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# Oxidation by Transition Metal Complexes. I. Oxidation of Styrene and Triphenylphosphine Catalyzed by $O_2$-Ir Complex

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In order to investigate the oxidation reaction which is catalyzed by transition metal complexes in a homogeneous system under mild conditions, the oxidation reactions of styrene and triphenylphosphine catalyzed by various iridium complexes have been studied. The Vaska complex ($IrX(CO)(PPh_3)_2$) and the biphosphine chelate complex have been found to be effective as oxidation catalyst. It was found that the $SnCl_3$ ligand which has a strong *trans* effect promotes the oxidation of styrene. For the sake of comparison with the iridium compounds, oxidation with palladium salts was also studied.

Extensive studies on heterogeneous oxidation reactions by means of various metal oxides or inorganic metal salts have been carried out.[1] Much less is known about oxidation reactions involving organo-transition metal compounds as a catalyst in homogeneous systems.

Recently, some transition metal complexes having

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[1] See, for example, K. B. Wiberg, Ed., "Oxidation in Organic Chemistry," Academic Press, New York (1965).

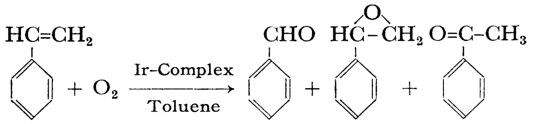
an oxygen molecule as a ligand were prepared.[2-6] These complexes could thus be expected to be effective as oxidation catalyst.

However, only a few workers have studied the homogeneous catalyzed oxidation reaction in the presence of these metal-oxygen complexes.[4-7] Collman has reported briefly that cyclohexene can be oxidized to cyclohexanone and cyclohexene oxide in the presence of the Vaska compelx.[7]

In order to investigate the oxidation reaction which is catalyzed by the transition metal-$O_2$ complexes in a homogeneous system under mild conditions, we have studied the oxidation reactions of styrene and triphenylphosphine catalyzed by various iridium complexes prepared by Vaska *et al.*[3,8] and others.[9-11]

It has been found that some organoiridium complexes can cause the oxidation reaction of styrene in the presence of oxygen to give styrene oxide, benzaldehyde or acetophenone catalytically. In addition, triphenylphosphine has been found to be easily oxidize to give triphenylphosphine oxide catalytically.

We report in this paper a study on oxidation reactions of styrene and triphenylphosphine by means of iridium complexes under an oxygen atmosphere.



## Results and Discussion

The oxidation reactions catalyzed by the iridium complexes were carried out under conditions where homogeneous solutions of reactant styrene (or triphenylphosphine) and iridium complexes in a solvent such as benzene or toluene are heated with a constant bubbling of oxygen for 8 hr.

**Oxidation of Triphenylphosphine.** Triphenylphosphine has been oxidized easily by the Vaska complexes ($IrX(CO)(PPh_3)_2$; X=Cl, Br, I) to afford triphenylphosphine oxide catalytically, and the catalyst is recovered without decomposition after the reaction. The results are summarized in Table 1.

TABLE 1. OXIDATION OF TRIPHENYLPHOSPHINE WITH VASKA COMPLEX

| Catalyst | Reaction temp. °C | Time, hr | Solvent | Triphenylphosphine oxide Yield[a] % |
|---|---|---|---|---|
| $IrClCO(PPh_3)_2$ | 110 | 9 | Toluene | 426 |
| $IrBrCO(PPh_2)_2$ | 110 | 9 | Toluene | 854 |
| $IrICO(PPh_3)_2$ | 110 | 9 | Toluene | 737 |

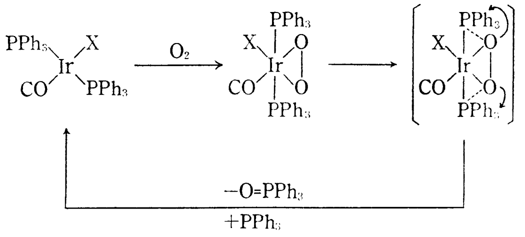
a) Yields are based on catalyst used.

Although it is well known that nickel, palladium, or platinum complexes are effective catalysts for the oxidation of phosphine,[4,5] the present result is the first example of the oxidation by iridium complex catalysts.

Of Vaska complexes, the yield of triphenylphosphine oxide increases in the order: $X=Cl<I<Br$ as shown in Table 1. The fact that the Vaska complexes coordinate with the oxygen molecule easily under oxygen atmosphere, suggests that the present oxidation reaction proceeds *via* an Ir-$O_2$ complex.

According to La Placa and Ibers[12], and McGinnety *et al.*,[13] the O–O bond lengths of the Ir-$O_2$ complexes prepared by Vaska *et al.* are 1.30 Å and 1.51 Å for the chloride complex and the analogous iodide complex respectively. That increasing bond length of O–O increases the yield of the oxide formed seems to show that the oxygen molecule is highly activated by coordinating with iridium(I) metal. Heating of Ir-$O_2$ complex resulted in the formation of triphenylphosphine oxide in the absence of oxygen.

From these results, it appears that the Vaska complex-catalyzed oxidation may proceed through the coordination of both oxygen and triphenylphosphine to iridium(I) metal as is shown in the following scheme:



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[2] L. Vaska, *Science*, **140**, 809 (1963).

[3] L. Vaska and D. L. Caton, *J. Amer. Chem. Soc.*, **88**, 5324 (1966).

[4] G. Wilke, H. Schott and P. Heimbach, *Angew. Chem.*, **79**, 62 (1967).

[5] S. Takahashi, K. Sonogashira and N. Hagihara, *Nippon Kagaku Zasshi*, **87**, 610 (1966).

[6] S. Otsuka, A. Nakamura and Y. Tatsuno, *Chem. Commun.*, **1967**, 836.

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

[8] L. Vaska and J. W. Diluzio, *ibid.*, **83**, 2784 (1961).

[9] P. B. Chock and J. Halpern, *ibid.*, **88**, 3511 (1966).

[10] R. C. Taylor, J. F. Young and G. Wilkinson, *Inorg. Chem.*, **5**, 20 (1966).

[11] R. S. Nyholm and K. Vrieze, *J. Chem. Soc.*, **1965**, 5337.

[12] S. J. LaPlaca and J. A. Ibers, *J. Amer. Chem. Soc.*, **87**, 2581 (1965).

[13] J. A. McGinnety, R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 2243 (1967).

Table 2. Oxidation of styrene with iridium compounds

| Catalyst | Reaction |  | Solvent | Product and yield,[a] % |  |  |
|---|---|---|---|---|---|---|
|  | Temp. °C | Time, hr |  | Benzaldehyde | Styrene oxide | Acetophenone |
| None | 110 | 8 | Toluene | 0 | 0 | 0 |
| IrClCO(PPh$_3$)$_2$ | 110 | 8 | Toluene | 0 | 0 | 84 |
| IrClCO(PPh$_3$)$_2$ | 100 | 8 | Toluene | 0 | 0 | 65 |
| IrClCO(PPh$_3$)$_2$ | 80 | 8 | Toluene | 0 | 0 | 37 |
| IrClCO(PPh$_3$)$_2$ | 6.5 | 8 | Toluene | 0 | 0 | 0 |
| IrClCO(PPh$_3$)$_2$ | 100 | 8 | Toluene[b] +Ethanol | 0 | 0 | 64 |
| IrClCO(PPh$_3$)$_2$ | 100 | 8 | Dioxane | 0 | 0 | 55 |
| IrClCO(PPh$_3$)$_2$ | 100 | 8 | Acetic acid | 1280 | 0 | 152 |
| IrBrCO(PPh$_3$)$_2$ | 110 | 8 | Toluene | 0 | 0 | 4 |
| IrICO(PPh$_3$)$_2$ | 110 | 8 | Toluene | 0 | 0 | 0 |
| Ir(P-P)$_2$Cl[d] | 110 | 8 | *n*-Propanol | 469 | 315 | 85 |
| Ir-SnCl$_3$ | 110 | 8 | Toluene | 1212 | 477 | trace |
| Ir-HgCl$_2$ | 110 | 8 | Toluene | 253 | 110 | trace |
| IrCl$_3$[c] | 110 | 8 | Toluene | 566 | 418 | 10 |
| IrCl$_3$ | 110 | 8 | Acetic acid | 1385 | 51 | 89 |

a) Yields are based on the catalyst utilized.
b) A mixture of 250 m*l* of toluene and 50 m*l* of ethanol was used.
c) Phenylethyleneglycol was also obtained in 102% yield.
d) [Ir(PPh$_2$CH$_2$CH$_2$PPh$_2$)$_2$]Cl

**Oxidation of Styrene.** Since the Vaska complexes have been found to be active catalysts for the oxidation of triphenylphosphine, we have undertaken a further study on the oxidation of olefins which are not easily oxidized especially under mild conditions.

It has been found that styrene can be smoothly oxidized by the use of iridium complexes under an oxygen atmosphere. The results are given in Table 2.

As apparent from Table 2, the Vaska complexes (X=Cl, and Br) can cause the oxidation of styrene to give acetophenone in considerable yields. In the absence of the complexes, no oxidation product was formed indicating that these complexes function as a catalyst for the oxidation of styrene.

**Solvent Effect.** The oxidation of styrene catalyzed by the iridium complexes appears to suffer no solvent effect. That is, styrene gave acetophenone in almost similar yields as in the cases of toluene, a non-polar solvent, ethanol, a protic solvent, or dioxane, a polar solvent. However, in the case of acetic acid, a different result was obtained, namely benzaldehyde was formed as a major product in 1280% yield and acetophenone in 152% yield.[14] This peculiar effect of acetic acid will be discussed in the following publication.

**Ligand Effect.** *1. Halide Ligand.* The effects of varying the halide ligands of the Vaska complex upon the styrene oxidation are shown in Table 2. The yield of acetophenone increases in the order: X=I<Br<Cl which is different from that observed in the oxidation of triphenylphosphine. This may be explained in the following way: Styrene is a weaker ligand than triphenylphosphine, and the steric hindrance of the halide ligand of the Vaska complex increases in the order, Cl<Br<I. Thus styrene is greatly hindered from coordinating with iridium metal because its forming an iridium-styrene-oxygen complex.

*2. SnCl$_3$ and HgCl Ligand.* The ligand effects are more clearly obtained when SnCl$_3$[15] or HgCl ligand is introduced to the iridium metal (Table 2).

With the iridium-tin chloride complex,[10] styrene gave 1212% yield of benzaldehyde, 477% yield of styrene oxide and a trace of acetophenone. The higher reactivity of the complex might arise from the strong *trans* effect of the SnCl$_3$ ligand which promotes the formation of an iridium-styrene-oxygen complex intermediate.

It is of interest that the oxidative cleavage of the C=C double bond of styrene takes place easily by the iridium complex catalyst under mild conditions indicating that oxygen is highly activated by coordinating with the iridium metal.[12,13] A similar result was obtained in the case of the HgCl ligand[11] though less reactive than the former.

An interesting aspect of the oxidation is that no benzoic acid is formed even under such an oxidative condition, though benzaldehyde is formed in a high

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[14] Yields of the oxidation products which appear hereafter in this paper are all based on the amount of the complexes ultilized.

[15] SnCl$_3$ ligand is known to have a large *trans* effect and to be a strong $\pi$-accepter and a weak donor.[16]

[16] R. V. Lindsey, Jr., G. W. Parshall and V. G. Stolberg, *J. Amer. Chem. Soc.*, **87**, 658 (1965).

TABLE 3. OXIDATION OF STYRENE WITH PALLADIUM SALTS

| Catalyst | Reaction | | Solvent | Product and yield[a)] % | | |
|---|---|---|---|---|---|---|
| | Temp. °C | Time, hr | | Benzaldehyde | Styrene oxide | Acetophenone |
| $PdCl_2$[b)] | 110 | 8 | Toluene | 1098 | 184 | 17 |
| $PdCl_2$ | 110 | 8 | Acetic acid | 969 | 19 | 60 |
| $Pd(OAc)_2$ | 110 | 8 | Toluene | 103 | 68 | 7 |
| $Pd_2(C_8H_8)Cl_4$[c)] | 110 | 8 | Toluene | 23 | 9 | 2 |

a) Yields are based on the catalyst used.

b) *trans*-Stilbene (64%) and unidentified compound (0.24 g, mp 77—79°C) were also obtained.

c) 1,3-Diphenylbutene (104%) and *trans*, *trans*-1,4-diphenylbutadiene (44%) were also formed.

yield. This was confirmed by the fact that when benzaldehyde was treated with $IrCl_3$ under the oxygen atmosphere, no benzoic acid was detected.

3 *Bisdiphenylphosphinoethane Ligand.* In the oxidation reaction catalyzed by the four coordinated biphosphine chelate complex,[3] bis,bis(1,2-diphenylphosphine)ethane iridium(III) monochloride, $[Ir(PPh_2CH_2CH_2PPh_2)_2]Cl$, styrene was also oxidized easily to give a similar result as above. In this case, an oxygen molecule will be also activated through coordination to iridium metal.[17]

**Oxidation with $IrCl_3$.** Oxidation of styrene catalyzed by iridium trichloride resulted in the formations of benzaldehyde, styrene oxide and acetophenone in high yields suggesting that the Vaska type complex is formed as an intermediate species[9] which causes the oxidation.

**Oxidation with Palladium Salts.** For the sake of comparison, the oxidation reactions of styrene using palladium(II) salts were performed. The data in Table 3 show that palladium(II) salts such as palladium(II) chloride can cause the oxidation of styrene to afford benzaldehyde, styrene oxide and acetophenone in excellent yields.

It is well known that acetophenone is obtained by the nucleophilic attack of the hydroxyl anion on the olefinic carbon atom of styrene in the presence of palladium(II) chloride and water.[19] The present oxidation reaction was carried out in the absence of water. Thus acetophenone formed can not be derived from the nucleophilic attack of the hydroxy anion on styrene suggesting that in the present system, an oxygen-palladium complex[4,5] is also formed which behaves as an oxidation catalyst.

In conclusion, it has been revealed that the Vaska complexes and some iridium complexes have a catalytic function for the oxidation of triphenylphosphine and styrene under an oxygen atmosphere.

## Experimental

**Materials and Analysis.** All temperatures were uncorrected. The IR-spectra were recorded on a Hitachi EPI-S2 spectrometer and NMR spectra were measured on a Japan Electron Optics JNM-4H-100 spectrometer. Chemical shifts are given in $\tau$ units together with splitting patterns and relative integrated area. The VPC analysis was made by a Yanagimoto GCG-3 gaschromatograph using an Apiezon L column. Iridium trichloride and palladium chloride were of commercial grade. $Pd(OAc)_2$ was prepared according to the method of Stephenson *et al.*[20] The styrene-$PdCl_2$ complex was prepared according to the method of Kharasch *et al.*[21]

Toluene was refluxed with sodium metal and distilled. Acetic acid was dried over phosphorus pentoxide and distilled. Styrene was dried over anhydrous magnesium sulfate and distilled.

**Preparation of Complexes. (1) *trans*-Chloro(carbonyl)bis(triphenylphosphine)iridium.** *The Vaska Complex.* *trans*-$IrCl(CO)(PPh_3)_2$ was prepared by a modification of the method of Vaska.[8] Iridium trichloride was dissolved in a mixture of triethyleneglycol and a ten fold excess triphenylphosphine. After heating the mixture at 280°C for 24 hr, the solvent was evaporated to dryness. The residue was recrystallized twice from benzene, affording a yellow crystalline complex (80%). IR: $\nu$(Nujol) 1950 cm$^{-1}$ (C=O) (lit,[8] 1950 cm$^{-1}$). NMR ($CDCl_3$): 2.00—2.90 (m).

Found: C, 57.23; H, 4.16%. Calcd for $C_{37}H_{30}OClP_2Ir$: C, 56.91; H, 3.88%.

**(2) *trans*-Bromo(carbonyl)bis(triphenylphosphine)iridium.** *trans*-$IrBr(CO)(PPh_3)_2$ was prepared by the method of Chock *et al.*[9] IR: $\nu$(Nujol) 1955 cm$^{-1}$ (C=O) (lit,[9] 1955 cm$^{-1}$). NMR ($CDCl_3$): 2.00—3.00 (m).

Found: C, 54.11; H, 3.95; Br, 9.34%. Calcd for $C_{37}H_{30}OBrP_2Ir$: C, 53.89; H, 3.67; Br, 9.69%.

**(3) *trans*-Iodo(carbonyl)bis(triphenylphosphine)iridium.** *trans*-$IrI(CO)(PPh_3)_2$ was prepared by the

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[17] The $O_2$-complex of this biphosphine chelate was synthesized by Vaska, and it has been reported that the O-O bond length in this complex is 0.45 Å larger than in free oxygen molecule.[18]

[18] J. A. Connor and E. A. V. Ebsworth, *Adv. Inog. Chem. Radiochem.*, **6**, 280 (1964).

[19] J. Smidt, W. Hafuer, R. Jira, R. Seiber, J. Sedlmeier and A. Sabel, *Angew. Chem.*, **71**, 176 (1959); **24**, 73 (1961), See also, A. Aguilo in "Advances in Organometallic Chemistry," Vol. 5, F. G. A. Stone and R. West, ed., Academic Press Inc., New York, N. Y. (1967), p. 321.

[20] J. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer and G. Wilkinson, *J. Chem. Soc.*, **1965**, 3632.

[21] M. S. Kharasch, R. C. Seiler and F. R. Mayo, *J. Amer. Chem. Soc.*, **60**, 882 (1938).

method of Chock *et al.*[9] IR: ν (Nujol) 1973 cm$^{-1}$ (C=O) (lit, 1975 cm$^{-1}$). NMR ($CDCl_3$): 2.05—2.80 (m).

Found: C, 50.66; H, 3.55%. Calcd for $C_{37}O_{30}OIP_2Ir$: C, 50.98; H, 3.47%.

(4) **Bis,bis(1,2-diphenylphosphino)ethane Iridium Monochloride.** $[Ir(Ph_2PCH_2CH_2PPh_2)]Cl$ was prepared according to the method of Vaska and Coton.[3] Mp 225—227°C (lit,[3] 225°).

Found: C, 60.62; H, 4.86; Cl, 3.80%. Calcd for $C_{52}H_{48}ClP_2Ir$: C, 60.94; H, 4.72; Cl, 3.46%.

(5) ***trans*-Dichloro(carbonyl)bis(triphenylphosphine)chloromercuryl Iridium.** *trans*-$IrCl_2(CO)(PPh_3)_2HgCl$ was prepared by the method of Nyholm and Vrieze.[11] IR: ν (Nujol) 2020 cm$^{-1}$ (C=O) (lit,[11] 2030 cm$^{-1}$).

Found: C, 42.58; H, 3.42%. Calcd for $C_{37}H_3OCl_3P_2HgIr$: C, 42.25; H, 2.88%.

(6) **Dichloro(carbonyl)triphenylphosphine Trichlorostanato Iridium.** $IrCl_2(CO)(PPh_3)(SnCl_3)$ was prepared by the method of Taylor *et al.*[10] IR: ν (Nujol) 2070 cm$^{-1}$ (C=O) (lit,[10] 2077, 2072 cm$^{-1}$). Mp 268—272°C (lit,[10] 270—275°C).

Found: C, 28.91; H, 2.16; Cl, 23.53%. Calcd for $C_{19}H_{15}OCl_5PSnIr$: C, 29.31; H, 1.95; Cl, 22.77%.

**General Procedure for Oxidation by the Iridium Complexes Catalysts.** The iridium complex and styrene (or triphenylphosphine) were dissolved in a solvent (usually, toluene). Oxygen was bubbled through the solution at reflux for 8 hr (in case of triphenylphosphine, 9 hr). After the evaporation of the solvent, the products were isolated by column or gaschromatography. Specific examples of reaction are given in detail below.

**Reaction of Vaska Complex with Triphenylphosphine.** In a 500-m*l*, three necked, round-bottomed flask, provided with condenser with a calcium chloride tube at the top and an oxygen inlet tube reaching nearly to the bottom, was placed a solution containing 300 m*l* of toluene, 2.00 g (7.6 mmol) of $PPh_3$ and 0.50 g (0.64 mmol) of $IrCl(CO)(PPh_3)_2$. The solution was refluxed with continued bubbling of oxygen for 9 hr and then the solvent was evaporated to dryness. The residue was subjected to a column chromatography of alumina (100 g). Elution with 500 m*l* of methanol resulted in 0.76 g (426%) of colorless crystals (I), which was assigned as triphenylphosphine oxide by comparison of IR spectrum and mixture melting point with those of an authentic sample. IR: ν (Nujol) 1420, 1185, 1115, 745, 692 and 535 cm$^{-1}$. After the reaction the Vaska complex catalyst used was recovered quantitatively.

**Reaction of Vaska Complex with Styrene.** In a flask similar to that mentioned above was placed a mixture containing 0.50 g (0.64 mmol) of $IrCl(CO)(PPh_3)_2$, 10.0 g (97 mmol) of styrene and 300 m*l* of toluene. The solution was refluxed with continued bubbling of oxygen for 8 hr. After evaporation of solvent under reduced pressure, the residual material was chromatographed on alumina (80 g). Elution with 500 m*l* of methanol and recrystallization gave 0.28 g (79%) of triphenylphosphine oxide (I). Although further elution with methanol resulted in no product, 0.2 g of an iridium complex remained at the upper part of the column, which was not further examined. From the solvent evaporated, we obtained styrene and 0.065 g (84%) of liquid substance (IIa) which was assigned as acetophenone by comparison of the IR spectrum and retention time with those of an authentic sample. IR: ν (neat) 1675, 1262, 759, 688, and 587 cm$^{-1}$.

**Reaction of Biphosphine Chelate Complex with Styrene.** In a 100 m*l* flask similar to that described above, was placed a mixture containing 0.66 g (0.64 mmol) of $[Ir(PPh_2CH_2CH_2PPh_2)_2]Cl$, 10.0 g (97 mmol) of styrene and 60 m*l* of *n*-propanol. The solution was refluxed with continued 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 IIa (0.065 g), IIb (0.32 g) and IIc (0.24 g). IIb was assigned as benzaldehyde by comparison of NMR spectrum, IR spectrum and retention time with those of an authentic sample. IR: ν (neat) 1675, 1573, 1200, 825, 744, 685 and 647 cm$^{-1}$. NMR ($CCl_4$): 0.15 (s,1) and 2.10—2.70 (m,5). IIc was assigned as styrene oxide by comparison of retention time with that of an authentic sample.

The solid substance was recrystallized from petroleum ether-benzene to give 0.46 g of white crystalline complex containing iridium metal. Its structure is not yet established.