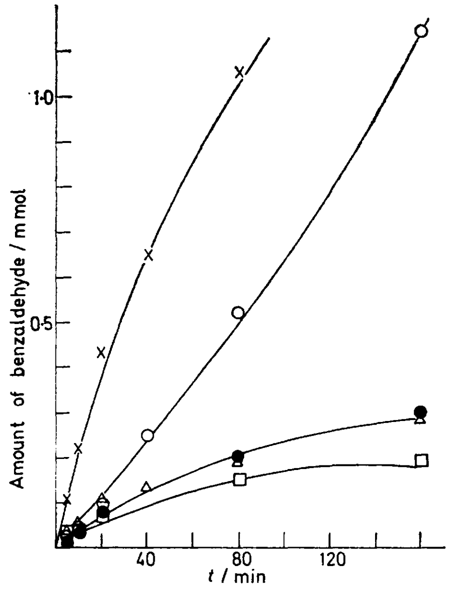

FIGURE 2 Influence of inhibitor on benzaldehyde formation (see legend of Figure 1 for significance of ○, ●, △, □, and ×)

(iv) *Effect of Added Cyclo-octa-*1,5-*diene.*—Addition of cyclo-octa-1,5-diene (cod) (0·2 mmol) to a typical reaction mixture, either before or during reaction, completely suppressed further formation of acetophenone and benzaldehyde. On adding the diene to the already reacting mixture, the solution changed colour from the deep red, always previously observed during successful rhodium-catalysed styrene oxidations, to a yellow-orange similar to that of solutions of [$\{RhCl(cod)\}_2$].

(v) *Role of Water in the Oxidation.*—(a) *Effect of cod on a Wacker oxidation.* Treatment of styrene (5 mmol) with $FeCl_3$ (4 mmol) in the presence of $RhCl_3{\cdot}H_2O$ (0·2 mmol) in oxygen-free dioxan–water mixtures (4 : 1, 14 ml) at 95 °C for 40 h, gave acetophenone (*ca.* 2 mmol), both in the presence and the absence of cod (0·2 mmol).

(b) *Effect of water concentration on rhodium*(I)*-catalysed and on Wacker oxidations.* Rhodium(I)-catalysed oxidation of styrene in oxygen-saturated tetralin gave products in yields independent of water concentration (which was constant during reaction) in the range 0·005 to 0·050%. Reaction of styrene at 95 °C with $RhCl_3$ in aqueous dioxan, and with oxygen catalysed by rhodium(I) in dry dioxan, gave acetophenone as indicated in Figure 3.

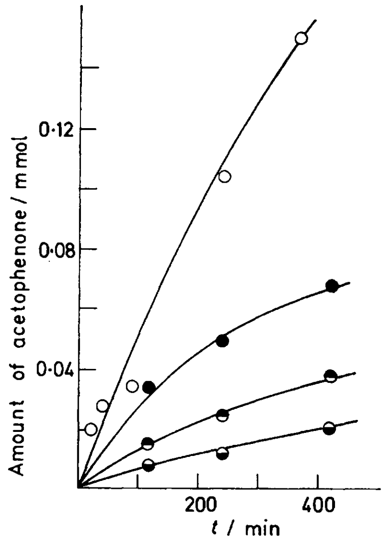

FIGURE 3 Acetophenone formation in aqueous dioxan (14 ml) containing styrene (0·5 ml) and Rh (2 × 10^{-4} g-atom) at 95 °C. ○, [$\{Rh(C_2H_4)_2Cl\}_2$], O_2, 0·1% H_2O; ●, $RhCl_3$, N_2, 28% H_2O; ◒, $RhCl_3$, N_2, 14% H_2O; ◓, $RhCl_3$, N_2, 7% H_2O

(c) *Tracer study.* A mixture of styrene (2·3 g) in tetralin (12 ml), saturated (0·07%) with $H_2{}^{18}O$ (0·6 mmol; 40% ^{18}O), was treated with [$\{RhCl(C_2H_4)_2\}_2$] (4 × 10^{-4} g-atom) under oxygen at 110 °C for 5 min. The resulting acetophenone (0·2 mmol) and benzaldehyde (0·1 mmol) were found to be free of ^{18}O by g.l.c. mass spectrometry, which would have detected a level of 2% of the label.

(vi) *Consumption of Styrene.*—An otherwise typical reaction mixture, but containing only 0·46 g of styrene, was treated at 110 °C and examined for benzaldehyde and acetophenone production and for consumption of styrene. Acetophenone formation was roughly parallel to, but less than, styrene loss; thus, after 60 min of reaction, the ratio of styrene lost to acetophenone formed was 1·7 : 1.

(vii) *Oxygen Absorption Studies.*—(a) *Stoicheiometry.* The rapid evolution (*ca.* 30 s) of ethylene from [$\{RhCl(C_2H_4)_2\}_2$] prevented accurate measurements of oxygen consumption during styrene oxidation, but readings taken after the initial evolution suggested that *ca.* 1 mol of oxygen was absorbed for each mol of acetophenone formed. More accurate values obtained using [$\{RhCl(PhCHCH_2)_2\}_2$] confirmed this stoicheiometry.

(b) *Rhodium–oxygen adducts.* Measurements were made at 33 °C with benzene as solvent. With [$\{RhCl(C_2H_4)_2\}_2$], there was no evidence for adduct formation or ethylene loss. Using [$\{RhCl(PhCHCH_2)_2\}_2$], in both the presence and the absence of added styrene, oxygen was absorbed reversibly during 2 h to give a plateau rhodium-dimer to oxygen ratio of 1·3 : 1. Slow oxidation of styrene in both cases accounted for only *ca.* 10% of the absorbed oxygen.

(viii) *Dependence of the Initial Rate of Acetophenone Production on the Concentration of Reactants.*—Each reactant was varied in turn in otherwise standard reaction mixtures which were heated at 110 °C. From graphs of acetophenone formation *versus* time, initial rates of reaction were estimated. Plots of log (initial rate) *versus* log (concentration of reactant) showed that:

$$\text{Initial rate } \alpha[\text{catalyst}]^{0\cdot98}\ [\text{styrene}]^{1\cdot04}\ [O_2]^{0\cdot8}$$

The linear dependence of the initial rates on the concentrations of catalyst and styrene was confirmed by plots of 1/rate *versus* 1/[reactant]. These plots passed through the origin, but the line resulting from similar treatment of the oxygen data was equivocal and a small positive intercept on the 1/rate axis was indicated. This intercept was confirmed by work using lower catalyst concentrations (10^{-4} g-atom Rh). A plot of 1/rate against the reciprocal of the fraction of oxygen in the gas stream was linear with an intercept of 63·2 ± 10·5 min mmol^{-1} and a slope of 30·1 ± 7·3 min mmol^{-1}.

All the kinetic data for initial rates of reaction conform to the expression

$$\text{Rate} = \frac{C[\text{styrene}][\text{catalyst}][O_2]}{1 + C'[O_2]} \qquad \text{(A)}$$

where C and C' are constants.

A series of reactions was carried out in syringes with limited quantities of oxygen. With $[\{Rh(PhCHCH_2)_2Cl\}_2]$ as the catalyst, and with initial [Rh] : $[O_2]$ ratios of up to *ca.* 15 : 1, it was found that the initial rates of reaction increased linearly with catalyst concentration with a gradient of 0·0060 ± 0·0006 mmol min^{-1} g-atom^{-1} and an intercept of −0·014 ± 0·004 mmol min^{-1}.

(ix) *Decay of Catalyst Activity.*—Using an otherwise standard reaction mixture, but containing $1{\cdot}25 \times 10^{-4}$ g-atom Rh, samples were removed at frequent intervals for analysis. Tangents were drawn to the acetophenone *versus* time curve, and from these tangents the rates of acetophenone formation at various times were estimated. It was found that catalyst activity so determined decayed in a first-order fashion over the first hour of reaction with a half life of 10 ± 1 min.

The effect of the concentrations of styrene and oxygen on the decay of catalyst activity was investigated. To help comparison with the above reaction, it was ensured that the initial rate of acetophenone formation was the same as in this experiment (this was accomplished by increasing the catalyst concentration five times and by reducing the concentration of styrene or of oxygen by the same factor). With the reduced styrene concentration the half-life of the catalyst during the first hour of reaction was *ca.* 13 min, but at reduced oxygen pressure the catalyst had a half-life of *ca.* 60 min.

(x) *Temperature Dependence of Acetophenone Formation.*—Otherwise standard reaction mixtures (14 ml) containing catalyst ($3{\cdot}5 \times 10^{-4}$ mol) were heated under oxygen at temperatures in the range 78—120 °C. Initial rates of acetophenone production were determined from which an activation energy of 70 ± 5 kJ mol^{-1} was calculated. The temperature dependence of benzaldehyde production did not vary appreciably from that of acetophenone.

Substituted Styrenes.—Reaction of various methyl styrenes (0·22 mmol) for 150 min at 110 °C in oxygen-saturated xylene (10 ml) containing inhibitor (2·4 g) and $[\{RhCl(C_2H_4)_2\}_2]$ (2×10^4 g-atom) gave the results shown in Table 2.

TABLE 2

Oxidation of substituted styrenes

Olefin	Product (yield) *
Styrene	PhCHO(1), PhCOMe(4)
o-Methylstyrene	MeC_6H_4CHO(1), MeC_6H_4COMe(3)
p-Methylstyrene	MeC_6H_4CHO(3), $MeC_6H_4COCH_3$(7)
α-Methylstyrene	No products detected
β-Methylstyrene	
cis-Stilbene	
trans-Stilbene	

* Mol/g-atom rhodium.

DISCUSSION

Initially, a number of potential catalysts were screened for activity in promoting the autoxidation of styrene (Table 1). Anhydrous conditions were used to reduce the chance of a Wacker cycle occurring and an inhibitor was added to suppress radical chains. These results were compared with those of typical radical-chain oxidations which gave benzaldehyde, styrene oxide, and polyoxide, but no acetophenone, and which were completely suppressed by addition of an inhibitor. Because catalyst activity decayed gradually, reaction times greater than the 16 h used in this screening study would not have given greatly increased turnover numbers. Various complexes, reported active by Takao,[5,6] were inactive in our study. Certain other complexes, not reported by Takao, were the most active species examined and one of these was chosen for more detailed study. Since tervalent phosphorus is a better oxygen acceptor than are olefins, further work with phosphine-containing species was avoided, and $[\{RhCl(C_2H_4)_2\}_2]$ was selected because this compound was both the most active and structurally the simplest catalyst. Thus, because ethylene is rapidly lost from this catalyst there was no need to determine whether any auxiliary (non-styrene) ligand was oxidised.*

Reactions with $[\{RhCl(C_2H_4)_2\}_2]$.—Since acetophenone was not produced in free-radical autoxidations of styrene, and because its yield in rhodium-catalysed reactions was independent of inhibitor concentration and of the presence of initiator (Figure 1), it was probably formed here by a route not involving a free-radical chain.

Acetophenone is formed from styrene during the Smidt reaction (Wacker Process), and this type of oxidation can be accomplished by rhodium(III) (Scheme 1). Therefore, it is necessary to show that the acetophenone in the catalytic reactions did not arise from

$$\text{Rh}^{I} + \tfrac{1}{2}O_2 + 2H^+ \longrightarrow \text{Rh}^{III} + H_2O \qquad \text{(a)}$$

$$\text{Rh}^{III} + H_2O + \text{olefin} \longrightarrow \text{Rh}^{I} + 2\,H^+ + \text{ketone} \qquad \text{(b)}$$

SCHEME 1

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* The rhodium-promoted oxidation of olefins with simultaneous oxygen transfer to phosphine has been proposed,[20] and we have noted that oxygenated solutions of $[(Ph_3P)(PhCHCH_2)_2IrCl]$ at 70 °C give acetophenone in nearly stoicheiometric yield (based on phosphine in the initial complex).

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

non-oxygen containing rhodium(III) species which were subsequently regenerated by oxygen. Such a species would have had to be formed very rapidly because no induction period was observed in these reactions; on the contrary, acetophenone production was fastest at the beginning of the reaction. Under the driest conditions used, the low and constant level of water (0·005%) was small compared with the acetophenone formed, and, had a Wacker mechanism operated, an average hydrogen ion would have passed through the cycle of Scheme 1 more than a hundred times. In addition, a ten-fold change in water concentration did not affect the rate of reaction under an atmosphere of oxygen, when the oxidation was also insensitive to oxygen concentration. Under these conditions, and in terms of Scheme 1, reaction (a) is not rate-determining, and the driest solutions contained sufficient water to ligate to only a fifth of the rhodium ions. Water is involved [21] in the rate-limiting step of the oxidation of olefins by palladium(II), and ligand water is essential for the rhodium(III) oxidation of ethylene.[22] Moreover, the data of Figure 3 show that production of acetophenone during the oxidation of styrene by rhodium(III) in aqueous dioxan exhibits an approximately first-order dependence on water concentration, and even with the highest water content accessible (28%) the rate is slower than that of a comparable rhodium(I)-catalysed autoxidation in dry dioxan. Furthermore, addition of cyclo-octa-1,5-diene in quantities sufficient to suppress the rhodium catalysis had no effect on a ferric ion-powered Wacker oxidation.

Finally, following a catalysed oxidation accomplished in the presence of $H_2{}^{18}O$, no label was detected in the organic products. Assumption that any water formed during step (a) would mix with the labelled water indicates that less than 7% of the carbonyl products resulted from a Wacker reaction. Thus, several independent results show that a Wacker mechanism does not contribute appreciably to the oxidation.

Benzaldehyde was not formed during an authentic Wacker oxidation but was formed during radical autoxidation. Moderate concentrations of inhibitor markedly reduced the benzaldehyde yield, but to a level similar to that achieved by 100 times that level of inhibitor (Figure 2). This residual yield was completely suppressed by the addition of cyclo-octa-1,5-diene. It appears that both acetophenone and the residual benzaldehyde result from a novel metal-centred oxidation.

The yields of acetophenone and of benzaldehyde were not linear functions of time, and the possibilities of catalyst poisoning by product or of product decomposition suggest themselves. However, the data of Figures 1 and 2 show that acetophenone production is insensitive to the presence of benzaldehyde, and addition of acetophenone to a typical oxidation mixture did not affect the course of reaction.

That acetophenone is not a decomposition product of initially formed styrene oxide was shown by addition of the latter to a reaction mixture, when benzaldehyde (*ca.* 17%) but no acetophenone was produced.

Table 1 shows that various complexes known to bind oxygen were not active, so co-ordination of oxygen alone is insufficient for reaction. In addition, iridium analogues of active rhodium complexes were ineffective, and this is possibly related to their greater stability. Moreover, the activity, or lack of it, displayed by the various rhodium complexes accords with the notion of a metal-centred oxygenation. The active complexes conceivably could yield intermediates in which oxygen and styrene are simultaneously co-ordinated to the metal, so the inactive rhodium complexes are of interest. Nixon and Pinkerton observed [23] that $[Rh(C_2H_4)_2(C_5H_5)]$ was inert to substitution by various ligands and this was attributed to the metal having an inert gas (18 electron) configuration whilst each analogous square-planar (16 electron) complex has a vacant orbital available to an incoming ligand, and these latter complexes frequently undergo ready substitution. On this basis, the inactivity of $[Rh(C_2H_4)_2(C_5H_5)]$ could be attributed to the inability of styrene to bind to the rhodium. However, that co-ordination of styrene, by itself, is insufficient for reaction is shown by the inactivity of $[Rh(PhCHCH_2)_2(C_5H_5)]$. Following the reasoning given above, this complex has no vacant orbital to accommodate an attacking oxygen. However, not all 16-electron rhodium species are active as was demonstrated by $[\{RhCl(cod)\}_2]$. Not only was this complex inactive, but addition of cod to a reacting mixture prevented further oxidation, and the associated colour change of the solution suggests that cod co-ordinated to the otherwise active rhodium. These observations strongly support the idea that acetophenone and residual benzaldehyde are produced at the metal centre. The inactivity of $[\{RhCl(cod)\}_2]$ is attributed to its stability and the resulting inability of the reactants to co-ordinate to the complex.* On heating a reaction mixture containing this species to 170 °C, however, acetophenone was produced with a turnover number of 15 within 25 h. Presumably, cod can be displaced at this temperature; its presence in solution was indicated by g.l.c.

Stoicheiometry of the Reaction.—In most of the experiments the conversion of styrene was of the order of only a few percent, and it was not possible to measure the consumption of styrene accurately. With an otherwise typical reaction mixture, but containing only one fifth of the usual quantity of styrene, it was found that *ca.* 1·7 styrene molecules were used for each acetophenone produced.

Although the rapid evolution of ethylene from $[\{RhCl(C_2H_4)_2\}_2]$ prevented accurate measurements of

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* N.m.r. spectroscopy showed this complex to be stable in styrene at 110 °C.

[21] P. H. Henry, *J. Amer. Chem. Soc.*, 1964, **86**, 3246.

[22] B. R. James and M. Kastner, *Canad. J. Chem.*, 1972, **50**, 1698, 1708.

[23] J. F. Nixon and A. A. Pinkerton, *J. Organometallic Chem.*, 1972, **37**, C47.

oxygen consumption during styrene oxidation, readings taken after the initial ethylene evolution suggested that *ca.* 1 mol of oxygen was absorbed for each mol of acetophenone produced. This ratio was confirmed using $[\{RhCl(PhCHCH_2)_2\}_2]$ which probably yields the same species in solution (see below). Thus, only about half the oxygen and styrene consumed appear as products. Permanent co-ordination to the rhodium cannot account for all the 'missing' styrene and oxygen. The instability of styrene oxide suggests that it may have been the precursor of residual benzaldehyde. Styrene oxide, formed at the metal centre in yield comparable to acetophenone, would have decomposed to benzaldehyde (*ca.* 17%) and polymer,[24] and would have led to the observed stoicheiometry.

Co-ordination to Rhodium.—The envisaged mechanism of oxygenation requires the entrance of both styrene and oxygen into the co-ordination sphere of the metal, and evidence was obtained for co-ordination of each reactant under conditions approaching those for reaction. At 110 °C, n.m.r. spectroscopy of oxygen-free solutions containing styrene and either $[\{RhCl(C_2H_4)_2\}_2]$ or $[\{RhCl(PhCHCH_2)_2\}_2]$ showed broad bands, centred at τ 3·5, 4·5, and 5·0, indicative of fast exchange between free and bound styrene. At 33 °C, oxygen uptake by $[\{RhCl(PhCHCH_2)_2\}_2]$ solutions pointed to the partial formation of a reversible 1 : 1 rhodium–oxygen adduct.

Reaction Kinetics.—Further support for the idea that acetophenone is formed in a metal-centred reaction of styrene with oxygen comes from the reaction kinetics. Since catalyst activity decayed gradually, ***initial*** rates only were considered. The initial rate of acetophenone production increases approximately linearly with increases in the concentrations of catalyst, styrene, and oxygen. This points to the coming together of molecules of two of the reactants to form a species which subsequently meets the third reactant and yields acetophenone. This process is represented by the sequence:

$$X + Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} XY$$

$$XY + Z \xrightarrow{k_2} P + \text{catalyst}$$

where P is the product (acetophenone) but X, Y, and Z have yet to be identified with the various reactants. Analysis of this scheme, using the steady-state approximation, neglecting regeneration of the catalyst, and with assumption that [Y] always approximated to $[Y_0]$, the initial value, yields expression (B),

$$\frac{d[P]}{dt} = \frac{k_2K[X][Y][Z]}{1 + K[Y] + k_2[Z]/k_{-1}} \qquad (B)$$

where $K \equiv k_1/k_{-1}$.

This expression agrees with the observed dependence of rate on reaction concentrations, equation (A), and, since only $[O_2]$ appears in the denominator of (A), oxygen can be identified with either Y or Z. The assumption concerning $[Y] \approx [Y_0]$ is reasonable since conditions were selected such that catalyst could not function as Y irrespective of whether styrene or oxygen acted as X. This was accomplished by using a large molar excess of styrene and by maintaining $[O_2]$ by continuous passage of oxygen-containing gases through the reaction solutions. Thus, catalyst was either X or Z. Had catalyst been Z, the rate could not have reached a plateau value with increase in $[O_2]$ because this could have resulted only if most of the styrene was present as an adduct (XY) with oxygen, and styrene shows no significant tendency to complex with oxygen. Therefore, X $\equiv$ catalyst, but the data so far presented do not allow the unambiguous identification of Y and Z. The observed kinetics result if either (i) at high $[O_2]$ a substantial fraction of catalyst forms an adduct with oxygen and the adduct reacts with styrene in the rate-limiting step, or (ii) the first step is a slow formation of a catalyst–styrene adduct which becomes rate-determining at high $[O_2]$.

The sequence of events in a related metal-centred oxidation has been determined[25] by studies of structurally similar substrates. This procedure is not applicable to the styrene oxidation because the catalytic species probably contains styrene and so would change as the olefin was varied. An alternative method is available. While oxygen plays a unique role in sequence (ii), in sequence (i) it would be expected that either $[O_2]$ or [catalyst] might appear in the denominator depending only on whether oxygen or catalyst was obliged to function as Y. Thus, if the reaction followed path (i), in the presence of only a limited quantity of oxygen, the rate would approach a plateau value with increasing [catalyst].

To limit the available oxygen, reactions were carried out within syringes with solutions previously saturated with oxygen. This technique eliminated the presence of gases in contact with the reaction mixtures, so the only oxygen available was that initially present in the aromatic solvent (*ca.* 8×10^{-3} mol l^{-1} *). With initial [rhodium] : $[O_2]$ ratios of up to 15, the rate of acetophenone formation remained a linear function of catalyst concentration. If all the rhodium complex yields catalytic species, sequence (i) is not tenable, and on this basis we suggest that the reaction sequence (ii) (Scheme 2) operates. Using this scheme, $k_1 = 2{\cdot}2 \times 10^{-3}$ l mol^{-1} s^{-1} and $k_{-1}/k_2 = 4 \times 10^{-3}$ mol l^{-1}.

$$\text{catalyst} + \text{styrene} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{catalyst–styrene}$$

$$\text{catalyst–styrene} + O_2 \xrightarrow{k_2} \text{products} + \text{catalyst}$$

SCHEME 2

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* This value was not measured but corresponds to literature values[26] of the solubility of O_2 in tetralin at 10—70 °C. The high boiling point of tetralin ensures that the solubilities of gases in this solvent at temperatures near 100 °C are not greatly temperature dependent.

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Temperature Dependence.—The slope of the Arrhenius plot corresponds to an activation energy of 70 kJ mol^{-1}. Because solutions were saturated with oxygen, when the rate is insensitive to oxygen pressure, this activation energy probably approximates to that necessary for the formation of the catalyst–styrene adduct of Scheme 2. Since the yields of both acetophenone and residual benzaldehyde responded similarly to changes of temperature and of reactant concentration, these products probably arise by oxidation of the same rhodium–styrene adduct. The marked temperature dependence of the reaction resolves the apparent conflict between two previous reports. Our findings broadly agree with those of Takao *et al.*[6] at 110 °C, and extrapolation of the results shows that the metal-centred oxygenation is very slow at 70 °C, the temperature used by Lyons and Turner.[8]

Decay of Catalyst Activity.—During the first hour of reaction at 110 °C, the activity of the catalyst decays in a first-order manner with a half-life which is insensitive to styrene concentration but which increases markedly with decrease in oxygen pressure. This suggests that the catalyst is deactivated oxidatively, but attempts to regenerate the spent catalyst with reducing agents were unsuccessful.

Steric Requirements.—Substitution of a methyl group on the aromatic nucleus does not greatly affect the oxidation, but substitution at the olefinic positions renders the resulting styrene unreactive (Table 2).

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