

THE OXIDATION OF STYRENE IN THE PRESENCE OF OXYGEN-CARRYING COMPLEXES

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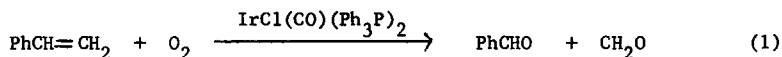
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Recently there has been considerable interest in the nature of olefin oxidation in the presence of oxygen-carrying group VIII metal complexes.<sup>1</sup> The role of the metal complex in the oxidation of styrene has been interpreted in two different ways. Sheldon<sup>2</sup> has recently implied that the role of  $\text{Pd}(\text{Ph}_3\text{P})_4$  in the oxidation of styrene is to decompose trace amounts of hydroperoxides to yield radical species which initiate autoxidation. Takao, *et al.*<sup>3,4</sup> have studied the oxidation of styrene in the presence of iridium and rhodium complexes, but these authors<sup>3,4</sup> suggest a mechanistic pathway involving coordination of molecular oxygen with the metal center causing an increased oxygen-oxygen bond length and enhanced reactivity with styrene in the coordination sphere of the metal. The mechanism suggested by Takao<sup>3,4</sup> is interesting since styrene, an olefin having no allylic hydrogen for radical abstraction, might undergo catalytic oxidation under mild conditions via a non-radical pathway in the presence of complexes which react reversibly with both oxygen and olefins.

Styrene is readily oxidized in the presence of many group VIII metal complexes in toluene<sup>5</sup> at 75°C, whereas little oxidation occurs in their absence. We have found that the product distribution which results from the oxidation of styrene in the presence of complexes of Ir(I), Rh(I), Ru(II), and Os(II) is markedly dependent on the metal complex which is used (Table I). For example, when oxidation is carried out in the presence of  $\text{RuCl}_2(\text{Ph}_3\text{P})_3$ , substantial quantities of styrene oxide are produced; whereas when  $\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$  is employed, cleavage products (benzaldehyde and formaldehyde) predominate, eq. 1. The latter behavior is consistent with



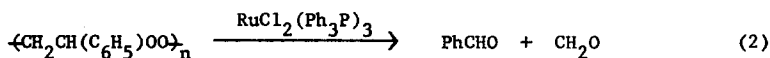
radical initiated autoxidation; however, the formation of large amounts of epoxide under these conditions is not (Table I). Nonetheless, 2,6-di-*t*-butyl-4-methylphenol (Ionol) was found to completely inhibit oxidation in both the iridium and the ruthenium cases indicating that both reactions were radical initiated.

Table I  
OXIDATION<sup>a</sup> OF STYRENE IN THE PRESENCE OF METAL COMPLEXES

Metal Complex	Radical Initiator <sup>b</sup>	Radical Inhibitor <sup>c</sup>	Time, Hr.	Conversion, %	Product Yields, %				
					Benzaldehyde	Formaldehyde	Acetophenone	Styrene Oxide	Polymer
			6.0	1	1	-	-	-	-
	AIBN		6.0	50	31	35	-	-	33 <sup>e</sup>
	AIBN	IONOL	6.0	0	-	-	-	-	-
IrCl(CO)(Ph <sub>3</sub> P) <sub>2</sub>			6.0	60	40	40	2	3	15
IrCl(CO)(Ph <sub>3</sub> P) <sub>2</sub>		IONOL	6.0	0	-	-	-	-	-
IrH(CO)(Ph <sub>3</sub> P) <sub>3</sub>			6.0	45	41	32	2	10	15
RhCl(CO)(Ph <sub>3</sub> P) <sub>2</sub>			5.0	59	44	18	4	23	11
RhCl(CO)(Ph <sub>3</sub> P) <sub>2</sub>		IONOL	5.0	0	-	-	-	-	-
RuCl <sub>2</sub> (Ph <sub>3</sub> P) <sub>3</sub>			3.5	54	43	16	2	26	13
RuCl <sub>2</sub> (Ph <sub>3</sub> P) <sub>3</sub>		IONOL	3.5	0	-	-	-	-	-
OsBr <sub>2</sub> (Ph <sub>3</sub> P) <sub>3</sub>			6.0	80	41	14	5	24	14

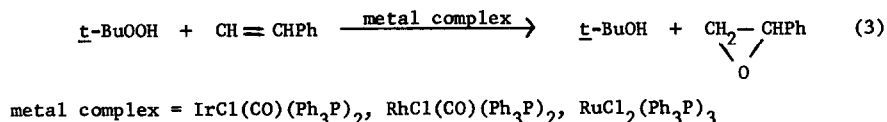
a. Oxygen bubbled through a solution of 6 ml styrene in 6 ml toluene containing 0.04 g of metal complex with stirring at 75°C. At the time designated above, volatile materials were collected by vacuum transfer at 0.1 mm from the reaction flask. A gummy residue (10-30% by weight of total product) was left behind. The volatile fraction contained toluene and 70-90% by weight of total reaction product which was analyzed by glpc. b. 0.04 g. c. 0.10 g. d. Sum of formaldehyde which distilled and paraformaldehyde which sublimed from reaction mixture. e. Approximately 50% styrene polyperoxide.

Since styrene oxide was formed in substantial quantities in the presence of RuCl<sub>2</sub>(Ph<sub>3</sub>P)<sub>3</sub>, but not when radical initiators were used, it was of interest to determine how this product arose. When styrene is oxidized in the presence of AIBN, benzaldehyde and formaldehyde are formed by decomposition of an intermediate polyperoxide, I.<sup>6</sup> When toluene solutions (3 ml) of I (10-30 mole %) were brought into contact with RuCl<sub>2</sub>(Ph<sub>3</sub>P)<sub>3</sub> (1 × 10<sup>-3</sup> M), an exothermic reaction occurred to give mainly benzaldehyde and formaldehyde, eq. 2. Greater than 90% of the polyperoxide was converted to cleavage products, but styrene oxide was formed in less than 3% yield.



It is unlikely, therefore, that much of the styrene oxide which is formed in the oxidation of styrene in the presence of RuCl<sub>2</sub>(Ph<sub>3</sub>P)<sub>3</sub> arose from decomposition of the polyperoxide, I.

It has been suggested<sup>6</sup> that the low yields of styrene oxide which can be detected during AIBN-initiated autoxidation at low oxygen pressure (<75 psi, 50°C),<sup>6</sup> resulted from epoxidation of styrene by an alkylperoxy radical. We have found that *t*-butylhydroperoxide reacts with styrene at 25°C in the presence of catalytic quantities of the complexes listed in Table I to form styrene oxide in 20-30% yield based on the hydroperoxide, eq. 3. This reaction does not proceed at an observable rate under these conditions in the absence of the metal complexes. This finding leaves open the possibility that some styrene oxide could arise from alkylperoxy species in these systems.



A variety of group VIII metal phosphine complexes proved to be effective in the oxidation of styrene (Table I). Benzaldehyde and formaldehyde were major reaction products and the extent of epoxide formation varied with the metal complex used. During the oxidation, however, styrene oxide was never detected until a substantial amount (>5%) of double bond cleavage had occurred. In addition, the formation of styrene oxide was accompanied by a correspondingly lower yield of formaldehyde. Formaldehyde, formed by oxidative cleavage of the double bond, could be further oxidized to species such as performic acid or the formylperoxy radical which are capable of epoxidizing styrene. Since benzaldehyde remained largely unchanged under the mild oxidation conditions employed, its role in epoxide formation must be minimal.

We conclude, therefore, that as with Pd(Ph<sub>3</sub>P)<sub>4</sub>,<sup>2</sup> the initial step in styrene oxidation in the presence of the Ir(I), Rh(I), Ru(II), and Os(II) complexes which we studied, is radical initiated autoxidation and that the unusually high epoxide yields which accompany some of these reactions are probably due to subsequent reactions which may be subject to metal catalysis. No evidence exists for coordination catalysis of oxidation as was previously<sup>3,4</sup> postulated.

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