The Kinetics of Formation and Catalytic Activity of Carbonyldioxygentris(diphenylmethylphosphine)iridium(I) Perchlorate

By **V. J. Choy** and **Charmian J. O'Connor,*** Chemistry Department, University of Auckland, Private Bag, Auckland, New Zealand

The kinetics of the uptake of dioxygen by $[Ir(CO)(PPh{\cdot}Me)_3][ClO_4]$ in acetone and dichloromethane have been studied and the Arrhenius parameters evaluated. Qualitative measurements on the homogeneous oxidation of triphenylphosphine and diphenylmethylphosphine by the dioxygen complex $[Ir(CO)(PPh_2Me)_3(O_2)][ClO_4]$ in a variety of solvents show that it is an inefficient catalyst.

THE electronic factors affecting dioxygen uptake by coordination compounds now appear to be well understood. An increase in electron density at the metal caused by changing the ligands or the metal improves uptake properties. The reactivities of three different metals in the same periodic group have been compared by Vaska *et al.*[1] who studied the reaction

$$[M(P\text{-}P)_2]^+ + XY \rightleftharpoons [(XY)M(P\text{-}P)_2]^+$$

where XY = O_2, HCl, H_2, CO, SO_2, and (P-P) = *cis*-1,2-bis(diphenylphosphino)ethylene, and found the unmistakable order of attraction of the univalent cations to dioxygen as $CO \gg Ir > Rh$. It was suggested that the reactivity of the d^8 M^I complexes is directly dependent on their ligand-field stabilisation energies.

Vaska and Chen[2] have also found that the rate of dioxygen addition to *trans*-$[IrCl(CO)(R_3P)_2]$ (R_3P = tertiary phosphine) and the stability of the resulting dioxygen adduct increase with the basicity of the substituent R. Halpern and Pickard[3] studied the rate of consumption of dioxygen by $Pt(PPh_3)_3$ and the mechanisms of the catalytic oxidations of triphenylphosphine by $Pt(PPh_3)_2(O_2)$[4] and $Ru(O_2)(NCS)(NO)(PPh_3)_2$[5] have been described. Roper *et al.*[6] recently reported the

---

[1] L. Vaska, L. S. Chen, and W. V. Miller, *J. Amer. Chem. Soc.*, 1971, **93**, 6671.

[2] L. Vaska and L. S. Chen, *Chem. Comm.*, 1971, 1080.

[3] J. Halpern and A. L. Pickard, *Inorg. Chem.*, 1970, **9**, 2798.

[4] J. P. Birk, J. Halpern, and A. L. Pickard, *J. Amer. Chem. Soc.*, 1968, **90**, 4491; *Inorg. Chem.*, 1968, **7**, 2672.

[5] B. W. Graham, K. R. Laing, C. J. O'Connor, and W. R. Roper, *Chem. Comm.*, 1970, 1272; *J.C.S. Dalton*, 1972, 1237.

[6] G. R. Clark, C. A. Reed, W. R. Roper, B. W. Skelton, and T. N. Waters, *Chem. Comm.*, 1971, 758.

isolation of the dioxygeniridium(I) cation $[Ir(O_2)(CO)(PPh_2Me)_3]^+$ and Reed [7] found that this cation acted as an homogeneous catalyst for the oxidation of diphenylmethylphosphine by dioxygen. In this paper we report the kinetics of the irreversible uptake of dioxygen by the $[Ir(CO)(PPh_2Me)_3]^+$ cation in acetone and dichloromethane, and a qualitative study of the catalytic homogeneous oxidation of PPh_2Me to $OPPh_2Me$.

RESULTS AND DISCUSSION

Formation Kinetics.—The red solutions of $[Ir(CO)(PPh_2Me)_3][ClO_4]$ in acetone and dichloromethane ($\lambda_{max.}$ 430 nm) absorbed O_2 readily at pressures up to 0·75 atm in the temperature range 5—25 °C. This absorption of O_2 was accompanied by a colour change from red to yellow, the colour of the O_2 adduct. In order to indicate that the rate measured was the rate of disappearance of the $[Ir(CO)(PPh_2Me)_3]^+$ cation, the rate laws have been written in terms of $-d[Ir]/dt$ [where $Ir = Ir(CO)(PPh_2Me)_3{}^+$].

Halpern *et al.*[3,4] have established the rate law for the addition of dioxygen to $Pt(PPh_3)_4$ and because the system in this study is also a dioxygen addition the rate law was expected to be similar [equation (1)], where

$$-d[Ir]/dt = k_2[Ir][O_2] \qquad (1)$$

k_2 is a second-order rate constant. However, under the present experimental conditions, there was a large excess of dioxygen and measurements were made under pseudo-first-order conditions [equation (2)], where k_1'

$$-d[Ir]/dt = k_1'[Ir] \qquad (2)$$

(a pseudo-first-order rate constant) $= k_2[O_2]$. Values of k_1' were evaluated from the slopes of first-order plots of $\log_{10}(E_t - E_\infty)$ against time, where E_t is the absorbance of the aliquot sample at time t, and E_∞ was taken as the absorbance of a separately prepared solution of the dioxygen complex. The data are shown in Figures 1 and 2. In all the kinetic runs the initial [Ir] was $3·0 \times 10^{-4}$M. Several runs with initial [Ir] equal to $1·5 \times 10^{-4}$M showed that the value of k_1' was not affected by small differences in the initial [Ir].

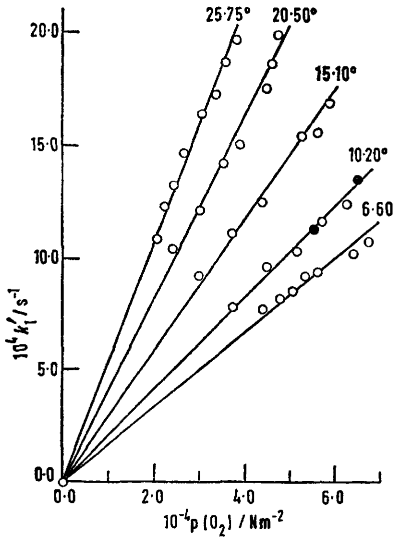

FIGURE 1 The dependence of k_1' {pseudo-first-order rate constant for the formation of $[Ru(O_2)(CO)(PPh_2Me)_3]^+$} on O_2 pressure in dichloromethane at different temperatures. [complex] = $3·0 \times 10^{-4}$M (○); $1·5 \times 10^{-4}$M (●)

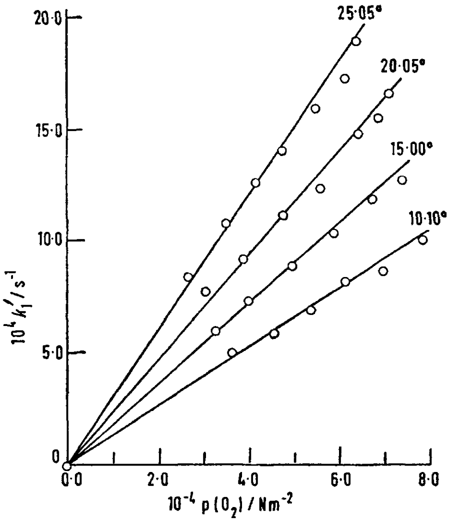

FIGURE 2 The dependence of k_1' {pseudo-first-order rate constant for formation of $[Ru(O_2)(CO)(PPh_2Me)_3]^+$} on O_2 pressure in acetone at different temperatures. [complex] = $3·0 \times 10^{-4}$M

TABLE 1

Values of k_2, the second-order rate constant for formation of $[Ir(O_2)(CO)(PPh_2Me)_3]^+$, derived from slopes of plots of k_1' {the pseudo-first-order rate constant of O_2 uptake by $[Ir(CO)(PPh_2Me)_3]^+$} against $p(O_2)$

Solvent	Temp. (°C)	k_2/l mol^{-1} s^{-1}
Dichloromethane	6·60	0·19
	10·20	0·24
	15·10	0·34
	20·50	0·46
	25·75	0·61
Acetone	10·10	0·15
	15·00	0·21
	10·05	0·26
	25·05	0·33

The second-order rate constants k_2 (Table 1) were obtained from the slopes of plots of k_1' against dioxygen partial pressure. The lines in Figures 1 and 2 were assumed to pass through the origin since no formation of $[Ir(CO)(PPh_2Me)_3(O_2)][ClO_4]$ was observed in an inert atmosphere (oxygen-free nitrogen) under comparable experimental conditions. The units of k_2 were converted into l mol^{-1} s^{-1} by converting the dioxygen pressure to concentration. Assuming Henry's law, the

---

[7] C. A. Reed, Ph.D. Thesis, University of Auckland, 1971.

solubility of O_2 in dichloromethane was calculated for the temperature range studied to be *ca.* $8{\cdot}9 \times 10^{-3}$M at N.T.P. by comparison with solubility data of O_2 in chloroform and carbon tetrachloride.[8] The solubility of O_2 in acetone [9] was found to be $9{\cdot}4 \times 10^{-3}$, $9{\cdot}1 \times 10^{-3}$, $8{\cdot}9 \times 10^{-3}$, and $8{\cdot}8 \times 10^{-3}$M at N.T.P. for the temperatures 25, 20, 15, and 10 °C respectively. Good Arrhenius plots of $\log_{10} k_2$ against $1/T$ were obtained and yielded the parameters $\Delta H^{\ddagger} = 9{\cdot}71$ kcal mol^{-1} and $\Delta S^{\ddagger} = -27{\cdot}1$ cal K^{-1} mol^{-1} at 25·75 °C in dichloromethane, and $\Delta H^{\ddagger} = 7{\cdot}99$ kcal mol^{-1} and $\Delta S^{\ddagger} = -34{\cdot}0$ cal K^{-1} mol^{-1} at 25·05 °C in acetone. These values are similar in magnitude to those obtained for the addition of O_2 to $[Ir(P\text{-}P)_2]^+$ in chlorobenzene at 25 °C ($\Delta H^{\ddagger} = 6{\cdot}5$ kcal mol^{-1}, $\Delta S^{\ddagger} = -38$ cal K^{-1} mol^{-1}),[1] and for the reversible reaction of O_2 with *trans*-$IrCl(CO)(R_3P)_2$ in chlorobenzene at 40 °C ($\Delta H^{\ddagger} = 8{\cdot}1$—$10{\cdot}8$ kcal mol^{-1}, $\Delta S^{\ddagger} = -31$ to -42 cal K^{-1} mol^{-1}).[2]

The uptake of O_2 by $[Ir(CO)(PPh_2Me)_3][ClO_4]$ has a small solvent effect; k_1', k_2, and $\Delta H^{\ddagger}$ are greater in dichloromethane than in acetone. This cannot be explained by the difference in solubility of O_2 in the two solvents since O_2 is slightly more soluble in acetone, and the reaction would, therefore, be expected to be faster in this solvent. However, reactive intermediates such as carbonium ions and carbanions are stabilised by solvation and the more negative entropy of activation in acetone suggests the importance of solvation in the present system, the reaction rate being smaller in the more polar solvent acetone. The small solvent effect leads us to conclude that the mechanism of O_2 uptake is the same in both solvents.

The values of k_2 obtained in the study of $[Ir(CO)(PPh_2Me)_3]^+$ (0·61 l mol^{-1} s^{-1} in dichloromethane and 0·33 l mol^{-1} s^{-1} in acetone at 25 °C) are almost the same as that obtained by Vaska [1] for $[Ir(P\text{-}P)_2]^+$ in chlorobenzene at 25 °C (0·47 l mol^{-1} s^{-1}). However, the formation of $[Ir(CO)(PPh_2Me)_3(O_2)]^+$ is irreversible whereas that of $[Ir(P\text{-}P)_2(O_2)]^+$ is reversible, the latter being more stable by 2—3 kcal mol^{-1}. The electronic properties of the ligands are similar; the phosphine ligands are all PPh_2R where R is a ' carbon chain ', but CO is a better π-acceptor than P so the electron density at Ir in $[Ir(CO)(PPh_2Me)_3]^+$ is slightly less than that in $[Ir(P\text{-}P)_2]^+$. Some of the difference in the values of k_2 for these complexes probably arises because of differences in solvent properties. The dielectric constants [10] of acetone, dichloromethane, and chlorobenzene are 20·7 (25 °C), 9·08 (20 °C), and 5·708 (20 °C) respectively. The lowest rate in acetone is explained by the superior co-ordinating ability of this solvent. In comparing k_2 values for reactions measured in dichloromethane and chlorobenzene the electronic factor is more important.

The uptake of O_2 by $Ru(PPh_3)_3Cl_2$ in benzene [11] is at least five times faster than that obtained for $[Ir(CO)(PPh_2Me)_3]^+$. Although the rate law initially followed by the two complexes is the same the observed rate with the former decreases markedly when about 0·8 moles of O_2 have been absorbed. The O_2 is actually added to $Ru(PPh_3)_2Cl_2$ in solution because $Ru(PPh_3)_3Cl_2$ dissociates readily into $Ru(PPh_3)_2Cl_2$ and PPh_3. It is not possible to make a direct comparison between the d^6 ruthenium and d^8 iridium systems, but a brief consideration of the π-acceptor ability of the ligands and the energies of the *d* orbitals shows that the ruthenium complex is electronically more favourable for O_2 addition.

The value of k_2 for dioxygen uptake by $[Ir(CO)(PPh_2Me)_3]^+$ is greater than the values obtained by Vaska [2] for *trans*-$IrCl(CO)(PR_3)_2$ (R = alkyl or aryl group) in chlorobenzene at 40 °C. In making this comparison the solubility of O_2 in the solvent may be an important factor since O_2 is only half as soluble in chlorobenzene as it is in dichloromethane and acetone. The comparison between the reactions of the ionic complex $[Ir(CO)(PPh_2Me)_3][ClO_4]$ and the non-ionic complexes *trans*-$IrCl(CO)(PR_3)_2$ is difficult because of their different properties in solution. However, the differences in k_2 are not so great as to suggest that there are different addition mechanisms involved.

Catalytic Oxidation of Diphenylmethylphosphine.—The catalytic oxidation of triphenylphosphine by $Ru(NCS)(NO)(PPh_3)_2(O_2)$ at 80 °C in xylene was investigated by O'Connor *et al.*[5] Similar conditions were first chosen for the study of the $[Ir(CO)(PPh_2Me)_3(O_2)]^+$–$PPh_2Me$ system so that a direct comparison of the two oxidations could be made. However, the catalyst was only sparingly soluble in hot xylene, and after *ca.* 2 h the slope of the $p(O_2)$ against time plot decreased to a value which was independent of catalyst concentration. Studies using dichloromethane as solvent ($[PPh_2CH_3] = 0{\cdot}22$M, catalyst concentration = 0·5mM, at 35 °C) showed that dichloromethane inhibits oxidation. No oxidation was observed in a run after 2½ days. There was no colour change to indicate catalyst decomposition, although at 90 °C the complex rapidly decomposes in dichloromethane. The catalyst was active in polar solvents, *e.g.* n-butanol and 2-methoxyethanol, and the reaction profiles for uptake of dioxygen were smooth continuous curves, but the catalytic efficiency was poor. At 59·3 °C in 2-methoxyethanol, using 0·5mM-$[Ir(CO)(PPh_2Me)_3(O_2)]^+$ and 0·22M-PPh_2Me, there was 26% conversion to $OPPh_2Me$ in 30 min. However, only 30% of this oxidation was *via* the catalytic pathway.

Oxidation of PPh_2Me occurred in the presence and absence of catalyst. There was a distinct solvent effect (Table 2). The oxidation observed in xylene in the absence of catalyst shows that the complex was probably catalytically inactive in this solvent. The same can be

---

[8] ' International Critical Tables,' McGraw-Hill, New York, 1928, **3**, 262.

[9] W. F. Linke, ' Solubilities of Inorganic and Metal Organic Compounds,' Amer. Chem. Soc., Washington D.C., 4th edn., 1965, **2**, 1235.

[10] ' Handbook of Chemistry and Physics,' The Chemical Rubber Co., 45th edn., 1964, E31.

[11] S. Cenini, A. Fusi, and G. Capparella, *J. Inorg. Nuclear Chem.*, 1971, **33**, 3576.

said for its activity in ethanol and dichloromethane but for a different reason. These solvents react with the catalyst to form a hydride or an Ir^{III} oxidation product and there is some evidence for the former. Thus, during the preparation of the catalyst, it was found that prolonged contact with hot ethanol caused the precipitation of a colourless solid whose i.r. spectrum was consistent with the compound $IrH(PPh_2Me)_3$. In the other solvents, 2-methoxyethanol, n-butanol, and acetone, there was no oxidation to Ir^{III}, nor was there hydride formation and catalysis was therefore possible. With the exception of the results in acetone, however, the results were difficult to reproduce and the inefficiency of the complex as an homogeneous oxidising agent did not warrant an extensive kinetic investigation.

TABLE 2

The dependence of catalysed and uncatalysed rates[a] of oxidation of PPh_2Me on solvent $\{[Ir(O_2)(CO)(PPh_2Me)]^+$ concentration = 0·5mM, $[PPh_2Me]$ = 0·22M$\}$

Temp. (°C)	Dioxygen pressure[b] $p(O_2)$/cmHg	Solvent	Rate (cmHg min^{-1})[c]	
			Catalysed	Un-catalysed
80	50	2-Methoxyethanol	1·7	1·3
		Xylene	*ca.* 0·2	*ca.* 0·2
59·3	40	2-Methoxyethanol	0·86[d]	0·57[d]
		Ethanol	0·13	0·13
		n-Butanol	0·44[d]	0·21[d]
35·0	25	Dichloromethane	0·0	0·0
25·5	30	Dichloromethane	0·0	0·0
30·3	45	Acetone	4·09 $\times 10^{-3}$[d]	1·30 $\times 10^{-3}$

[a] The initial maximum slope of the plot $p(O_2)$ against time was taken as a measure of the rate. [b] Approximate values only. [c] The experimental units are used since this is a semi-quantitative study. Conversion factors (*e.g.*, 1·32 × 10^{-5} at 30 °C) are necessary to convert these values into units of l mol^{-1} s^{-1}. [d] Mean value of a number of measurements.

$[Ir(O_2)(CO)(PPh_2Me)_3]^+$ Was also found to catalyse the oxidation of PPh_3 at 80 °C. In 2-methoxyethanol and n-butanol the catalysed rate was approximately four times greater than the uncatalysed rate and similar to the rate of oxidation of PPh_3 catalysed by $[Ir(CO)(PPh_3)_3]^+$ at 80 °C. Cross-catalysis of reactants which are not initially ligands of the dioxygen compound has been observed with $Ni(O_2)(Bu^tNC)_2$ which catalyses the oxidation of PPh_3.[12] This complex forms a new compound with both Bu^tNC and PPh_3 ligands. $[Ir(O_2)(CO)(PPh_2Me)_3]^+$ Was probably similarly converted into a triphenylphosphine–diphenylmethylphosphine complex which then acted as a catalyst.

EXPERIMENTAL

Materials.—The complexes $[Ir(CO)(PPh_3)_3]ClO_4$, $[Ir(CO)(PPh_2Me)_3]ClO_4$, and $[Ir(O_2)(CO)(PPh_2Me)_3]ClO_4$ were prepared by the methods of Reed and Roper.[6,7] PPh_2Me Was prepared by a Grignard reaction on PPh_2Cl (Alfa Inorganics Ltd.). All solvents were dried before use in kinetic work.

Measurement of Reaction Rates.—The method used for following the rate of homogeneous oxidation by uptake of dioxygen has been described previously;[5] the rate of formation of the dioxygen complex was monitored using the same vacuum line. Samples were removed from the thermostatted reaction vessel, through a rubber septum held by a screw-down PVC cap fitted to the apparatus immediately above the reaction flask, using a glass syringe fitted with a 25-cm stainless-steel needle, and were analysed on a Shimadzu QV50 spectrophotometer by following the decrease in absorbance at 430 nm. (The dioxygen complex absorbed light strongly at 284 nm. The presence of a small excess of diphenylmethylphosphine intensified this absorption and shifted the peak to *ca.* 300 nm.)

We are grateful to Drs. C. A. Reed and W. R. Roper for assistance.

[2/626 *Received*, 17*th March*, 1972]

---

[12] S. Otsuka, A. Nakamura, and Y. Tatsuno, *Chem. Comm.*, 1967, 836; *J. Amer. Chem. Soc.*, 1969, **91**, 6994.