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Oxidation by Transition Metal Complexes. II. Oxidation of Styrenes Catalyzed by Rhodium Compounds

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Catalytic activities of chlorotris(triphenylphosphine)rhodium(I) and rhodium(III) chloride for the oxidation of olefins have been studied. It has been found that the complex and $RhCl_3$ can cause catalytically the oxidation of aliphatic olefins such as styrene, α-methylstyrene or β-methylstyrene to produce carbonyl compounds under oxygen atmosphere. A remarkable solvent effect was observed in the reaction.

We have reported the catalytic oxidation of styrene and triphenylphosphine by means of some organoiridium complexes under oxygen stream.[1] In connection with this work, the catalytic function of oxidation by some rhodium compounds which form O_2-complexes, were investigated.

It was found that the complex ($RhX(PPh_3)_3$), especially chlorotris(triphenylphosphine)rhodium (I) can oxidize styrenes in the presence of oxygen to produce carbonyl compounds.[2] Styrene gave similar products to those reported in the case of organoiridium complex catalysts,[1] α-methylstyrene gave acetophenone, α-phenylpropionaldehyde and formaldehyde, and β-methylstyrene gave benzaldehyde and acetaldehyde in good yields. In the present paper catalytic oxidation with the rhodium complex, $RhCl(PPh_3)_3$ and $RhCl_3$ will be presented.

Results and Discussion

As the general method of oxidation catalyzed by rhodium compounds, mixtures of the reactant styrene and the rhodium complex in toluene, ethanol or other solvents were heated for 8 hr under a constant bubbling of oxygen.

It was found that styrene can be easily oxidized with the use of $RhCl(PPh_3)_3$ or $RhCl_3$ to give similar oxidation products as those obtained with the use of iridium complexes.[1a] The results are summarized in Table 1. This is the first example of oxidation of aliphatic olefins with the use of rhodium complexes. It is remarkable that the oxidation differing from cases with iridium complexes,[1a] is affected by the solvent polarity. Thus, in dioxane (polar solvent) the oxidation resulted in the cleavage of the C=C double bond of styrene to give benzaldehyde as a main product in 611% yield based on the Rh-complex used.[5]

In contrast to this, in ethanol (protic solvent) acetophenone was obtained in excellent yield with a small amount of the double bond-cleavage product, and in toluene (non-polar solvent) the main products were both acetophenone (348%) and benzaldehyde (148%). This is different from results for dioxane and ethanol. In acetic acid and pyridine only a small amount of oxidation products was detected.

Table 1 shows a similar solvent effect in the

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[1] a) K. Takao, Y. Fujiwara, T. Imanaka and S. Teranishi, This Bulletin, **43**, 1153 (1970). b) K. Takao, Y. Fujiwara, T. Imanaka, M. Yamamoto, K. Hirota and S. Teranishi, *ibid.*, **43**, 2249 (1970).

[2] Although the complex ($RhX(PPh_3)_3$) was used only in the oxidation of ethylbenzene[3] and cyclohexene[4], no application of the complex to any other olefins has been reported.

[3] J. Blum, *Tetrahedron Lett.*, **1967**, 3665.

[4] J. P. Collman, M. Kubota and J. W. Hosking, *J. Amer. Chem. Soc.*, **89**, 4809 (1967).

[5] Formaldehyde was also obtained from the outlet gas.

TABLE 1. OXIDATION OF STYRENE WITH RHODIUM COMPOUNDS

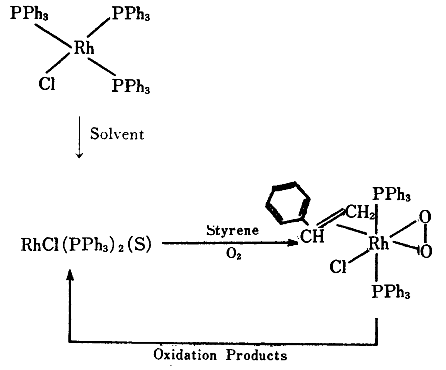
Catalyst	Reaction		Solvent	Product and yield,[a] %		
	Temp. °C	Time, hr		Benzaldehyde	Styrene oxide	Acetophenone
$RhCl(PPh_3)_3$	110	8	Toluene	148	trace	348
$RhCl(PPh_3)_3$	80	8	Toluene	213	trace	13
$RhCl(PPh_3)_3$	80	8	Dioxane	611	161	55
$RhCl(PPh_3)_3$	80	8	Tetrahydrofuran	225	106	103
$RhCl(PPh_3)_3$	80	8	Ethanol	17	trace	752
$RhCl(PPh_3)_3$	80	8	Pyridine	trace	trace	trace
$RhCl(PPh_3)_3$	110	8	Acetic acid	trace	trace	trace
$RhCl_3$	110	8	Toluene	867	1232	trace
$RhCl_3$	80	8	Ethanol	48	10	158
$IrCl_3$[1a)]	110	8	Toluene	566	418	10
$IrCl_3$	80	8	Ethanol	trace	trace	45

a) Yields are based on the catalyst utilized.

case of the $RhCl_3$ catalyst, but the product distribution differs from that of $RhCl(PPh_3)_3$. The yields of styrene oxide and benzaldehyde increased in toluene, and the total yields decreased in ethanol. A similar result was obtained in the case of $IrCl_3$. The question of catalytic oxidation of styrene with rhodium complexes undergoing a remarkable solvent effect is now being investigated. It seems that the species $RhCl(PPh_3)_2$ (II) which is derived from the dissociation of $RhCl(PPh_3)_3$ has an important role in the reaction.[6)]

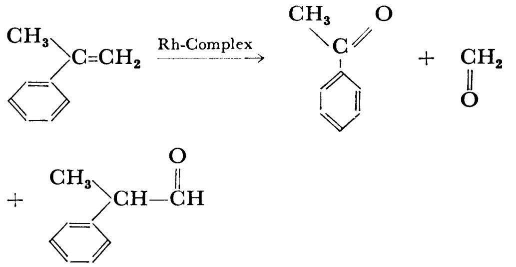
$$\underset{\text{(I)}}{RhCl(PPh_3)_3} \underset{PPh_3}{\overset{\text{Solvent}}{\rightleftarrows}} \underset{\text{(II)}}{RhCl(PPh_3)_2} + PPh_3$$

Species II has a vacant site which may be essential to catalytic activity and will be coordinated easily with oxygen molecule under oxygen atmosphere.[6)] We have postulated that oxidation might proceed *via* the coordination of both oxygen and styrene to Rh(I) metal as shown below.



S: Solvent

Oxidation of α-Methylstyrene. The catalytic oxidation of α-methylstyrene with the Rh-complex was also investigated. The results are summarized in Table 2. Oxidation of α-methylstyrene gave acetophenone, formaldehyde, and α-phenylpropionaldehyde in considerable yields. Formations of acetophenone and formaldehyde are derived from the C=C double-bond cleavage of methylstyrene, and the formation of α-phenylpropionaldehyde corresponds to that of acetophenone in styrene. However, no epoxide type product such as styrene oxide could be obtained. The results differ from those of the Wacker process. In the Wacker process, in which $PdCl_2$ is used as an essential catalyst, α-methylstyrene gave only acetophenone and α-phenylpropionaldehyde.[7)]



When iridium trichloride was used in the oxidation of α-methylstyrene a similar oxidation mixture (acetophenone and α-phenylpropionaldehyde) was obtained but the yields decreased in comparison with $RhCl_3$.

Oxidation of β-Methylstyrene. β-Methylstyrene was oxidized to benzaldehyde and acetaldehyde. The formation of acetaldehyde was confirmed by converting it to 2,4-dinitrophenylhydrozone. The results are shown in Table 3. We also tried the oxidation of *trans*-stilbene using the Rh-complex in toluene, but no oxidation product was obtained. From the results, it is clear that the reactivities to oxidation of styrenes

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

7) R. Hüttel, J. Kratzer and M. Bechter, *Chem. Ber.*, **94**, 766 (1961).

Table 2. Oxidation of α-methylstyrene with rhodium compounds and iridium compound

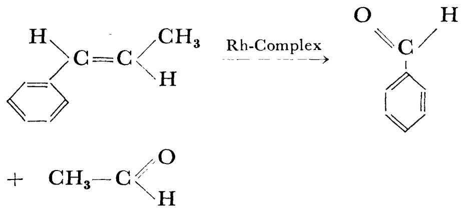
Catalyst	Reaction		Solvent	Product and yield,[a] %	
	Temp. °C	Time, hr		Acetophenone	α-Phenylpropionaldehyde
$RhCl(PPh_3)_3$	110	8	Toluene	67	23
$RhCl(PPh_3)_3$	80	8	Ethanol	0	0
$RhCl_3$	110	8	Toluene	466	227
$RhCl_3$	80	8	Ethanol	96	trace
$IrCl_3$	110	8	Toluene	177	107

a) Yields are based on the catalyst utilized.

Table 3. Oxidation of β-methylstyrene with rhodium compounds

Catalyst	Reaction		Solvent	Benzaldehyde yield,[a] %
	Time hr	Temp. °C		
$RhCl(PPh_3)_3$	110	8	Toluene	134
$RhCl(PPh_3)_3$	80	8	Ethanol	trace
$RhCl_3$	110	8	Toluene	19
$RhCl_3$	80	8	Ethanol	9

a) Yields are based on the catalyst utilized.



decrease as follows: styrene>α-methylstyrene>β-methylstyrene≫*trans*-stilbene. This suggests that a more sterically hindered olefin is difficult to coordinate with rhodium(I) and hence is less reactive to oxidation.

In conclusion, it has been found that the rhodium complex and rhodium trichloride have a catalytic function for the oxidation of styrene and methylstyrenes under oxygen atmosphere and that the product distribution undergoes a solvent effect.

Experimental

Materials and Analysis. All temperatures were uncorrected. VPC analysis was made by a Yanagimoto G-8 gas chromatograph usingan Apiezon L column. Rhodium trichloride trihydrate and iridium trichloride were of commercial grade. Toluene and acetic acid were purified as described previously.[1a] Ethanol was refluxed with calcium oxide and distilled. Pyridine was dried over barium oxide and distilled. Tetrahydrofuran was refluxed with sodium metal and distilled. Dioxane was purified by the method of Hess and Frahm.[8] Styrene, α-methylstyrene and β-methylstyrene were dried over anhydrous magnesium sulfate and distilled.

Preparation of Chlorotris(triphenylphosphine)-rhodium. $RhCl(PPh_3)_3$ was prepared by the method of Osborn *et al.*[6] Mp 160—161°C (lit,[6] 157—158°C).

Oxidation of Styrene by Rhodium Complex. In a flask similar to that mentioned previously[1a], was placed a mixture containing 2.65 g (2.87 mmol) of $RhCl(PPh_3)_3$, 15 g (0.146 mol) of styrene, and 150 m*l* of toluene. The reaction was carried out at 110°C with continuous bubbling of oxygen for 8 hr. After evaporation of the solvent under reduced pressure, the residual material was chromatographed on alumina (80 g). Elution with 600 m*l* of ether and recrystallization gave 0.82 g of triphenylphosphine oxide. Further elution with methanol gave 0.24 g of an unidentified green complex.

From the solvent evaporated, we obtained styrene, 1.20 g of acetophenone, 0.45 g of benzaldehyde and a trace of styrene oxide.

Oxidation of α-Methylstyrene by Rhodium Complex. The apparatus was similar to that described above, except that the outlet gas from a condenser was bubbled into 2,4-dinitrophenylhydrazine solution. In a flask was placed a mixture containing 2.65 g (2.87 mmol) of $RhCl(PPh_3)_3$, 17 g (0.146 mol) of α-methylstyrene and 150 m*l* of toluene. The solution was refluxed with continuous bubbling of oxygen for 8 hr. Resulting reaction mixture was treated as usual, and the liquid phase was analysed and separated by VPC to give Ia (0.23 g) and Ib (0.09 g). Ia was assigned as acetophenone by comparison of NMR spectrum and retention time with those of an authentic sample. Ib was assigned as α-phenylpropionaldehyde by comparison of NMR spectrum and retention time with those of an authentic sample.

The solid phase was chromatographed on alumina (80 g). Elution with 2 *l* of ether and recrystallization gave 0.90 g of triphenylphosphine oxide. From 2,4-dinitrophenylhydrazine solution, 2,4-dinitrophenylhydrazone of formaldehyde was obtained as yellow crystals.

Oxidation of β-Methylstyrene by Rhodium Complex. The apparatus was similar to that described for α-methylstyrene. In a flask was placed mixture containing 0.55 g (0.60 mmol) of $RhCl(PPh_3)_3$, 2.27 g (19.2 mmol) of β-methylstyrene, and 45 m*l* of toluene. The solution was refluxed with continuous bubbling of oxygen for 8 hr. Resulting reaction mixture was treated as usual, and the liquid phase was separated by VPC to give 0.063 g of benzaldehyde. From 2,4-dinitrophenylhydrazine solution, 2,4-dinitrophenylhydrazone of acetaldehyde was obtained as yellow crystals.

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[8] K. Hess and H. Frahm, *Ber.*, **71**, 2627 (1938).