Reactions Involving Transition Metals. Part VIII.^{1,2} Decomposition of Hydroperoxides catalysed by Iridium(1) and by Rhodium(1) Complexes

By Brian L. Booth, Robert N. Haszeldine,* and Geoffrey R. H. Neuss, Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester, M60 1QD

The complexes IrCl(CO)(PPh₃)₂ and RhCl(PPh₃)₃ catalyse decomposition of the hydroperoxides PhMe₂C·OOH and Me₃C·OOH to oxygen and the corresponding alcohols. Decomposition of Me₃C·OOH by IrCl(CO) (PPh₃)₂ is completely inhibited by phenol present in a molar ratio of phenol : iridium(i) complex of ≥ 5 : 1. 2.6-Di-t-butylp-cresol causes an induction period, the length of which varies with the cresol concentration, but thereafter the rate of decomposition is equivalent to that observed in the absence of inhibitor. Low concentrations of pyridine also inhibit this reaction. while similar concentrations of anisole and 2.6-lutidine are ineffective. The results are discussed in terms of a homolytic decomposition pathway in which co-ordination of the hydroperoxide to the metal atom is an important first step.

MANY d^8 and d^{10} transition metal complexes have been found to catalyse the homogeneous autoxidation of aralkyl or olefinic hydrocarbons.³ The highest yields of oxidation products are usually found with the rhodium(I) complexes RhCl(PPh₃)₃⁴⁻¹⁰ or RhCl(CO)-(PPh₃)₂,^{11,12} although other complexes such as PtO₂- $(PPh_3)_2$,⁴ Pt $(PPh_3)_4$,¹³ IrCl $(N_2)(PPh_3)_2$,⁴ IrX $(CO)(PPh_3)_2$ (X = I⁴ or Cl^{9,11-14}), Ru $(O_2)(NCS)(NO)(PPh_3)_2$,¹⁵ and RuCl₂(PPh₃)₃^{12, 16} also show catalytic activity. Various mechanisms have been proposed for these reactions, and in some cases there is some evidence to suggest that oxidation occurs via metal-dioxygen compounds.4,10,12 In the majority of reactions investigated, however, it appears that the function of the transition metal complex is to catalyse the decomposition of hydroperoxide impurities in the organic substrate, thus forming radicals which initiate autoxidation. If the organic starting material is rigorously purified, or if a radical trapping agent is added, oxidation is retarded or inhibited.9,12,14,17

Prior to this investigation the reactions of hydroperoxides with d^8 or d^{10} metal complexes had not been reported. Recently, however, several workers have mentioned briefly that complexes such as IrCl(CO)- $(PPh_3)_2$ and $Pd(PPh_3)_4$ cause the decomposition of α, α -dimethylbenzyl and t-butyl hydroperoxides.¹²⁻¹⁴ We now report some more detailed observations on the decomposition of hydroperoxides catalysed by complexes of the type trans-MX(CO)(PPh₃)₂ (M = Rh or Ir, X = Cl, Br, or I).

When aa-dimethylbenzyl hydroperoxide was added to a catalytic amount of trans-IrCl(CO)(PPh₃)₂ (molar ratio of hydroperoxide : catalyst 78:1), in the absence of any solvent, a rapid exothermic reaction occurred to give 2-phenylpropan-2-ol as the major product, together with traces of acetophenone and a-methyl-¹ Part VII, R. N. Haszeldine, R. J. Lunt, and R. V. Parish,

J. Chem. Soc. (A), 1971, 3711. ² Preliminary communication, B. L. Booth, R. N. Haszeldine,

and G. R. H. Neuss, J.C.S. Chem. Comm., 1972, 1074. ³ R. Jira and W. Freiesleben, Organometallic Reactions, 1972,

8, 1. ⁴ J. P. Collman, M. Kubota, and J. W. Hosking. J. Amer.

Chem. Soc., 1967, 89, 4809. ⁵ J. Blum, H. Rosenman, and E. D. Bergmann, Tetrahedron

Letters, 1967, 3665.

V. P. Kurkov, J. Z. Pasky, and J. B. Lavigne, J. Amer.

Chem. Soc., 1968, 90, 4743. ⁷ J. Blum, J. Y. Becker, H. Rosenman, and E. D. Bergmann, *J. Chem. Soc.* (B), 1969, 1000. ⁸ A. J. Birch and G. S. R. Subba Rao, *Tetrahedron Letters*, 1968, 2917.

styrene, and the evolution of oxygen. The gaseous product was characterised by molecular weight measurement (Regnault's method) and by mass spectrometry, and was shown definitely to be oxygen, rather than carbon dioxide, which was previously reported 13 to be the major gaseous product of this reaction. A quantitative estimation of the oxygen evolution has established the stoicheiometry:

$$2PhMe_2C \cdot OOH \longrightarrow 2PhMe_2COH + O_2$$

No $IrCl(CO)(PPh_3)_2$ could be detected at the end of the reaction, and an impure green residue obtained after removal of the organic products showed a weak band in its i.r. spectrum at $ca. 2050 \text{ cm}^{-1}$ indicative of an iridium(III)-carbonyl complex.

t-Butyl hydroperoxide, which contained 30% di-tbutyl peroxide, also reacted with IrCl(CO)(PPh₃)₂ (molar ratio 112:1) to give oxygen and t-butyl alcohol according to the above stoicheiometry and in agreement with previous findings.¹² A control experiment confirmed that pure di-t-butyl peroxide is completely unaffected by IrCl(CO)(PPh₃)₂ under similar conditions. The solid residue recovered after reaction of the hydroperoxide again showed a weak i.r. band at ca. 2050 cm⁻¹ corresponding to an iridium(III)-carbonyl species. The decomposition of aa-dimethylbenzyl and t-butyl hydroperoxides to oxygen and the corresponding alcohols also occurs in the presence of RhCl(PPh₃)₃, although at a much reduced rate (see Table).

An interesting effect was observed when phenols were added to the mixtures of t-butyl hydroperoxide and $IrCl(CO)(PPh_3)_2$. In order to ensure homogeneity these reactions were carried out in benzene solution at 295 ± 1 K with a molar ratio of hydroperoxide to

9 A. Fusi, R. Ugo, F. Fox, A. Pasini, and S. Cenini, J. Organometallic Chem., 1971, 28, 417. ¹⁰ K. Takao, M. Wayaku, Y. Fujiwara, T. Imanaka, and S.

Teranishi, Bull. Chem. Soc. Japan, 1970, 43. 3898: 1972, 45. 1505; K. Takao, H. Azuma, Y. Fujiwara, T. Imanaka, and S. Tera-

nishi, *ibid.*, 1972, **45**, 2003. ¹¹ L. W. Fine, M. Grayson, and V. H. Suggs, *J. Organometallic Chem.*, 1970, **22**, 219.

J. E. Lyons and J. O. Turner, J. Org. Chem., 1972. 37, 2881.
E. W. Stern, Chem. Comm., 1970, 736.

 ¹⁴ R. A. Sheldon, *Chem. Comm.*, 1971, 788.
¹⁵ B. W. Graham, K. R. Laing, C. J. O'Connor, and W. R. Roper, J.C.S. Dalton. 1972, 1237. ¹⁸ S. Cenini, A. Fusi, and G. Capparella, Inorg. Nuclear Chem.

Letters, 1972, 8, 127.

¹⁷ J. E. Lyons and J. O. Turner, Tetrahedron Letters, 1972, 2903.

catalyst of ca. 300:1. Under these standard conditions, and in the absence of phenol, the hydroperoxide decomposed smoothly over 3 h to give t-butyl alcohol

Decompositio	n of hydroperoxide	es by transit	ion metal
	complexes		
	•	Time taken	
		for	O,
Hydro-		evolution	[mmol,
peroxide		of O ₂	conversion
(mmol)	Complex (mmol)	(min)	(%)]
ButOOH	IrCl(CO)(PPh _s),	70	$3 \cdot 20$ (83)
(7.6)	(0.64)		. ,
ButOÓH	IrCl(CO)(PPh _a) ₂	100	2.50(80)
(6-4)	(0.13)		
PhMe ₂ C·ÓOH	IrCl(ĊO)(PPh ₃) ₂	20	0.94 (76)
(2.5)	(0.13)		
ButOOH	RhCl(PPh ₃) ₃	480	$2 \cdot 15$ (50)
(8 ⋅ 6)	(0.11)		
PhMe ₂ C·OOH	RhCl(PPh ₃) ₃	210	1.77 (77)
(4 ·6)	(0.05)		

and oxygen (81%) according to the stoicheiometry established previously for the reactions carried out in the absence of benzene. Addition of phenol in the ratio



of phenol: catalyst $\geq 5:1$ resulted in the complete inhibition of oxygen evolution over the same time period, while with phenol: catalyst ratios of $\leq 2:1$ slow evolution of oxygen occurred over 19 h. Even with a phenol: catalyst ratio of 1:10 the rate of oxygen evolution was markedly slower (see Figure 1). A control experiment established that a 1:1 mixture of phenol and IrCl(CO)(PPh₃)₂ in benzene shows no changes in its i.r. spectrum after 2 h at room temperature, and the starting materials are recovered unchanged after this period.

One explanation of these results is that iridium(I)catalysed decomposition of t-butyl hydroperoxide occurs by a homolytic mechanism, and that the phenol simply acts as a scavenger of t-butylperoxyl and t-butoxyl radicals. The action of the phenol must, however, be more complex than this, since the addition of 2,6-di-tbutyl-*p*-cresol in the ratio of cresol : catalyst of 4.5 : 1 to the reaction of Bu^tOOH and IrCl(CO)(PPh₃)₂ under similar conditions, caused complete inhibition of reaction for a period of 15 min, but thereafter oxygen evolution took place at a rate comparable to that which occurred in the absence of added cresol. When the ratio of the cresol to catalyst was increased to 10:1 the induction period correspondingly increased to 90 min before oxygen evolution commenced (see Figure 2).



FIGURE 2 Effect of 2,6-di-t-butyl-*p*-cresol on the decomposition of Me₃C·OOH by IrCl(CO)(PPh₃)₂: A, in the absence of cresol; B, cresol (1·15 × 10⁻⁴ mol), cresol : Ir^I complex $4\cdot5:1$; C, cresol (2·56 × 10⁻⁴ mol), cresol : Ir^I complex 10:1

These results are apparently paradoxical in that 2,6di-t-butyl-*p*-cresol, which is known ¹⁸ to be a far better scavenger of peroxyl and alkoxyl radicals than phenol, causes only temporary inhibition unlike phenol which inhibits reaction completely.

Other compounds have been investigated as inhibitors for hydroperoxide decomposition, including anisole, which has no effect on oxygen evolution even when present in a 100:1 excess over $IrCl(CO)(PPh_3)_2$. On the other hand, a similar excess of pyridine over the iridium catalyst greatly reduced the rate of hydroperoxide decomposition, and even a pyridine : catalyst



FIGURE 3 Effect of pyridines on the decomposition of Me₃C-OOH by IrCl(CO)(PPh₃)₂: A, in the absence of inhibitor; B, 2,6-butidine (2.56 \times 10⁻⁴ mol), butidine: Ir^I complex 10: 1; C, 2,6-butidine (2.56 \times 10⁻³ mol), butidine: Ir^I complex 100: 1; D, pyridine (2.56 \times 10⁻⁴ mol), pyridine: Ir^I complex 100: 1; E, pyridine (2.56 \times 10⁻³ mol), pyridine: Ir^I complex 100: 1; E, pyridine (2.56 \times 10⁻³ mol), pyridine: Ir^I complex 100: 1; C, pyridine (2.56 \times 10⁻³ mol), pyridine: Ir^I complex 100: 1; E, pyridine (2.56 \times 10⁻³ mol), pyridine: Ir^I complex 100: 1; E, pyridine (2.56 \times 10⁻³ mol), pyridine: Ir^I complex 100: 1; E, pyridine (2.56 \times 10⁻³ mol), pyridine: Ir^I complex 100: 1; E, pyridine (2.56 \times 10⁻³ mol), pyridine: Ir^I complex 100: 1; E, pyridine (2.56 \times 10⁻³ mol), pyridine: Ir^I complex 100: 1; E, pyridine (2.56 \times 10⁻³ mol), pyridine: Ir^I complex 100: 1; E, pyridine (2.56 \times 10⁻³ mol), pyridine: Ir^I complex 100: 1; E, pyridine (2.56 \times 10⁻³ mol), pyridine: Ir^I complex 100: 1; E, pyridine (2.56 \times 10⁻³ mol), pyridine: Ir^I complex 100: 1; E, pyridine (2.56 \times 10⁻³ mol), pyridine: Ir^I complex 100: 1; E, pyridine (2.56 \times 10⁻³ mol), pyridine: Ir^I complex 100: 1; E, pyridine (2.56 \times 10⁻³ mol), pyridine: Ir^I complex 100: 1; E, pyridine (2.56 \times 10⁻³ mol), pyridine: Ir^I complex 100: 1; E, pyridine (2.56 \times 10⁻³ mol), pyridine: Ir^I complex 100: 1; E, pyridine (2.56 \times 10⁻³ mol), pyridine: Ir^I complex 100: 1; E, pyridine (2.56 \times 10⁻³ mol), pyridine: Ir^I complex 100: 1; E, pyridine (2.56 \times 10⁻³ mol), pyridine: Ir^I complex 100: 1; E, pyridine (2.56 \times 10⁻³ mol), pyridine (2.56 \times 10

ratio of 10:1 caused a considerable retardation in reaction rate. 2,6-Lutidine has a much less marked ¹⁸ G. Scott, 'Atmospheric Oxidation and Antioxidants,' Elsevier, Amsterdam, 1965. effect, even when using a ratio of lutidine : catalyst of 100:1 (see Figure 3). The possibility that the oxygen adduct IrCl(CO)(PPh₃)₂O₂ may be important in these reactions can be discounted, since no reaction occurs between the oxygen adduct and Bu^tOOH in benzene over a period of several hours.

DISCUSSION

Both bis-(1,10-phenanthroline)copper(II)¹⁹ and lead tetra-acetate²⁰ are known to cause decomposition of aa-dimethylbenzyl and t-butyl peroxides into oxygen and the corresponding alcohols. There is sound evidence that in these reactions decomposition takes place by the initial formation of alkylperoxyl radicals, formed according to the general Haber-Weiss equation, and these then undergo a bimolecular self-reaction to alkoxyl radicals (and hence alcohols) and oxygen.^{21, 22} At room temperature there is evidence to suggest that this bimolecular reaction affords an unstable tetraoxide intermediate, which can decompose to alkoxyl radicals or a peroxide, the ratio of these products depending upon the rate of diffusion of the alkoxyl radicals from the solvent cage (see Scheme 1), which in turn is dependent upon solvent viscosity and temperature.^{21, 22}

 $2ROOH + 2M^{(x+1)+} - 2ROO^{-} + 2M^{x+} + H^{+}$ $2ROO: [ROOOOR] \longrightarrow [RO + O_2 + OR] cage$ $2ROO: \frac{2ROOH}{2ROO} = 2ROO + O_2$ ROOR + 02 2R00 $2R0 + 0_{2}$ + 2 ROH

SCHEME 1

It seems reasonable to assume from our work, and that of others, that the decomposition of hydroperoxides by d^8 rhodium(I) and iridium(I) complexes also involves alkylperoxyl radical intermediates. In benzene or the hydroperoxide itself, which are both low viscosity solvents, the rate of formation of peroxide will be relatively unimportant compared with the rate of diffusion of the alkoxyl radicals from the solvent cage ²¹ and alcohol formation might be expected to predominate, as is found in the reactions with IrCl(CO)(PPh₃)₂. It is possible that a small amount of peroxide is also formed, but this would be difficult to detect especially in the reaction using Bu^tOOH, which was contaminated with 30% Bu^tOOBu^t impurity.

The origin of the alkylperoxyl radicals from the alkyl hydroperoxides when iridium(I) or rhodium(I) catalysts are used requires some consideration, since these metals are already in their lowest stable oxidation state and redox mechanisms proposed for the copper(II) and lead(IV) catalysed reactions cannot be applicable. It is possible, however, that reaction is initiated by alkoxyl radicals formed according to the reactions in Scheme 2.

¹⁹ H. Berger and A. F. Bickel, Trans. Faraday Soc., 1961, 57, 1325.

²⁰ H. Hock and H. Kropf, Chem. Ber., 1958, 91, 1681.
²¹ D. Lindsay, J. A. Howard, E. C. Horswill, L. Iton, K. U. Ingold, 'T. Cobbley, and A. II', Canad. J. Chem., 1973, 51, 870.

It should be noted that the metal complex is only required to produce the first few alkylperoxyl radicals,

$$ROOH + M^{II} \longrightarrow RO \cdot + M^{II} + -OH$$
$$ROOH + M^{II} \longrightarrow ROO \cdot + M^{II} + H^{+}$$
$$RO \cdot + ROOH \longrightarrow ROH + ROO \cdot$$
$$SCHEME 2$$

and thereafter subsequent decomposition of the hydroperoxide can be autocatalytic and follow the pathway outlined in Scheme 1. The fact that the iridium(I) catalyst is eventually transformed into an iridium(III) species is probably not mechanistically significant, as hydroperoxides have been shown to form diperoxyiridium(III) complexes with IrCl(CO)(PPh₃)₂ by a side reaction;² these complexes do not catalyse the breakdown of hydroperoxides.

The temporary inhibition of hydroperoxide decomposition caused by addition of 2,6-di-t-butyl-p-cresol is explained by assuming that the cresol does not prevent the initial formation of alkylperoxyl radicals by reaction of the hydroperoxide with the iridium(I) complex, but once formed these radicals are efficiently scavenged by the cresol before decomposition to alkoxyl radicals and autocatalysis can occur. When all the cresol is consumed in this way, decomposition of the hydroperoxide proceeds at the same rate as the uninhibited reaction. In agreement with this idea, an increase in the amount of cresol inhibitor causes an increase in the inhibition period but does not affect the rate of oxygen evolution once decomposition commences. The action of phenol is rather different, in that, despite the fact that it is a poorer scavenger for alkylperoxyl radicals than 2,6-di-tbutyl-p-cresol, it is capable of completely inhibiting the reaction. This suggests that an important prerequisite for hydroperoxide decomposition by an iridium(I) or rhodium(I) complex may be the availability of a vacant co-ordination site on the metal atom, and that the inhibitory action of phenol may be to block this site by co-ordination to the metal atom via the lone-pair electrons on the oxygen atom. The equilibrium

 $IrCl(CO)(PPh_3)_2 + PhOH \implies (PhOH)IrCl(CO)(PPh_3)_2$

probably favours the four co-ordinate species, and with molar ratios of phenol: iridium(I) complex of 5:1, sufficient IrCl(CO)(PPh₃)₂ is evidently present in solution to cause some hydroperoxide decomposition, but at a much reduced rate due, in part, to the reduced rate of metal-catalysed initiation and also, to some extent, to the radical scavenging effect of the phenol. An examination of molecular models has shown that with 2,6-di-t-butyl-p-cresol the non-bonding interaction between the bulky ortho-butyl groups and the triphenylphosphine ligands on the metal atom prevents coordination of the phenolic oxygen to the metal atom and limits the inhibitory action of the cresol to radical scavenging. With anisole the presence of the methyl

²² J. E. Bennett and J. A. Howard, J. Amer. Chem. Soc., 1973, 95, 4008; A. Factor, C. A. Russell, and T. G. Traylor, *ibid.*, 1965, 87, 3692; R. Hiatt and T. G. Traylor, *ibid.*, p. 3766.

group attached to oxygen is again sufficient to prevent co-ordination.

Some support for these assumptions comes from the experiments carried out using pyridine and 2,6-lutidine. Pyridine, unlike phenol or 2,6-di-t-butyl-p-cresol, is not a scavenger for alkylperoxyl radicals and yet it is an efficient inhibitor of hydroperoxide decomposition in agreement with the idea that inhibition can be caused by blocking of the co-ordination site on the metal atom. With 2,6-lutidine, the methyl substituents prevent co-ordination of the nitrogen atom to iridium, and this compound has little effect on the rate of decomposition of the hydroperoxide even at high concentrations.

Kaneda *et al.*²³ have recently reported that pyridine or triphenylphosphine oxide depress the rate of the RhCl(PPh)₃-catalysed oxidation of cyclohexene. They attribute this to prevention of oxygen co-ordination to the rhodium atom, but our results suggest that prevention of co-ordination of cyclohexenyl hydroperoxide is an alternative explanation.

EXPERIMENTAL

t-Butyl hydroperoxide was a practical sample containing 30% di-t-butyl peroxide, which was dried and used as supplied. $\alpha\alpha$ -Dimethylbenzyl hydroperoxide, which contained *ca*. 17% cumene, was dried and filtered to remove the sodium hydrogen carbonate added as a stabiliser. *trans*-Chlorocarbonylbis(triphenylphosphine)iridium(1),⁷ and chlorotris(triphenylphosphine)rhodium(1) ²⁴ were prepared and purified by literature methods.

Reaction of $\alpha\alpha$ -Dimethylbenzyl Hydroperoxide with trans-IrCl(CO)(PPh₃)₂.—Dry $\alpha\alpha$ -dimethylbenzyl hydroperoxide (4.01 g, 21.9 mmol) was added dropwise over 2 h to crystals of trans-chlorocarbonylbis(triphenylphosphine)iridium(I) (0.23 g, 0.28 mmol) stirred at 20° in vacuo. The volatile products were condensed in a trap at -78° and oxygen (0.25 g, 7.81 mmol, 71%) was adsorbed onto charcoal at -196° , and identified by mass spectrometry and molecular weight determination. G.l.c. and mass spectrometry of the organic products from the trap and the reaction flask revealed unchanged cumene (0.68 g, 5.66 mmol, 100%)

²³ K. Kaneda, T. Itoh, X. Fujiwara, and S. Teranishi. Bull. Chem. Soc. Japan, 1973. **48**. 3810. recovery), α -methylstyrene (0.07 g, 0.59 mmol, 3%), and a mixture of acetophenone and 2-phenylpropan-2-ol (3.01 g), which could not be satisfactorily separated but was shown by i.r. spectroscopy to consist mainly of the alcohol. Removal of the organic materials by pumping for several hours at 60° *in vacuo* gave a sticky green residue which showed a weak metal carbonyl absorption at 2050 cm⁻¹ in the i.r. spectrum.

Catalytic Decomposition of Hydroperoxides by Transition Metal Complexes.—(a) In the absence of solvent. Weighed crystals of the transition metal complex were placed in a 3-necked flask (50 ml) which was fitted with a thermometer and a rubber serum cap and contained a magnetic stirrer, and one neck was connected to a mercury manometer. A known weight of hydroperoxide was then injected via the serum cap and the total volume of oxygen evolved was measured at constant pressure, until no further change had occurred for at least 0.25 h. The results are given in the Table.

(b) In benzene solution. t-Butyl hydroperoxide (0.90 g practical sample; *ca*. 7.0 mmol) was added to *trans*-chlorocarbonylbis(triphenylphosphine)iridium(I) (0.10 g, 0.13 mmol) in benzene (10 ml) to give oxygen (2.76 mmol).

(c) In the presence of phenols, anisole, and pyridines. The apparatus consisted of a 3-necked 100 ml flask fitted with a swivel tip-head, a thermometer, and connected to a vacuum line containing a capillary tube mercury manometer. A benzene solution (10 ml) of trans-chlorocarbonylbis(triphenylphosphine)iridium(I) (0.02 g, 2.5×10^{-5} mol) and a benzene solution of the phenol, anisole, or pyridine in the required concentration (10 ml) were pipetted into the flask. t-Butyl hydroperoxide (1.00 g practical sample); ca. 7.8 mmol) and benzene (5 ml) were placed in the tiphead. The system (total volume 232 cm³) was then evacuated and left stirring for 0.5 h to equilibrate at a temperature of 295 + 1 K. After this time the contents of the tip-head were added, and the oxygen evolution was recorded at various time intervals. The results are presented graphically in Figures 1-3.

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²⁴ J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.* (A), 1966, 1711.