

Liquid Phase Oxidation of Benzaldehyde Catalyzed by Low-Valent Transition Metal Complexes

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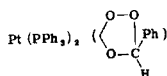
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Catalytic activities of d^8 and d^{10} noble metal complexes for the oxidation of benzaldehyde to benzoic acid and perbenzoic acid were investigated in benzene solution under oxygen atmosphere. The catalytic activity of the complex catalysts was in the order of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2 > \text{PdO}_2(\text{PPh}_3)_2 \approx \text{Pd}(\text{PPh}_3)_4 > \text{RhCl}(\text{PPh}_3)_3 > [\text{RhCl}(\text{PPh}_3)_2]_2 > \text{IrO}_2\text{Cl}(\text{CO})(\text{PPh}_3)_2 \approx \text{PtO}_2(\text{PPh}_3)_2$. From the kinetic studies using $\text{PdO}_2(\text{PPh}_3)_2$ catalyst, the initial rate of oxygen consumption was described by the following equation;

$$-\left(\frac{d\text{O}_2}{dt}\right)_0 = \frac{C_1[\text{PdO}_2(\text{PPh}_3)_2]_0[\text{PhCHO}]_0 P_{\text{O}_2}}{1 + C_2[\text{PhCHO}]_0}$$

where C_1 and C_2 are constants. The reaction was completely inhibited by free phosphine and markedly retarded by perbenzoic acid. The catalytic activity of $\text{Pd}(\text{PPh}_3)_4$ after preoxidation treatment was similar to that of $\text{PdO}_2(\text{PPh}_3)_2$, suggesting the participation of the oxygen complex in this oxidation reaction.



was found to have the comparable activity to that of $\text{PtO}_2(\text{PPh}_3)_2$. On the basis of these results, a tentative reaction mechanism for this catalysis was proposed.

INTRODUCTION

The square planar complexes of low-valent metal ions of d^8 or d^{10} configuration such as Ir(I), Rh(I), Pd(0) and Pt(0) are well known to add molecular oxygen to form the so-called "oxygen complex." This fact has stimulated many attempts to use them as catalysts for homogeneous oxidation reactions. Actually, catalytic activities of several oxygen complexes have been reported in the homogeneous oxidation of hydrocarbons so far (1). For such catalytic reactions, there has been postulated a

radical chain mechanism in which the role of the catalysts was to initiate the reaction either by hydrogen abstraction with the coordinated oxygen (2, 3) or by the decomposition of hydroperoxide (4). However, recent investigations indicated that the oxidative cleavage of carbon-carbon double bond of vinyl esters catalyzed by a rhodium complex was considered to take place via an intermediate which contained both olefin and oxygen in its coordination sphere (5).

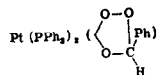
The authors found that some transition metal complexes showed high catalytic activities for the oxidation of benzaldehyde to benzoic acid and perbenzoic acid in ben-

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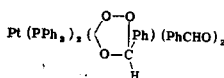
zene solution. The catalysis with these complexes showed different features from those with cobalt salts, which were known to accelerate the same reaction by a radical chain mechanism (6). In this paper, the kinetic study with $\text{PdO}_2(\text{PPh}_3)_2$ catalyst and the comparative study of catalytic activities of some oxygen complexes including a benzaldehyde-peroxy chelate complex of platinum are reported and discussed in relation to the reaction mechanism.

EXPERIMENTAL METHOD

$\text{Pd}(\text{PPh}_3)_4$ (7), $\text{PdO}_2(\text{PPh}_3)_2$ (7), $\text{Pt}(\text{PPh}_3)_4$ (7), $\text{PtO}_2(\text{PPh}_3)_2$ (7), $\text{IrO}_2\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (8), $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ (9), $\text{RhCl}(\text{PPh}_3)_3$ (10), and $[\text{RhCl}(\text{PPh}_3)_2]_2$ (10) were prepared according to standard procedures described in the literature. Their analyses were listed in Table 1.



was obtained by recrystallizing $\text{PtO}_2(\text{PPh}_3)_2$ from benzaldehyde. Analysis of the precipitate supported the formula of



(Anal. Calcd: C 63.92; H 4.53%, Found: C 63.42; H 4.91%). The solvating PhCHO was detected by NMR. The proton NMR in CDCl_3 showed a singlet at $\tau = 4.07$ assigned to a hydrogen bound to the chelate ring (11). Benzaldehyde was refined by

vacuum distillation. Triphenylphosphine was purified by recrystallization from ethanol.

The reaction was followed by measuring the oxygen consumption in 50 ml of benzene solution at constant temperatures (30–50°C) under a constant total pressure (1 atm). Products were quantitatively analyzed by titrations, i.e., iodometric for the amount of perbenzoic acid and neutralization for the total amount of benzoic acid and perbenzoic acid using thymolphthalein indicator.

RESULTS

Catalytic Activities of Palladium Complexes

Figure 1 shows a typical reaction curve for the oxidation of benzaldehyde in the

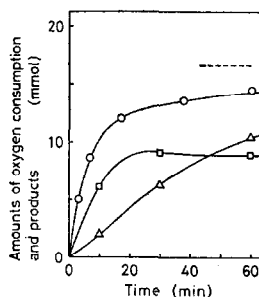
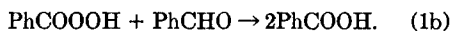
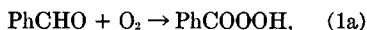


Fig. 1. Oxidation of benzaldehyde with $\text{PdO}_2(\text{PPh}_3)_2$. The dotted line represents the oxygen consumption at 100% conversion of benzaldehyde. $\text{PdO}_2(\text{PPh}_3)_2$ 0.0527 mmole and PhCHO 24.7 mmole in 50 ml of benzene solution at 30°C under 624 mmHg of O_2 . ○ Amount of oxygen consumption; □ amount of perbenzoic acid; Δ amount of benzoic acid.

TABLE 1
ANALYTICAL DATA

	Found (%)		Required (%)		Color
$\text{Pd}(\text{PPh}_3)_4$	C 75.58	H 5.44	C 74.82	H 5.24	yellow
$\text{PdO}_2(\text{PPh}_3)_2$	C 65.14	H 4.78	C 64.95	H 4.53	pale blue
$\text{Pt}(\text{PPh}_3)_4$	C 69.03	H 5.11	C 69.44	H 4.82	yellow
$\text{PtO}_2(\text{PPh}_3)_2$	C 57.28	H 4.23	C 57.47	H 3.99	pale yellow
$\text{IrO}_2\text{Cl}(\text{CO})(\text{PPh}_3)_2$	C 53.98	H 4.27	C 54.71	H 3.73	yellow
$\text{RhCl}(\text{CO})(\text{PPh}_3)_2$	C 64.48	H 5.07	C 64.31	H 4.39	yellow
$\text{RhCl}(\text{PPh}_3)_3$	C 69.87	H 5.24	C 70.09	H 4.91	russet
$[\text{RhCl}(\text{PPh}_3)_2]_2$	C 65.31	H 5.23	C 65.22	H 4.57	reddish brown

presence of a catalytic amount of $\text{PdO}_2(\text{PPh}_3)_2$ in benzene solution. As seen in the figure, perbenzoic acid increased rapidly at the earlier stage of the reaction, while benzoic acid increased gradually over the whole reaction period, suggesting the following consecutive reactions.



Since the amount of oxygen incorporated into the two acids was well balanced by the observed oxygen consumption, it was concluded that there was no other significant product.

The initial rate of oxygen consumption was first order in oxygen pressure and catalyst concentration, whereas it showed a Michaelis-Menten type of dependence on benzaldehyde concentration as shown in Fig. 2. Thus, the initial rate of benzaldehyde oxidation was expressed as follows.

$$-\left(\frac{d\text{O}_2}{dt}\right)_0 = \frac{C_1[\text{PdO}_2(\text{PPh}_3)_2]_0[\text{PhCHO}]_0 P_{\text{O}_2}}{1 + C_2[\text{PhCHO}]_0}, \quad (2)$$

where C_1 and C_2 are constants and the suffix "0" means the initial value.

It should be mentioned that a marked retardation of the reaction was observed at the latter stage, especially after the conversion of benzaldehyde reached 40–50%. Since this retardation became more and more pronounced as the reaction proceeded, the rate of the reaction was quite small at

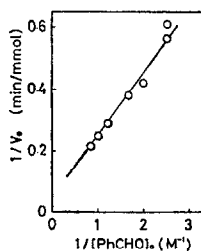


Fig. 2. The linear relationship between the reciprocal of the initial rate of oxygen consumption, $1/V_0$, and that of the concentration of benzaldehyde, $1/[\text{PhCHO}]_0$. $\text{PdO}_2(\text{PPh}_3)_2$, 0.0526 mmole in 50 ml of benzene solution at 30°C under 624 mmHg of O_2 .

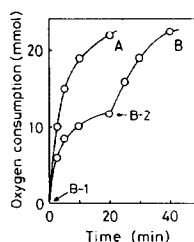


Fig. 3. The restoration of catalytic activity by addition of the fresh reactant. $\text{Pd}(\text{PPh}_3)_4$, 0.0779 mmole in 50 ml of benzene solution at 40°C under 572 mmHg of O_2 . A. PhCHO 60 mmole; B. B-1. Starting PhCHO 30 mmole; B-2. Additional PhCHO 30 mmole.

the conversion level of ca. 70%, in contrast to the usual case of autoxidation catalyzed by cobalt salts in which the reaction was completed in 20 min under similar conditions. The retardation was not due to the exhaustion of the catalyst because the catalytic activity was restored by the addition of the fresh reactant (Fig. 3). Hence,

it was probable that the retardation was related to the accumulation of the products. For this point, experiments showed that the addition of perbenzoic acid to the reaction system lowered the initial rate to a great extent as shown in Fig. 4, while benzoic acid had no effect. This suggests that the oxidation reaction proceeds via an intermediate complex containing both oxygen and benzaldehyde in its coordination sphere

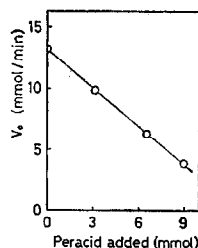


Fig. 4. The lowering of the initial rate, V_0 , of benzaldehyde oxidation by addition of perbenzoic acid. $\text{PdO}_2(\text{PPh}_3)_2$, 0.0779 mmole and PhCHO 19.8 mmole in 50 ml of benzene solution at 30°C under 624 mmHg of O_2 .

rather than via a radical chain mechanism, and that perbenzoic acid shows the retardation effect by coordinating competitively with benzaldehyde, for it is unlikely that hydroperoxides have a retardation effect on a radical chain reaction in which they are known to act as initiators or re-oxidizing agents. In fact, no retardation effect by perbenzoic acid was observed in the benzaldehyde oxidation with cobalt acetate catalyst.

Although the catalytic activity of Pd(PPh₃)₄ was negligible without oxygen treatment (preoxidation) of benzaldehyde before the addition of the catalyst into the reaction system, its activity after preoxidation was nearly equal to that of PdO₂(PPh₃)₂. The amount of oxygen required for the preoxidation was about three times as much as the catalyst added. That the color of the solution in the case of Pd(PPh₃)₄ catalysts even without preoxidation was similar to that in the case of PdO₂(PPh₃)₂, suggested the formation of PdO₂(PPh₃)₂ from Pd(PPh₃)₄ dissociating free triphenylphosphine which might inhibit the reaction. Actually, addition of triphenylphosphine was observed to prevent the activity of PdO₂(PPh₃)₂, too. It appears that an enough amount of perbenzoic acid was produced during the preoxidation to oxidize the free phosphine.

Catalytic Activities of Platinum Complexes

Platinum complexes catalyzed the oxidation of benzaldehyde although their activity

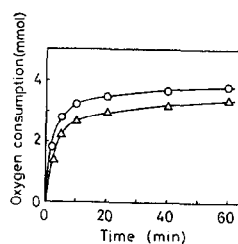
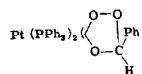


FIG. 5. A comparison of catalytic activities between (Δ) platinum oxygen complex, PtO₂(PPh₃)₂, and (○) platinum aldehyde-peroxy chelate complex,



Cat. 0.0390 mmole and PhCHO 39.6 mmole in 50 ml of benzene solution at 50°C under 520 mmHg of O₂.

was much smaller than palladium complexes. Following observations with platinum complexes were quite similar to those with palladium complexes. (a) Pt(PPh₃)₄ and PtO₂(PPh₃)₂ had similar catalytic activities to each other, although (b) preoxidation was required for Pt(PPh₃)₄ catalyst. (c) A small amount of triphenylphosphine contained as impurity in PtO₂(PPh₃)₂ inhibited the reaction. (d) Retardation of the reaction due to perbenzoic acid was observed after the conversion of benzaldehyde went up to 10%.

The coordinated oxygen molecule of PtO₂(PPh₃)₂ is known to react with carbonyl group of benzaldehyde to form an

TABLE 2
CATALYTIC ACTIVITIES OF COMPLEXES FOR THE BENZALDEHYDE OXIDATION

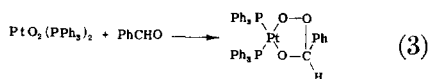
	Temp. (°C)	Cat. ^a (mmole)	PhCHO ^a (mmole)	Initial rate ^b (mmole/min)	Conversion ^c (%)
PdO ₂ (PPh ₃) ₂	40	0.078	19.8	1.80	72
PtO ₂ (PPh ₃) ₂	40	0.078	39.6	0.34	14
RhCl(CO)(PPh ₃) ₂	40	0.078	19.8	2.30	78
RhCl(PPh ₃) ₃	40	0.078	19.8	1.40	83
[RhCl(PPh ₃) ₂] ₂	40	0.041	19.8	0.29	71
IrO ₂ Cl(CO)(PPh ₃) ₂	40	0.075	19.8	0.12	45

^a The amount in 50 ml of benzene solution.

^b The initial rate of oxygen consumption.

^c The benzaldehyde conversion after 1 h.

aldehyde-peroxy chelate ring (Eq. (3)) (11). Such a chelate complex may be one of



The reaction of perbenzoic acid with benzaldehyde described at step 4 is well known.

Assuming stationary states in this reaction mechanism from step 1 to 3, the following rate equation for the initial reaction is derived.

$$V_0 = \frac{K_1 K_2 k_3 [\text{ML}_2\text{O}_2]_0 [\text{PhCHO}]_0 \text{P}_{\text{O}_2}}{1 + K_1(1 + K_2) [\text{PhCHO}]_0 + (1 + (k_2/k_{-1}) + K_1 [\text{PhCHO}]_0) (k_3/k_{-2}) \text{P}_{\text{O}_2}} \quad (4)$$

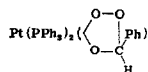
intermediate species in this oxidation reaction. The catalytic activity of this chelate complex was found to be nearly equal to that of $\text{PtO}_2(\text{PPh}_3)_2$ (Fig. 5).

Catalytic Activities of Rhodium and Iridium Complexes

The catalytic activities of these transition metal complexes are summarized in Table 2. The catalytic activity was in the sequence of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2 > \text{PdO}_2(\text{PPh}_3)_2 > \text{RhCl}(\text{PPh}_3)_3 > [\text{RhCl}(\text{PPh}_3)_2]_2 > \text{IrO}_2\text{Cl}(\text{CO})(\text{PPh}_3)_2 \approx \text{PtO}_2(\text{PPh}_3)_2$. It was also observed that free phosphine and perbenzoic acid hindered the reaction.

DISCUSSION

The similarity in catalytic activity between $\text{PdO}_2(\text{PPh}_3)_2$ and $\text{Pd}(\text{PPh}_3)_4$ and that between $\text{PtO}_2(\text{PPh}_3)_2$ and

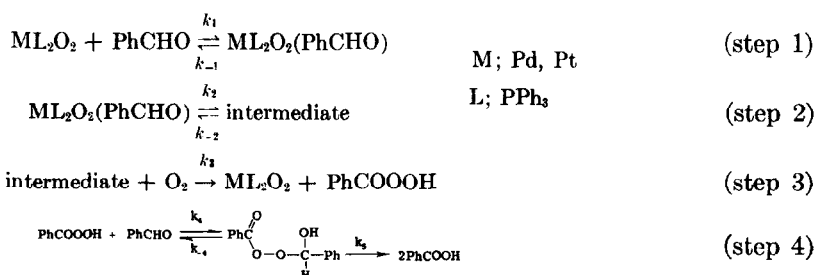


suggest the following reaction steps (a radical-chain mechanism seems unlikely as mentioned earlier):

where k_1 , k_{-1} , k_2 , k_{-2} and k_3 are rate constants, $K_1 = k_1/k_{-1}$ and $K_2 = k_2/k_{-2}$. If step 3 is assumed to be rate-determining (that is, $k_{-2} \gg k_3$), Eq. (4) is consistent with the experimental equation.

Some observations in the present study can be explained by this reaction scheme in the following way: (a) The low activity of platinum complex is interpreted in terms of the high stability of intermediate complex. (b) Free phosphine and perbenzoic acid may hinder the benzaldehyde oxidation by preventing the coordination of benzaldehyde to the catalyst in step 1. (c) A small amount of perbenzoic acid produced during the preoxidation may oxidize free phosphine into phosphine oxide which shows low coordination ability to the catalyst complex. However, it seems difficult to explain the difference in catalytic activity between $\text{RhCl}(\text{PPh}_3)_3$ and $[\text{RhCl}(\text{PPh}_3)_2]_2$, both of which are expected to form the same oxygen complex, $\text{RhO}_2\text{Cl}(\text{PPh}_3)_2$ (10), in the reaction system. Detailed kinetic studies are in progress.

In conclusion, it seems apparent that the benzaldehyde oxidation using oxygen complexes proceeds by a reaction mechanism



in which molecular oxygen reacts with benzaldehyde with the assistance of the central metal atom.

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