

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

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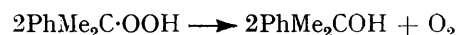
The complexes $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ and $\text{RhCl}(\text{PPh}_3)_3$ catalyse decomposition of the hydroperoxides $\text{PhMe}_2\text{C}\cdot\text{OOH}$ and $\text{Me}_3\text{C}\cdot\text{OOH}$ to oxygen and the corresponding alcohols. Decomposition of $\text{Me}_3\text{C}\cdot\text{OOH}$ by $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ is completely inhibited by phenol present in a molar ratio of phenol : iridium(I) complex of $\geq 5 : 1$. 2,6-Di-*t*-butyl-*p*-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 $\text{RhCl}(\text{PPh}_3)_3$ ⁴⁻¹⁰ or $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$,^{11,12} although other complexes such as $\text{PtO}_2(\text{PPh}_3)_2$,⁴ $\text{Pt}(\text{PPh}_3)_4$,¹³ $\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2$,⁴ $\text{IrX}(\text{CO})(\text{PPh}_3)_2$ ($\text{X} = \text{I}^4$ or $\text{Cl}^{9,11-14}$), $\text{Ru}(\text{O}_2)(\text{NCS})(\text{NO})(\text{PPh}_3)_2$,¹⁵ and $\text{RuCl}_2(\text{PPh}_3)_3$ ^{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 $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ and $\text{Pd}(\text{PPh}_3)_4$ 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 $\text{trans-MX}(\text{CO})(\text{PPh}_3)_2$ ($\text{M} = \text{Rh}$ or Ir , $\text{X} = \text{Cl}$, Br , or I).

When α,α -dimethylbenzyl hydroperoxide was added to a catalytic amount of $\text{trans-IrCl}(\text{CO})(\text{PPh}_3)_2$ (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 α -methyl-

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 reported¹³ to be the major gaseous product of this reaction. A quantitative estimation of the oxygen evolution has established the stoichiometry:



No $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ 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 cm^{-1} indicative of an iridium(III)-carbonyl complex.

t-Butyl hydroperoxide, which contained 30% di-*t*-butyl peroxide, also reacted with $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (molar ratio 112 : 1) to give oxygen and *t*-butyl alcohol according to the above stoichiometry and in agreement with previous findings.¹² A control experiment confirmed that pure di-*t*-butyl peroxide is completely unaffected by $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ 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 α,α -dimethylbenzyl and *t*-butyl hydroperoxides to oxygen and the corresponding alcohols also occurs in the presence of $\text{RhCl}(\text{PPh}_3)_3$, 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 $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$. In order to ensure homogeneity these reactions were carried out in benzene solution at 295 ± 1 K with a molar ratio of hydroperoxide to

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⁹ A. Fusi, R. Ugo, F. Fox, A. Pasini, and S. Cenini, *J. Organometallic Chem.*, 1971, **26**, 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. Teranishi, *ibid.*, 1972, **45**, 2003.

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¹⁶ 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

Decomposition of hydroperoxides by transition metal complexes

| Hydroperoxide (mmol) | Complex (mmol) | Time taken for evolution of O ₂ (min) | O ₂ [mmol, conversion (%)] |
|-------------------------------|---|--|---------------------------------------|
| Bu ^t OOH (7.6) | IrCl(CO)(PPh ₃) ₂ (0.64) | 70 | 3.20 (83) |
| Bu ^t OOH (6.4) | IrCl(CO)(PPh ₃) ₂ (0.13) | 100 | 2.50 (80) |
| PhMe ₂ C·OOH (2.5) | IrCl(CO)(PPh ₃) ₂ (0.13) | 20 | 0.94 (76) |
| Bu ^t OOH (8.6) | RhCl(PPh ₃) ₃ (0.11) | 480 | 2.15 (50) |
| PhMe ₂ C·OOH (4.6) | RhCl(PPh ₃) ₃ (0.05) | 210 | 1.77 (77) |

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

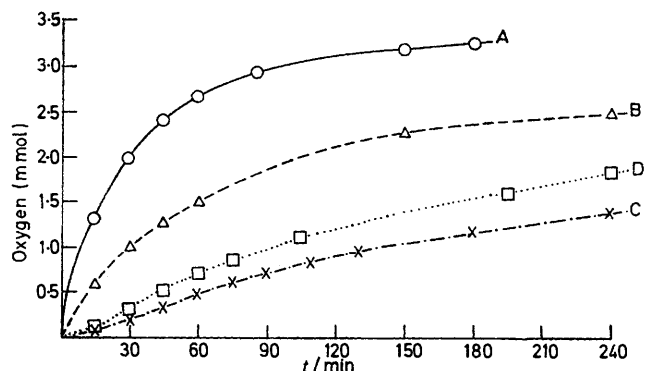


FIGURE 1 Effect of phenol on the decomposition of Me₃C·OOH by IrCl(CO)(PPh₃)₂: A, in the absence of phenol; B, phenol (2.56×10^{-6} mol), phenol : Ir^I complex 1 : 10; C, phenol (5.12×10^{-6} mol), phenol : Ir^I complex 2 : 1; D, phenol (2.56×10^{-6} mol), phenol : Ir^I complex 1 : 1

of phenol : catalyst ≥ 5 : 1 resulted in the complete inhibition of oxygen evolution over the same time period, while with phenol : catalyst ratios of ≤ 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-*t*-butyl-*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).

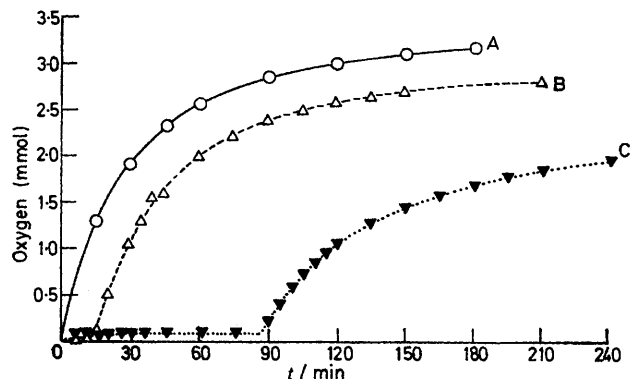


FIGURE 2 Effect of 2,6-di-*t*-butyl-*p*-cresol on the decomposition of Me₃C·OOH by IrCl(CO)(PPh₃)₂: A, in the absence of cresol; B, cresol (1.15×10^{-4} mol), cresol : Ir^I complex 4.5 : 1; C, cresol (2.56×10^{-4} mol), cresol : Ir^I complex 10 : 1

These results are apparently paradoxical in that 2,6-di-*t*-butyl-*p*-cresol, which is known¹⁸ to be a far better scavenger of peroxy and alkoxy 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)(PPh₃)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

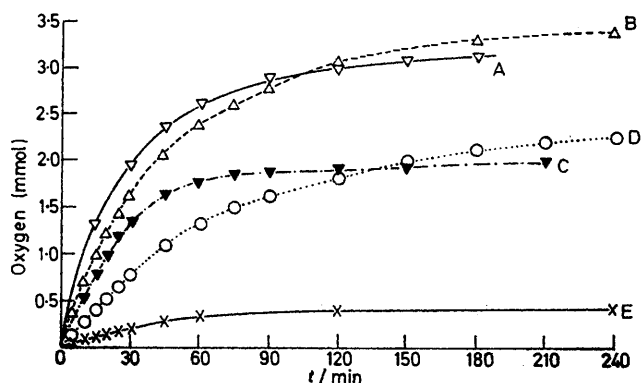


FIGURE 3 Effect of pyridines on the decomposition of Me₃C·OOH by IrCl(CO)(PPh₃)₂: A, in the absence of inhibitor; B, 2,6-butidine (2.56×10^{-4} mol), butidine : Ir^I complex 10 : 1; C, 2,6-butidine (2.56×10^{-3} mol), butidine : Ir^I complex 100 : 1; D, pyridine (2.56×10^{-4} mol), pyridine : Ir^I complex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

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.

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(I),⁷ and chlorotris(triphenylphosphine)rhodium(I)²⁴ were prepared and purified by literature methods.

Reaction of $\alpha\alpha$ -Dimethylbenzyl Hydroperoxide with trans-IrCl(CO)(PPh)₃.—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, **46**, 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 tip-head. 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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