CHEMISTRY LETTERS, pp. 1217-1220, 1973. Published by the Chemical Society of Japan

TRICHLOROVANADIUM(III)-CATALYZED OXIDATION OF TRIPHENYLPHOSPHINE

Yasuo CHIMURA, Hiroyoshi KANAI, Satohiro YOSHIDA, and Kimio TARAMA
Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University
Sakyo-Ku, Kyoto 606

VCl_3 catalyzes the oxidation of PPh_3 to $OPPh_3$ with oxygen in CH_3CN. By kinetic investigation the mechanism involving a dioxygen complex of VCl_3 as an intermediate is proposed and its reactivity toward PPh_3 is shown to be greater than that of $Pt(PPh_3)_2O_2$.

In recent years many low valent complexes of the group VIII elements have been known to catalyze the oxidation of PPh_3, and a few reports have described the mechanism of the reaction.[1,2] There have scarcely been the reports on the catalytic action of complexes of high valent transition metals in the oxidation of PPh_3, thus only two papers are reported.[3,4] It is much interesting to compare the catalysis by low valent complexes with that by high valent complexes in the oxidation of PPh_3. We found recently the catalytic activity of VCl_3, one of high valent complexes, in the oxidation of PPh_3, and compared the reactivity of a dioxygen complex of VCl_3, which is an intermediate in the reaction, toward PPh_3 with that of a dioxygen complex of platinum, which is one of the typical intermediates in the low valent complex-catalyzed oxidations of PPh_3.

Experimental procedure: PPh_3-CH_3CN solution was introduced into a oxygen-filled reaction flask equipped with a gas buret, and the reaction was initiated by the injection of VCl_3-CH_3CN solution into the above solution. The volume of oxygen taken up at constant pressure was measured. Experimental conditions: 20.0 ^{o}C; the volume of the reaction solution, 40.7 ml; $[VCl_3]_o$, $(5.7\text{—}22.6)\times10^{-3}$ M; $[PPh_3]_o$, $(0.0\text{—}1.5)\times10^{-1}$ M; the partial pressure of oxygen, 176—687 mmHg.

The time course of the oxygen uptake represented a sigmoid curve. The reaction solution was homogeneous at the early stage of the reaction, changing its color from green to yellow. At the later stage blue-green powders, identified as $VOCl_2(OPPh_3)_2$, precipitated. The oxygen uptake ceased before the oxygen necessary to convert all PPh_3 to $OPPh_3$ was taken up. From this reaction solution, initial PPh_3 was found as $OPPh_3$

and unreacted PPh_3; initial VCl_3 as the above precipitates and $VOCl_2$ in solution; and oxygen taken up as $OPPh_3$ and the both $VOCl_2$ species.[5)]

The effects of initial reactant concentrations on r_o were examined, where r_o was defined as the extrapolated value of the gradient of the above sigmoid curve to zero reaction time. A plot of r_o *vs.* $[VCl_3]_o$ and that of r_o *vs.* $[O_2]$ were straight lines which started from origins, while that of r_o *vs.* $[PPh_3]_o$ was a hyperbolic curve as shown in Figure. Hence, r_o could be expressed as Eq.(1):

$$r_o = a[VCl_3]_o[O_2]\left(1 - \frac{c}{b + [PPh_3]_o}\right) \qquad (1)$$

From the data in Figure, the values of a, b, and c in Eq.(1) were estimated as 0.45±0.02 $M^{-1}sec^{-1}$, 0.055±0.002 M, and 0.051±0.001 M, respectively.

No interaction between VCl_3 and PPh_3 under the atmosphere of nitrogen was observed by infrared and visible spectra.

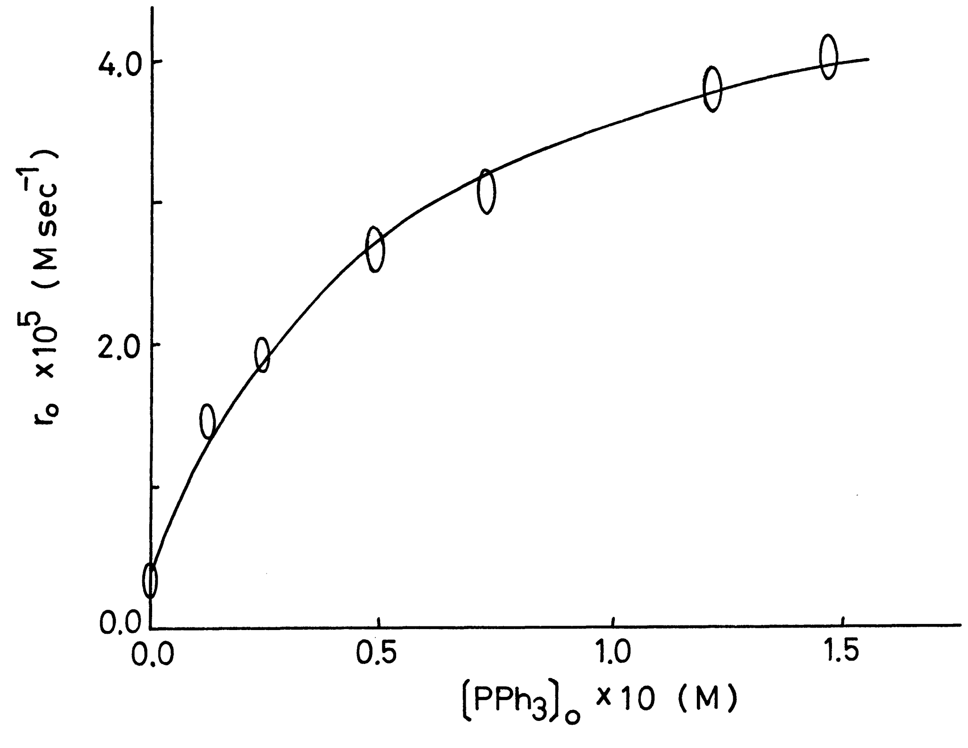
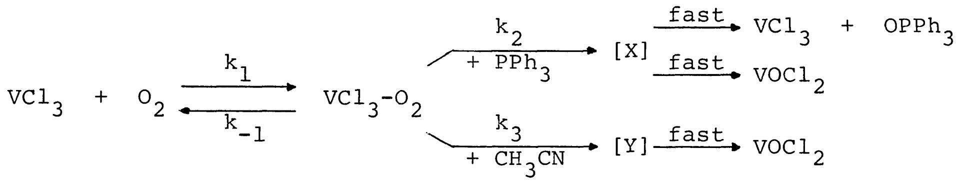


Figure r_o *vs.* $[PPh_3]_o$ 20 °C; $[VCl_3]_o$, 1.27×10^{-2} M; $[O_2]$, 9.21×10^{-3} M. The solid line represents the calculated one by Eq.(1) with the values of a, b, and c in the text.

The addition of 2,6-di-*t*-butyl-*p*-cresol, a radical inhibitor, had no influence on the reaction. Therefore, the reaction is not a radical chain one.

r_o was increased by the addition of $OPPh_3$ at the start of the reaction, reaching maximum at about a 4-fold excess of $OPPh_3$ in relation to VCl_3. This suggests that the change of the reaction rate with time, especially the initial rate increase, may be caused partly by $OPPh_3$ produced in the reaction.

From the above experiments, the following scheme involving a dioxygen complex of VCl_3[6) as an intermediate is proposed.



$$VCl_3 + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} VCl_3\text{-}O_2 \qquad VCl_3\text{-}O_2 \xrightarrow[+\,PPh_3]{k_2} [X] \xrightarrow{\text{fast}} VCl_3 + OPPh_3,\quad [X] \xrightarrow{\text{fast}} VOCl_2 \qquad VCl_3\text{-}O_2 \xrightarrow[+\,CH_3CN]{k_3} [Y] \xrightarrow{\text{fast}} VOCl_2$$

Making use of a steady-state approximation for the concentration of $VCl_3\text{-}O_2$, the initial rate is derived as follows:

$$r_o = k_1[VCl_3]_o[O_2]\left(1 - \frac{k_{-1}/k_2}{(k_{-1}+k_3)/k_2 + [PPh_3]_o}\right) \qquad (2)$$

Eq.(2) explains the results of kinetic experiments. Comparison between Eq.(1) and Eq.(2) leads to: k_1= a, $(k_{-1} + k_3)/k_2$= b, and k_{-1}/k_2= c.

Let us compare the reactivity of $VCl_3\text{-}O_2$ toward PPh_3 with that of $Pt(PPh_3)_2O_2$, one of the typical dioxygen complexes of low valent metals. As shown in Ref.(1), the dependence of the rate of $Pt(PPh_3)_3$-catalyzed oxidation of PPh_3 on $[O_2]$ is not linear, differing from that of VCl_3-catalyzed oxidation. This difference may arise from that the concentration of $Pt(PPh_3)_2O_2$ is comparable with that of $Pt(PPh_3)_3$ in contrast to the negligible small concentration of $VCl_3\text{-}O_2$. Since the rates of formation of these two dioxygen complexes do not much differ, the difference in the concentrations of these dioyygen complexes may be caused by the great difference in the rates of disappearance of these dioxygen complexes. In the case of VCl_3-catalyzed oxidation, since $(k_{-1} + k_3)/k_2[PPh_3]_o$ has the value of 0.75±0.03 at $[PPh]_o$=0.0737 M,[7) the reaction between $VCl_3\text{-}O_2$ and PPh_3 should be most responsible for the rate of disappearance of $VCl_3\text{-}O_2$. Therefore, it seems that $VCl_3\text{-}O_2$ is more reactive than $Pt(PPh_3)_2O_2$ toward PPh_3.

It is the most important feature of the catalysis by VCl_3 that $VCl_3\text{-}O_2$ has, in spite of its reversibility, greater reactivity toward PPh_3 than $Pt(PPh_3)_2O_2$ has.

We are now investigating the effects of other halogen ligands of vanadium(III) complexes, and those of the substituents of PPh_3 on the reaction.

Notes and References

(1) J. P. Birk, J. Halpern, and A. L. Pickard, *J. Amer. Chem. Soc.*, 90, 4492 (1968); J. Halpern and A. L. Pickard, *Inorg. Chem.*, 9, 2798 (1970).

These papers have described the following scheme and rate equation.

$$\mathrm{Pt(PPh_3)_3 + O_2 \xrightarrow{k_1} Pt(PPh_3)_2O_2 + PPh_3}$$

$$\mathrm{Pt(PPh_3)_2O_2 + PPh_3 \xrightarrow{k_2} [Pt(PPh_3)_3O_2] \xrightarrow[fast]{2PPh_3} Pt(PPh_3)_3 + 2OPPh_3}$$

$$\mathrm{rate} = \frac{k_1k_2[\mathrm{Pt}]_{\mathrm{total}}[\mathrm{PPh_3}][\mathrm{O_2}]}{k_1[\mathrm{O_2}] + k_2[\mathrm{PPh_3}]}$$

where $[\mathrm{Pt}]_{\mathrm{total}} = [\mathrm{Pt(PPh_3)_3}] + [\mathrm{Pt(PPh_3)_2O_2}]$

$k_1 = 2.6 \pm 0.1\ \mathrm{M^{-1}sec^{-1}}$, $k_2 = 0.15 \pm 0.01\ \mathrm{M^{-1}sec^{-1}}$, at 25 °C in benzene.

(2) B. W. Graham, K. R. Laing, J. O'Connor, and W. R. Roper, *J. Chem. Soc. Dalton*, 1237 (1972).

(3) K. Tarama, S. Yoshida, H. Kanai, and S. Osaka, *Bull. Chem. Soc. Japan*, 41, 1271 (1968).

(4) R. Barral, C. Bocard, I. Sérée de Roch, and L. Sajus, *Tetrahedron Lett.*, 1693 (1972).

(5) One example: initial $\mathrm{VCl_3}$, 0.515 mmole; initial $\mathrm{PPh_3}$, 5.00 mmole; $\mathrm{O_2}$ taken up, 1.63 mmole; total $\mathrm{OPPh_3}$, 3.00 mmole; unreacted $\mathrm{PPh_3}$, 2.00 mmole; $\mathrm{VOCl_2(OPPh_3)_2}$, 0.39 mmole; $\mathrm{VOCl_2}$ in solution, 0.11 mmole.

(6) A dioxygen complex of V(III) was kinetically characterized in the reaction between $\mathrm{O_2}$ and V(III)-chelate: J. H. Swinehart, *Chem. Commun.*, 1443 (1971).

(7) The concentration at which r_0 *vs.* $[\mathrm{O_2}]$ was measured.

(Received September 10, 1973)