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Homogeneous Oxidation of Benzaldehyde Catalyzed by Bis (triphenylphosphine)oxygenopalladium(II) Complex

In the studies of the homogeneous oxidation of organic substrates catalyzed by metal complexes (*1*), oxygen activation by metal complexes, direct oxygen transfer from metal–dioxygen complexes to organic substrates, and/or nonradical oxidation processes have been of current interest. Recently, the report by Hojo *et al.* (*2*) attracted our attention, because they proposed the nonradical mechanism for the catalytic oxidation of benzaldehyde by $PdO_2(PPh_3)_2$. We have restudied the same reaction and found that the reaction proceeds via free radical intermediates.

Figure 1 shows a typical reaction curve in the presence and absence of $PdO_2(PPh_3)_2$ [Anal. Found: C, 64.81%; H, 4.79%; Calcd: C, 65.22%; H, 4.56%; color was green as in Ref. (*3*), while pale blue was reported in Ref. (*2*)]. To know the feature of the initial stage of the reaction, we used the lower concentration of the complex (1.51×10^{-4} *M*) and the smaller volume of the reaction solution (10 ml) than those used in Ref. (*2*). Chlorobenzene was used as a solvent in place of benzene. The results of our kinetic studies were different from those of Hojo *et al.* in some points. As shown in Fig. 1, we observed an induction period. The rate of the catalytic oxidation was determined at the maximum slope of the oxygen uptake curve, ignoring the uncatalyzed oxidation. The rate equation (1) obtained from the results in Figs. 2 and 3 is very different from that previously reported (*2*), but rather similar to that obtained for the radical autoxidation of benzaldehyde catalyzed by Co(III) (*4*).

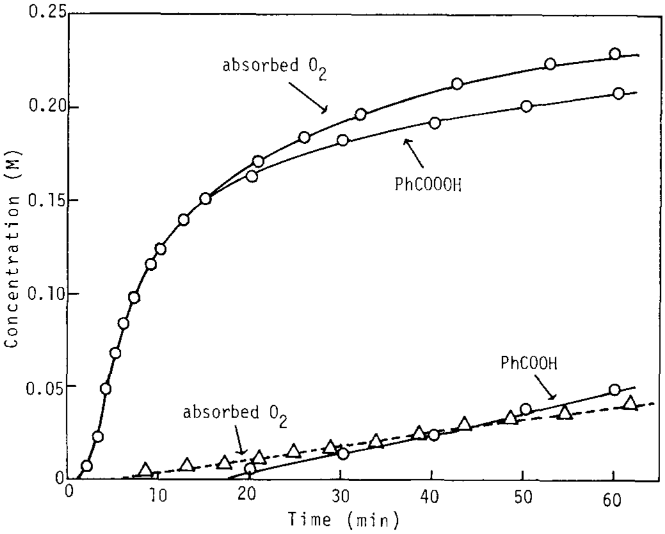

FIG. 1. Oxidation of benzaldehyde. (○) with $PdO_2(PPh_3)_2$ (1.51×10^{-4} *M*), (△) without $PdO_2(PPh_3)_2$, $[PhCHO]_0 = 0.490$ *M*, $P_{O_2} = 747$ mm Hg, at 25°C.

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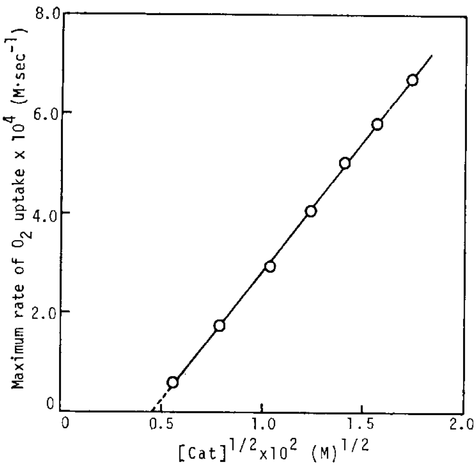


FIG. 2. Dependence of the maximum rate on the catalyst concentration. $[PhCHO]_0 = 0.490$ *M*, $P_{O_2} = 747$ mm Hg, at 25°C.

$$-d[O_2]/dt = K[PdO_2(PPh_3)_2]^{\frac{1}{2}} \times [PhCHO]^{\frac{3}{2}} P_{O_2}^{\frac{1}{2}}. \quad (1)$$

A marked retardation of the catalytic oxidation was observed after the conversion of benzaldehyde reached about 30%. Hojo *et al.* explained the result as the effect of accumulation of product (perbenzoic acid). But the addition of perbenzoic acid or benzoic acid did not affect the rate significantly. Since the addition of benzaldehyde after 1 hr of the reaction only slightly increased the oxygen uptake, the retardation may be due to the decomposition of the catalyst. The result that the straight line in Fig. 2 did not intercept origin is also explained by the decomposition of the catalyst. No retardation by perbenzoic acid and results similar to those shown in Fig. 2 were reported in the case of Co(III) (*4*).

Although Hojo *et al.* did not study the effect of the addition of radical inhibitors, we observed the retardation or stop of the reaction by the addition of Ionol(2,6-di-*tert*-butyl-*p*-cresol). Furthermore, the formation of a radical intermediate was demonstrated by the radical trapping technique. When the solution of nitroso-*tert*-butane (NtB) (*5*) or phenyl-*tert*-butylnitrone (PBN) (*6*) was added to the reaction solution at the maximum rate of oxygen uptake, the reaction stopped immediately. After nitrogen was bubbled

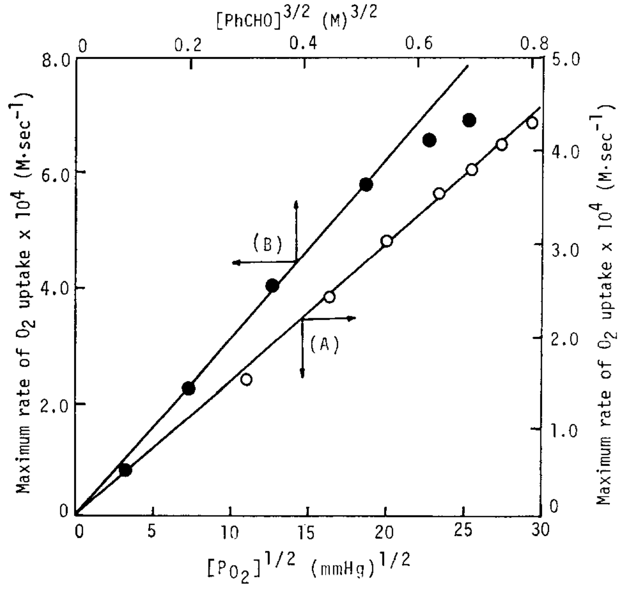
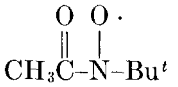


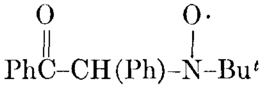
FIG. 3. Dependence of the maximum rate on the oxygen pressure and benzaldehyde concentration at 25°C. (A) $[Cat]_0 = 1.51 \times 10^{-4}$ *M*, $[PhCHO]_0 = 0.490$ *M*. (B) $[Cat]_0 = 1.51 \times 10^{-4}$ *M*, $P_{O_2} = 747$ mm Hg.

through the solution to remove oxygen, esr spectra were taken on a JEOL PE-2X spectrometer modified with a JEOL ES-SCXA gunn diode microwave unit at room temperature. A fine triplet (g-factor, 2.0068; a_N, 8.0 G) in the case of NtB and double triplets (g-factor, 2.0063; a_N, 13.4 G; $a_{\beta-\mathrm{H}}$, 1.56 G) in the case of PBN were observed. By comparing the g-factors and hyperfine coupling constants with those of



$CH_3C(=O)-N(O\cdot)-Bu^t$

(g-factor, 2.0068; a_N, 8.0 G in benzene) (*7*) and



$PhC(=O)-CH(Ph)-N(O\cdot)-Bu^t$

(a_N, 12.85 G; $a_{\beta-\mathrm{H}}$, 1.48 G in benzene) (*6a*), the free radical trapped by NtB and PBN was identified as $Ph\dot{C}O$.

To explain these results, we propose Mechanism 1 [Eqs. (2)–(7)], in which Cat denotes $PdO_2(PPh_3)_2$.

$$\mathrm{Cat} + \mathrm{PhCHO} + \mathrm{O_2} \xrightarrow{k_i} \mathrm{Cat} + \mathrm{Ph\dot{C}O} + \text{inert product}, \quad (2)$$

$$\mathrm{Ph\dot{C}O} + \mathrm{O_2} \xrightarrow{k} \mathrm{PhCOOO\cdot}, \quad (3)$$

$$\mathrm{PhCOOO\cdot} + \mathrm{PhCHO} \xrightarrow{k_p} \mathrm{PhCOOOH} + \mathrm{Ph\dot{C}O}, \quad (4)$$

$$\mathrm{PhCOOO\cdot} + \mathrm{PhCOOO\cdot} \xrightarrow{k_t} \mathrm{O_2} + \text{inert product}, \quad (5)$$

$$\mathrm{Cat} \xrightarrow{k_d} \text{inactive form}, \quad (6)$$

$$\mathrm{PhCOOOH} + \mathrm{PhCHO} \xrightarrow{k_a} 2\mathrm{PhCOOH}. \quad (7)$$

When the steady-state approximation is applied while ignoring the steps (6) and (7), the constant K in Eq. (1) corresponds to $k_p(k_i/2k_t)^{\frac{1}{2}}$, which value was obtained from the lines in Figs. 2 and 3 [1.83 from Fig. 2 and from line A in Fig. 3, and 1.66 from line B in Fig. 3. Oxygen concentration in chlorobenzene was evaluated in Ref. (*8*). Effective catalyst concentration was evaluated to 6.2×10^{-5} M by supposing the first-order decomposition of the catalyst.]. The fair agreement of K values may support the present mechanism.

In conclusion, it is clear that the oxidation of benzaldehyde catalyzed by $PdO_2(PPh_3)_2$ proceeds by the radical mechanism rather than by the nonradical mechanism. The detailed mechanism of each step should further be studied.

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REFERENCES

1. Sheldon, R. A., and Kochi, J. K., *in* "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. 25, p. 272. Academic Press, New York, 1976; and references therein.
2. Hojo, J., Yuasa S., Yamazoe, N., Mochida, I., and Seiyama, T., *J. Catal.* **36**, 93 (1975).
3. Nyman, J., Wymore, C. E., and Wilkinson, G., *J. Chem. Soc.* (*A*) 561 (1968).
4. Bawn, C. E. H., and Jolley, J. E., *Proc. Roy. Soc.* *A* **237**, 297 (1956).
5. Holman, R. J., and Perkins, M. J., *J. Chem. Soc.* (*C*) 2195 (1970).
6. (a) Janzen, E. G., and Blackburn, B. J., *J. Amer. Chem. Soc.* **91**, 4481 (1969); (b) Emmons, W. D., *J. Amer. Chem. Soc.* **79**, 5739 (1957).
7. Mackor, A., Wajer, T. A. J. W., and De Boer, T. J., *Tetrahedron* **24**, 1623 (1968).
8. Stephen, H., and Stephen, T. (Eds.), "Solubilities of Inorganic and Organic Compounds," Vol. 1, Part 1, p. 573. Pergamon, New York, 1963.

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