Dioxygen Complexes of Ruthenium as Homogeneous Catalysts for the Oxidation of Triphenylphosphine

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The complexes $Ru(NCS)(CO)(NO)(PPh_3)_2$ (I) and $Ru(O_2)(NCS)(NO)(PPh_3)_2$ (II) have been shown to be efficient catalysts for the homogeneous oxidation of PPh_3 to $OPPh_3$. In xylene solution rate $\propto$ [catalyst] and rate^{-1} $\propto$ $[PPh_3]^{-1}$. The rate depends on $p(O_2)$ for (I) but not for (II). A mechanism is suggested which accommodates these facts.

In recent years a number of compounds containing dioxygen co-ordinated to one metal centre (as distinct from bridging dioxygen in *e.g.* $[Co(NH_3)_5O_2Co(NH_3)_5]^{4+}$ ref. 1) have been described. The prototype for these complexes is $Ir(O_2)Cl(CO)(PPh_3)_2$ [2] and other typical examples are $Pt(O_2)(PPh_3)_2$ [3] and $Ru(O_2)Cl(NO)(PPh_3)_2$.[4] The co-ordinated dioxygen is reactive and various ligand oxidations have been achieved using these compounds. Examples include phosphine to phosphine oxide,[5] isocyanide to isocyanate,[6] carbon monoxide to chelated carbonate [7] or carbon dioxide,[8] nitric oxide to nitrite [9] or nitrate,[7] and sulphur dioxide to chelated sulphate.[10,11] Most of these reactions are stoicheiometric but if further ligand can replace the oxidised product the process may become catalytic. Such a possibilty exists for phosphine to phosphine oxide oxidation. There has been one kinetic investigation of a reaction of this type. Halpern [12,13] has studied the oxidation of triphenylphosphine using $Pt(O_2)(PPh_3)_2$ as catalyst and the results are consistent with the following mechanism:

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[1] W. P. Schaefer and R. E. Marsh, *Acta Cryst.*, 1966, **21**, 735.

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

[3] S. Takahashi, K. Sonagashira, and N. Hagihara, *J. Chem. Soc. Japan*, 1966, **87**, 610.

[4] K. R. Laing and W. R. Roper, *Chem. Comm.*, 1968, 1556.

[5] G. Wilke, H. Schott, and P. Heimbach, *Angew. Chem. Internat. Edn.*, 1967, **6**, 92.

[6] S. Otsuka, A. Nakamura, and Y. Tatsuno, *J. Amer. Chem. Soc.*, 1969, **91**, 6994.

[7] K. R. Laing and W. R. Roper, *Chem. Comm.*, 1968, 1568.

[8] J. A. Stanko, G. Petrov, and C. K. Thomas, *Chem. Comm.*, 1969, 1100.

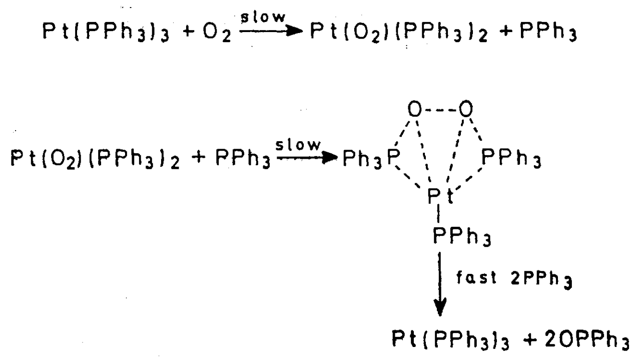
[9] J. P. Collman, M. Kubota, and J. W. Hosking, *J. Amer. Chem. Soc.*, 1967, **89**, 4809.

[10] R. W. Horn, E. Weissberger, and J. P. Collman, *Inorg. Chem.*, 1970, **9**, 2367.

[11] J. J. Levison and S. D. Robinson, *J. Chem. Soc.* (*A*), 1971, 762.

[12] J. P. Birk, J. Halpern, and A. L. Pickard, *J. Amer. Chem. Soc.*, 1968, **90**, 4491.

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

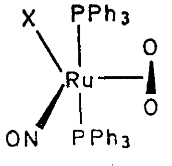


In order to extend these observations to dioxygen complexes of different co-ordination number and geometry we have studied $Ru(O_2)Cl(NO)(PPh_3)_2$, $Ru(O_2)(OH)(NO)(PPh_3)_2$, $Ru(O_2)(CN)(NO)(PPh_3)_2$, and $Ru(O_2)(NCS)(NO)(PPh_3)_2$ as catalysts for the homogeneous oxidation of triphenylphosphine to triphenylphosphine oxide. A preliminary report of this work has appeared.[14] These dioxygen compounds are obtained from the corresponding carbonyl compounds[15] by stirring solutions of the latter under dioxygen pressure. It is possible, therefore, to use the carbonyl compounds as catalysts for the same oxidation reactions with the dioxygen compounds being formed *in situ*.

Of the dioxygen complexes the cyanide and thiocyanate compounds are the most effective as catalysts at, or near, room temperature. However, the preparation of the cyanide compound gave a poor yield (*ca.* 17%) so that it was not suitable for a kinetic investigation of this kind.

The chloride and hydroxide dioxygen compounds were also tested for catalytic activity. These were both found to be inactive for the triphenylphosphine oxidation at temperatures up to 80 °C, which was the practical limit of the apparatus used in this work. The chloride complex was an effective catalyst for the oxidation of the triphenylarsine to triphenylarsine oxide in boiling toluene (110 °C), thus suggesting that it should also be effective with triphenylphosphine at higher temperatures.

All the dioxygen complexes are believed to have the following geometry:



This has been confirmed for $Ru(O_2)Cl(NO)(PPh_3)_2$ by *X*-ray crystallographic investigation,[16] the overall geometry being quite similar to that of $Ir(O_2)Cl(CO)(PPh_3)_2$.

EXPERIMENTAL

I.r. spectra (4000—400 cm^{-1}) were recorded as Nujol mulls on a Shimadzu IR 27G spectrometer, calibrated with Polystyrene. M.p.s were measured on a Reichert hot-stage apparatus. Least-squares analyses were performed on an I.B.M. 1130 computer. Ruthenium trichloride (hydrated) was from Johnson Matthey Chemicals Limited. Triphenylphosphine was recrystallised from ethanol. Florisil was a B.D.H. reagent, 100—200 U.S. Mesh, for chromatographic analysis.

The compounds $RuX(CO)(NO)(PPh_3)_2$ (X = Cl, OH, NCS) were prepared by the methods of Laing and Roper.[15] The dioxygen compounds were prepared from these as follows:

Dioxygenhydroxynitrosylbis(triphenylphosphine)ruthenium(0), $Ru(O_2)(OH)(NO)(PPh_3)_2$.—A solution of $Ru(OH)(CO)(NO)(PPh_3)_2$ (0·3 g) in dichloromethane (20 ml) and ethanol (10 ml) was stirred, in a glass pressure-bottle under dioxygen pressure (1 atm), for 20 min. The green solution darkened to a deep red-brown. After venting the bottle the solution was evaporated under reduced pressure and dark brown crystals (0·25 g, 83%) of $Ru(OH)(O_2)(NO)(PPh_3)_2$ were deposited (Found: C, 60·7; H, 4·5; N, 1·4. $C_{36}H_{31}NO_4P_2Ru$ requires C, 61·35; H, 4·4; N, 2·0%).

Dioxygenchloronitrosylbis(triphenylphosphine)ruthenium(0), $Ru(O_2)Cl(NO)(PPh_3)_2$.—$RuCl(CO)(NO)(PPh_3)_2$ (0·3 g) was treated in a similar manner to the above and dark brown crystals (0·28 g, 93%) of $Ru(O_2)Cl(NO)(PPh_3)_2$ were obtained (Found: C, 59·3; H, 4·3; N, 1·7. $C_{26}H_{30}ClNO_3P_2Ru$ requires C, 59·8; H, 4·2; N, 1·8%).

Dioxygen-N-*thiocyanatonitrosylbis(triphenylphosphine)ruthenium*(0), $Ru(O_2)(NCS)(NO)(PPh_3)_2$.—(1) $Ru(NCS)(CO)(NO)(PPh_3)_2$ (0·3 g) was treated as above to yield green-brown crystals of an impure product. Chromatography on Florisil (3-in column, eluted with CH_2Cl_2) followed by evaporation of the solvent yielded green-brown crystals (0·19 g, 63%) of $Ru(O_2)(NCS)(NO)(PPh_3)_2$.

(2) $Ru(NCS)(CO)(NO)(PPh_3)_2$ (0·3 g) was treated as in (1) in the presence of triphenylphosphine (1·0 g). Triphenylphosphine oxide (0·5 g) was produced in the reaction and both this and triphenylphosphine were removed from the solid product of the reaction by washing with ethanol (50 ml), to yield green-brown crystals (0·24 g, 80%) of $Ru(O_2)(NCS)(NO)(PPh_3)_2$ (Found: C, 59·7; H, 4·2; N, 3·7. $C_{37}H_{30}N_2O_3P_2RuS$ requires C, 59·6; H, 4·05; N, 3·75%).

The purpose of the triphenylphosphine in (2) was to reduce the decomposition of the dioxygen complex as it was formed in solution.

Dioxygencyanonitrosylbis(triphenylphosphine)ruthenium(0), $Ru(O_2)(CN)(NO)(PPh_3)_2$.—$Ru(OH)(CO)(NO)(PPh_3)_2$ (0·35 g) in dichloromethane (20 ml) and sodium cyanide (0·03 g) in aqueous ethanol (10 ml) were mixed and the solution was stirred under oxygen as above. The solution was evaporated under reduced pressure until dark brown crystals were deposited. These crystals were chromatographed as above and two fractions were collected. Ethanol (10 ml) was added to the first fraction (yellow-brown) and evaporation of the solution under reduced pressure afforded dark brown crystals (0·21 g, 60%) of $Ru(O_2)(OH)(NO)(PPh_3)_2$.

n-Hexane was added to the second fraction (pinkish purple) and evaporation of the solution under reduced pressure yielded grey-green crystals (0·06 g, 17%) of

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[14] B. W. Graham, K. R. Laing, Charmian J. O'Connor, and W. R. Roper, *Chem. Comm.*, 1970, 1272.

[15] K. R. Laing and W. R. Roper, *J. Chem. Soc.* (*A*), 1970, 2149.

[16] J. A. Ibers, personal communication.

Ru(O$_2$)(CN)(NO)(PPh$_3$)$_2$ (Found: C, 61·9; H, 4·2; N, 3·7. $C_{37}H_{30}N_2O_3P_2Ru$ requires: C, 62·3; H, 4·2; N, 3·9%).

Kinetic runs were carried out in a glass reaction flask fitted with a glass water jacket, and the system was held at a constant temperature by a Churchill Laboratory Thermo Circulator with an accuracy of ±0·5°. The experimental techniques used were similar to those described for following the absorption of gas during homogeneous hydrogenation reactions.[17] The catalyst was added to a solution of substrate in xylene (degassed by evacuation and saturation with dioxygen) at the partial pressure of the solvent. The dioxygen pressure was adjusted so that the pressure at which readings were required was reached after 1—2 min of rapid stirring-in of dioxygen. The overall reproducibility of the kinetic runs is *ca.* 5%.

The rate of dioxygen uptake was obtained at a standard pressure (*e.g.* 50 cm) from the tangent to the plot of the dioxygen pressure against time. Conversion to the rate of consumption of substrate in mol l^{-1} s^{-1} was made using the stoicheiometric relationship, $-2\mathrm{d}[O_2]/\mathrm{d}t = -\mathrm{d}[PPh_3]/\mathrm{d}t$. The solubility of dioxygen was taken as constant from run to run, and assumed to obey Henry's Law. The consumption of the substrate at the time of measurement is <1% in all cases, and is considered negligible. Under the experimental conditions there was no oxidation of the solvent and in the absence of catalyst no detectable oxidation of triphenylphosphine to triphenylphosphine oxide.

RESULTS

Semiquantitative Tests for Catalytic Activity.—Ru(O$_2$)(OH)(NO)(PPh$_3$)$_2$ (0·0173 g) did not oxidise triphenylphosphine (1·28 g) in refluxing benzene (50 ml) in air during 1 h.

Ru(O$_2$)Cl(NO)(PPh$_3$)$_2$ (0·0197 g) did not oxidise triphenylphosphine (0·64 g) at room temperature in benzene (50 ml) under 1 atm dioxygen pressure within 12 h but 0·08 g oxidised *ca.* 50% of triphenylarsine (1·5 g) to triphenylarsine oxide in refluxing toluene (50 ml) during 30 min. The catalyst appeared to have decomposed and a trace of OPPh$_3$ was detected.

Ru(O$_2$)(CN)(NO)(PPh$_3$)$_2$ (0·015 g) oxidised triphenylphosphine (1 g) in ethanol (10 ml)–dichloromethane (20 ml) under reflux in an atmosphere of dioxygen for 15 min. The catalyst was recovered unchanged from the reaction.

Quantitative Measurements.—The reactions were studied in xylene solution with sub-atmospheric pressures of dioxygen and at temperatures between 50 and 80 °C. Rates of reaction were determined by studying the change in dioxygen pressure with time, but the results are given in terms of $-\mathrm{d}[PPh_3]/\mathrm{d}t$; *i.e.* the rate of consumption of triphenylphosphine. Typical runs are shown in Figure 1. The initial rates of each reaction were obtained by measuring the initial gradients of these graphs. Usually the amount of dioxygen added to the system was such that the initial dioxygen partial pressure was *ca.* 50 cmHg, so that the results applied to a constant dioxygen pressure. The reaction rates obtained in this way were in units of cmHg min^{-1} but a conversion factor of $1{\cdot}21 \times 10^{-5}$ was used to express these results in terms of mol l^{-1} s^{-1}.

It seems from the curves shown in Figure 1 that the two catalysts differ from each other, in that the gradient of the curve for Ru(O$_2$)(NCS)(NO)(PPh$_3$)$_2$ slowly decreases, whereas the gradient of the curve for Ru(NCS)(CO)(NO)(PPh$_3$)$_2$ first increases, and then decreases. This difference in behaviour may be attributed to the effect of triphenylphosphine oxide. As this is produced in the reactions it may effectively compete with triphenylphosphine in the first step of the catalytic cycle in the Scheme [*i.e.* (II) ⟶ (III)]. Since the oxide is a better electron donor than triphenylphosphine it will tend to accelerate the reaction by increasing k_1. Thus there are two conflicting effects producing the observed behaviour: the reaction rate should decrease with time due to the decrease in [PPh$_3$], but at the same time should increase in the presence of triphenylphosphine oxide. Figure 2 shows that at a triphenylphosphine concentration of *ca.* 0·5M the effect on the reaction rate of a decrease in the concentration of triphenylphosphine is greater for the dioxygen compound than for the carbonyl compound. The effect of triphenylphosphine oxide is probably much the same for both catalysts. Thus it is proposed that for the dioxygen catalyst the two effects almost cancel each other, while for the carbonyl compound the effect of triphenylphosphine oxide is greater than the effect of triphenylphosphine.

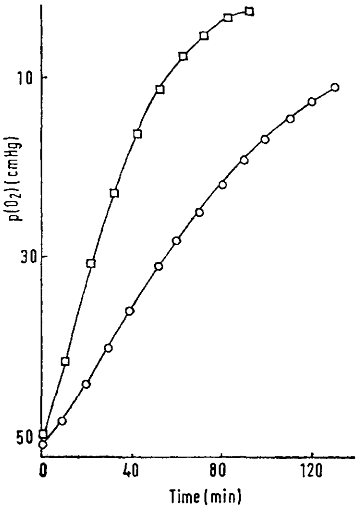

FIGURE 1 Typical runs for homogeneous oxidation of triphenylphosphine (0·5M) at 80 °C in xylene using □ Ru(O$_2$)(NCS)(NO)(PPh$_3$)$_2$ (2·0 mM) and ○ Ru(NCS)(CO)(NO)(PPh$_3$)$_2$ (1·25 mM)

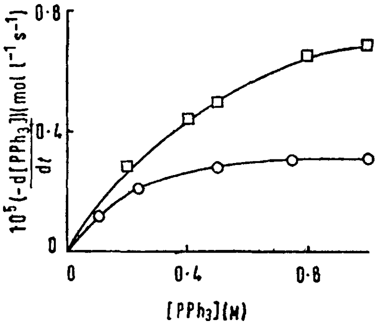

FIGURE 2 Rate of oxidation of triphenylphosphine as a function of triphenylphosphine concentration in xylene at 80 °C, and at 50 cm O$_2$ pressure: □ Ru(O$_2$)(NCS)(NO)(PPh$_3$)$_2$ (1·0 mM) and ○ Ru(NCS)(CO)(NO)(PPh$_3$)$_2$ (1·0 mM)

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[17] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1711.

Participation in the equilibrium governed by K_1 must be a major factor for the difference in behaviour of the carbonyl compound.

TABLE 1

Effect of triphenylphosphine oxide on the catalytic oxidations of triphenylphosphine

$[PPh_3]$ (M)	$[OPPh_3]$ (M)	10^2 × Initial rate (mol l^{-1} s^{-1})
Catalyst: $Ru(O_2)(NCS)(NO)(PPh_3)_2$		
0·5	0·0	0·484
0·4	0·1	0·465
0·3	0·2	0·406
Catalyst: $Ru(NCS)(CO)(NO)(PPh_3)_2$		
0·5	0·0	0·274
0·4	0·1	0·387
0·3	0·2	0·412

(Data apply for [Catalyst] = 1·0 mM, $p(O_2)$ = 50 cmHg, 80 °C.)

Support for this idea came from performing a number of runs with each catalyst with triphenylphosphine oxide added to the solutions. The total concentration of phosphine in solution was kept constant however by varying the ratio $[PPh_3]:[OPPh_3]$. The results shown in Table 1 were obtained from this study.

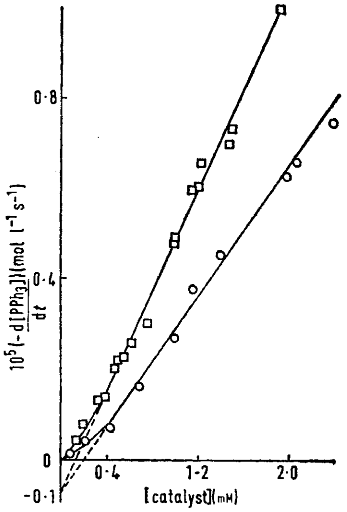


FIGURE 3 Rate of oxidation of triphenylphosphine (0·5M) as a function of catalyst concentration in xylene at 80 °C and at 50 cm O_2 pressure: □ $Ru(O_2)(NCS)(NO)(PPh_3)_2$ and ○ $Ru(NCS)(CO)(NO)(PPh_3)_2$

These results clearly show that triphenylphosphine oxide has the predicted effect on the reactions since otherwise the rates of the reactions with $[PPh_3]$ = 0·4 and 0·3M would be much lower than the rate for $[PPh_3]$ = 0·5M, with each catalyst.

Catalyst Concentration Dependence.—Figure 3 shows the dependence of the reaction rate on catalyst concentration for both the dioxygen complex and the carbonyl compound. The reaction is first order in catalyst concentration for both compounds, at concentrations greater than, *ca*. 0·4 mM. The behaviour at lower concentrations is considered later. The graph shows that $Ru(O_2)(NCS)(NO)(PPh_3)_2$ is a more efficient catalyst than the corresponding carbonyl compound, and also that the efficiencies of the two catalysts differ by a constant factor (*ca*. 0·8) since the two straight lines intersect at zero catalyst concentration. This agrees with the 80% yield obtained in the preparation of the dioxygen complex from $Ru(NCS)(CO)(NO)(PPh_3)_2$.

Triphenylphosphine Concentration Dependence.—The graphs in Figure 4 show that for both of the catalysts 1/rate is proportional to $1/[PPh_2]$. In both cases plots of rate *vs*. $[PPh_3]$ were curved (Figure 2).

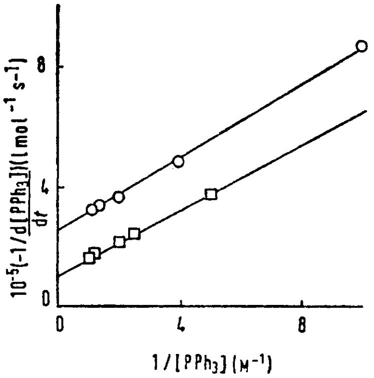


FIGURE 4 Plot of reciprocal of rate of oxidation of triphenylphosphine against the reciprocal of triphenylphosphine concentration in xylene at 80 °C and at 50 cm O_2: □ $Ru(O_2)(NCS)(NO)(PPh_3)_2$ (1·0 mM) and ○ $Ru(NCS)(CO)(NO)(PPh_3)_2$ (1·0 mM)

Dioxygen Pressure Dependence.—The two catalysts differ in the dependence of their reaction on dioxygen pressure. Figure 5 shows that for $Ru(NCS)(CO)(NO)(PPh_3)_2$ a plot of 1/rate *vs*. $1/p(O_2)$ is linear. [A plot of rate *vs*. $p(O_2)$ was curved.] In contrast to this behaviour the dioxygen-catalysed reactions are independent of dioxygen pressure [$p(O_2)$ between 10 and 60 cmHg]. This difference in behaviour suggests that the dioxygen pressure dependence of the carbonyl compound is a consequence of its initial reaction to form the dioxygen complex, since once that process has occurred the two compounds should show essentially the same behaviour.

Temperature Dependence.—Arrhenius parameters were determined for the reactions of the dioxygen catalyst, by studying the dependence on triphenylphosphine concentration at a number of different temperatures. The plots of 1/rate *vs*. $1/[PPh_3]$ are shown in Figure 6. The overall rate constant k' ($=k_1K_2$) was calculated from the slopes of these plots {since slope $= 1/(k_1K_2[RuO_2])$}, Arrhenius parameters calculated from a plot of $\log_{10}k'$ *vs*. $1/T$ are $\Delta H^{\ddagger} = 21{\cdot}6 \pm 0{\cdot}7$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -7{\cdot}1$ e.u.

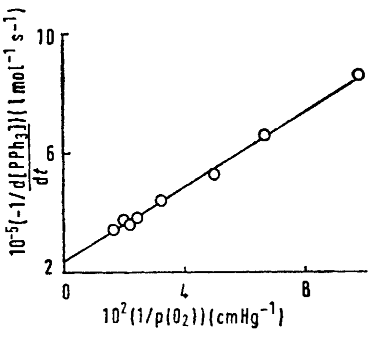


FIGURE 5 Dependence of rate of oxidation of triphenylphosphine (0·5M) with dioxygen pressure in xylene with 1·0 mM $Ru(NCS)(CO)(NO)(PPh_3)_2$ at 80 °C

Catalytic Oxidations of Other Substrates.—In view of the mechanism proposed in the Scheme it seemed likely that $Ru(O_2)(NCS)(NO)(PPh_3)_2$ would be an effective catalyst for the oxidation of other substrates—in particular triphenylarsine, triphenylstibine, isocyanides, and unsaturated organic compounds. The first three of these compounds could exchange with the $OPPh_3$ ligands in intermediate (IV), while the last one could take the place of PPh_3 in the pre-equilibrium step (II) ⟶ (III).

Triphenylarsine and Triphenylstibine Substrates.—Triphenylarsine was oxidised readily in the presence of $Ru(O_2)(NCS)(NO)(PPh_3)_2$; the initial rate of oxidation being 3 to 4 times greater than the corresponding rate for triphenylphosphine oxidation under the same conditions. However, the rate of oxidation was rapidly diminished by decomposition of the catalyst, so that in a short time (*ca.* 30 min) the catalyst was virtually ineffective.

With triphenylstibine as substrate the catalyst decomposed almost immediately on being dissolved in solution, and no oxidation was observed.

Isocyanide Substrate.—p-Tolyl isocyanide was tested as a substrate but as with triphenylstibine the catalyst decomposed before any oxidation took place.

Olefin Substrates.—Hex-1-ene and cyclohexene were tested as substrates with $Ru(O_2)(NCS)(NO)(PPh_3)_2$. With hex-1-ene the test was carried out at 60 °C in benzene (since the boiling point of hex-1-ene is 64 °C) and a small dioxygen uptake was observed, corresponding to *ca.* 1·5% oxidation, after which no further reaction occurred.

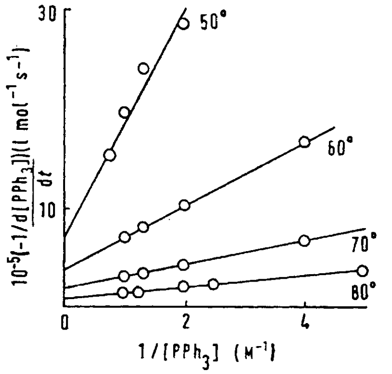
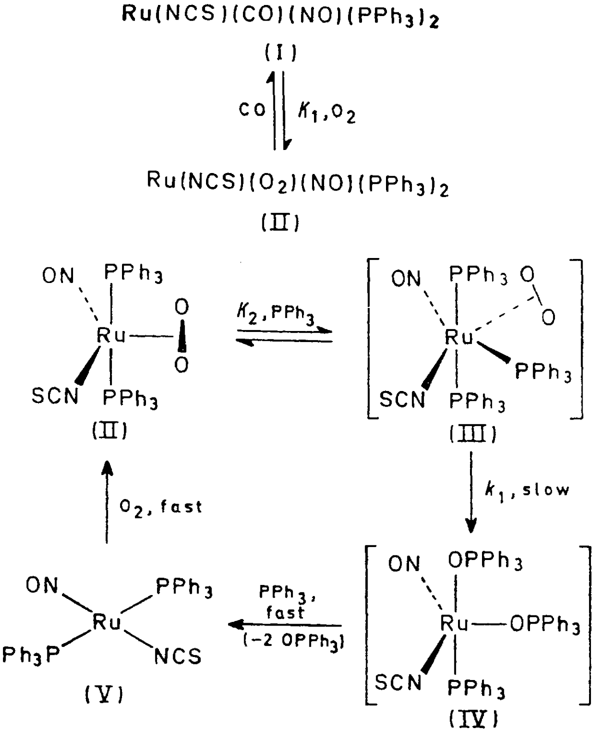


FIGURE 6 Plot of reciprocal of rate of oxidation of triphenylphosphine against the reciprocal of triphenylphosphine concentration in xylene with 1·0 mM $Ru(O_2)(NCS)(NO)(PPh_3)_2$ at 50 cm O_2

The test of cyclohexene oxidation was carried out at 80° in xylene solution and continuous oxidation was observed for 4 h. The products of the reaction were identified as water, cyclohexene oxide, cyclohex-1-en-3-one, and cyclohex-1-en-3-ol, *i.e.* the same products found by Collman *et al.*[9] for the oxidation of cyclohexene in the presence of $RhCl(PPh_3)_3$, $RhCl(CO)(PPh_3)_2$, $PtO_2(PPh_3)_2$, $IrI(CO)(PPh_3)_2$, and $IrCl(N_2)(PPh_3)_2$. This result suggested that the ruthenium catalyst was simply initiating a free-radical process, similar to that observed by Collman *et al.*[9] During the reaction a black solid was precipitated in the reaction flask, indicating decomposition of the catalyst. This precipitate did not appear to have any effect on the rate of oxidation however, which was continually increasing until the dioxygen supply diminished. As a test for a free-radical process β-naphthol, a known free-radical inhibitor,[18] was added to a run containing cyclohexene, identical in every other respect to the test described above. Now there was no dioxygen uptake at all in 2 h, but the same black solid was precipitated in the flask. This test confirmed that the catalyst was simply initiating a free-radical process.

DISCUSSION

The reaction sequence proposed for the oxidation of triphenylphosphine using $Ru(NCS)(CO)(NO)(PPh_3)_2$ and



SCHEME

$Ru(O_2)(NCS)(NO)(PPh_3)_2$ as catalysts is shown in the Scheme.

The first step of the mechanism (I) ⟶ (II) applies only for the carbonyl compound as catalyst, and the actual catalytic cycle involves the remaining steps [*i.e.* (II) ⟶ (III) ⟶ (IV) ⟶ (V) ⟶ (II)]. Thus the rate equations for this mechanism are:

$$-\frac{d[PPh_3]}{dt} = \frac{k_1K_2[RuO_2][P]}{1 + K_2[P]}$$

for the dioxygen compound, and:

$$-\frac{d[PPh_3]}{dt} = \frac{k_1K_1K_2[RuCO][P][O_2]}{[CO] + K_1[O_2] + K_1K_2[P][O_2]}$$

for the carbonyl compound, where P = PPh_3, RuO_2 = $Ru(O_2)(NCS)(NO)(PPh_3)_2$, and RuCO = $Ru(NCS)(CO)(NO)(PPh_3)_2$. Analysis of the data on the basis of these equations yields $k_1 = 1{\cdot}26 \pm 0{\cdot}03 \times 10^{-2}\ s^{-1}$, and $K_2 = 1{\cdot}63 \pm 0{\cdot}04\ l\ mol^{-1}$.

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[18] W. O. Lundberg, 'Autoxidation and Autoxidants,' vol. I, Interscience, New York, 1961.

In contrast to the rate law observed by Halpern *et al.*[12,13] where the rate of oxidation of triphenylphosphine by $Pt(O_2)(PPh_3)_2$ depended linearly on $[PPh_3]$, the above two rate equations require that the reciprocal of the rate depends on $[PPh_3]^{-1}$. Similar inverse dependence has also been observed for the homogeneous oxidation of t-butyl isocyanide using $Ni(Bu^tNC)_4$ as catalyst.[19]

The catalytic cycle is initiated by the entry of triphenylphosphine into (II) to form (III). The intermediate (III) is reasonably formulated as a six-co-ordinate derivative of Ru^{II}, the nitrosyl ligand being bound as NO^-. This implies that the Ru–N–O linkage will be bent [in (II) it is linear] and it seems likely that this special capacity of the nitrosyl ligand to adapt its ligand properties (from three-electron donor when linear to one-electron donor when bent) is here playing a special role in allowing the triphenylphosphine to co-ordinate. There is precedent for a dioxygen complex of ruthenium(II) in $Ru(O_2)Cl_2(AsPh_3)_3$.[20] The corresponding iridium dioxygen complex, $IrX(O_2)(CO)(PPh_3)_2$, presumably could not function by this same mechanism since the carbonyl ligand does not have the flexibility of the nitrosyl ligand in its bonding requirements.

The rate-determining step in the Scheme is the oxygen-atom-transfer process to give a triphenylphosphine oxide complex (IV). This species must be unstable and readily undergoes ligand exchange to produce the co-ordinatively unsaturated Ru^0 complex, (V) which, in turn, readily takes up dioxygen to re-form the catalyst (II). Thus two molecules of triphenylphosphine are oxidised to triphenylphosphine oxide by one molecule of dioxygen in one catalytic cycle.

We have previously reported[7] that although the dioxygen complex $Ru(O_2)Cl(NO)(PPh_3)_2$ can be prepared from $RuCl(CO)(NO)(PPh_3)_2$ by reaction with dioxygen the reverse reaction of $Ru(O_2)Cl(NO)(PPh_3)_2$ with CO yields $Ru(NO_3)Cl(CO)_2(PPh_3)_2$. This evidence suggests that the formation of the dioxygen complex from $Ru(NCS)(CO)(NO)(PPh_3)_2$ should be an irreversible process. However, the kinetic results require this to be reversible, as shown in the Scheme. This apparent discrepancy can be explained if one considers that the reaction of (I) with dioxygen to form (II), and the reaction of (II) with carbon monoxide to form $Ru(NO_3)(NCS)(CO)_2(PPh_3)_2$ occur by two entirely different processes. The efficiency of the catalyst can be calculated by relating the total pressure change to the amount of triphenylphosphine oxidised. Thus for the run shown in Figure 1 a 40 cmHg change occurred in 1 h. This corresponds to a 60% conversion into triphenylphosphine oxide.

On the basis of the proposed Scheme, we have K_1 and K_2 as the equilibrium constants for the formation of (II) and (III), respectively, and k_1 is the rate constant for the rate-determining step (III) ⟶ (IV).

The rate expression reasonably accommodates the experimental results.

(1) *The Dependence of the Rate on Catalyst Concentration should be linear.*—Although as Figure 3 shows, the dependence is linear over a wide range of concentration the line does not pass through the origin, as required by this equation.

The behaviour of the catalysts at low concentrations has been investigated by studying the dependence on triphenylphosphine concentration at a catalyst concentration of 0·15 mM, using the dioxygen catalyst. A plot of rate *vs.* $[PPh_3]$ gave a straight line with a non-zero intercept. (Contrast this behaviour with that shown in Figure 2 for a catalyst concentration of 1·0 mM.) This may be explained if one considers that as the catalyst concentration becomes small the reverse process of (III) ⟶ (II) becomes negligible. In the limit of this trend the reaction should be independent of triphenylphosphine and give a straight line parallel to the $[PPh_3]$ axis, in a graph of rate *vs.* $[PPh_3]$. However, this limit may only be reached at zero catalyst concentration so that it may not be possible to observe it. But one does indeed observe behaviour intermediate between the expected limits. Thus the curve in the graph of rate *vs.* [Catalyst] in Figure 3 is due to this change in the triphenylphosphine concentration dependence of the reaction.

A least-squares analysis carried out on the data above 0·25 mM yielded for $Ru(O_2)(NCS)(NO)(PPh_3)_2$ a slope = $0{\cdot}56 \pm 0{\cdot}01 \times 10^{-2}\ s^{-1}$ and intercept = $-0{\cdot}08 \pm 0{\cdot}01 \times 10^{-5}$ mol $l^{-1}\ s^{-1}$ and for $Ru(NCS)(CO)(NO)(PPh_3)_2$ a slope = $0{\cdot}35 \pm 0{\cdot}01 \times 10^{-2}\ s^{-1}$ and intercept = $-0{\cdot}07 \pm 0{\cdot}02\ 10^{-5}$ mol $l^{-1}\ s^{-1}$.

(2) *Calculation of Rate Constants.*—*Catalyst:* $Ru(O_2)(NCS)(NO)(PPh_3)_2$.

The rate constants in the Scheme were calculated from the data for $Ru(O_2)(NCS)(NO)(PPh_3)_2$ as catalyst, as follows.

Since the linear part of the plot of Rate *vs.* [Catalyst] (Figure 2) does not pass through the origin, the rate equation may be conveniently expressed by the equation

$$\text{Rate} = \frac{k_1K_2[\text{P}]([\text{RuO}_2] - [\text{RuO}_2]_0)}{1 + K_2[\text{P}]}$$

where $[RuO_2]_0$ is the value of $[RuO_2]$ when Rate = 0. For this catalyst, $[RuO_2]_0$ = 0·13 mM. Now, since 1/Rate is linearly dependent on $1/[PPh_3]$ (Figure 4),

$$\textit{i.e.}\ \frac{1}{\text{Rate}} = \frac{1}{k_1K_2([\text{RuO}_2] - [\text{RuO}_2]_0)[\text{P}]} + \frac{1}{k_1([\text{RuO}_2] - [\text{RuO}_2]_0)},$$

$$\text{then, slope} = \frac{1}{k_1K_2([\text{RuO}_2] - [\text{RuO}_2]_0)}$$

$$= 0{\cdot}56 \pm 0{\cdot}01 \times 10^5\ \text{s, and}$$

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[19] S. Otsuka, personal communication.

[20] M. M. Taqui Khan, (Miss) R. K. Andal, and P. T. Manoharan, *Chem. Comm.*, 1971, 561.

$$\text{intercept} = \frac{1}{k_1([\mathrm{RuO_2}] - [\mathrm{RuO_2}]_0)}$$

$$= 0{\cdot}91 \pm 0{\cdot}03 \times 10^5\ \mathrm{l\ mol^{-1}\ s}$$

$$\text{Thus,}\quad \frac{\text{intercept}}{\text{slope}} = K_2 = 1{\cdot}63 \pm 0{\cdot}04\ \mathrm{l\ mol^{-1}}$$

$$\text{and}\quad \frac{1}{\text{intercept}} \times \frac{1}{([\mathrm{RuO_2}] - [\mathrm{RuO_2}]_0)} = k_1,$$

i.e. $k_1 = 1{\cdot}26 \pm 0{\cdot}03 \times 10^{-2}\ \mathrm{s^{-1}}$.

As a check of these values one can consider the dependence of the rate on the concentration of catalyst (Figure 2), in which:

$$\text{slope} = \frac{k_1K_2[\mathrm{P}]}{1 + K_2[\mathrm{P}]}$$

Substituting the above values of k_1 and K_2 and using $[\mathrm{P}] = 0{\cdot}5\mathrm{M}$ in this expression, one obtains a value for the slope of $0{\cdot}566 \times 10^{-2}\ \mathrm{s^{-1}}$. This may be compared with the experimentally determined value for the slope of $0{\cdot}56 \times 10^{-2}\ \mathrm{s^{-1}}$.

Catalyst: $\mathrm{Ru(NCS)(CO)(NO)(PPh_3)_2}$. The data for this catalyst were analysed using the equation:

$$\text{Rate} = \frac{k_1K_1K_2[\mathrm{O_2}][\mathrm{P}]([\mathrm{RuCO}] - [\mathrm{RuCO}]_0)}{[\mathrm{CO}] + K_1[\mathrm{O_2}] + K_1K_2[\mathrm{P}][\mathrm{O_2}]}$$

where $[\mathrm{RuCO}]_0$, the value of [RuCO] when Rate = 0, is equal to 0·195 mM. However, in order to analyse the data it was necessary to convert $p(\mathrm{O_2})$ into $[\mathrm{O_2}]$—*i.e.* one needed to know the solubility of dioxygen in xylene. An approximate value of this was obtained by extrapolation of the Ostwald coefficient for the solubility of dioxygen in benzene[21] to 80°, and this was used as the approximate value of the Ostwald coefficient in xylene. At 80 °C, 50 cmHg, $p(\mathrm{O_2})$ was converted into $[\mathrm{O_2}] = 0{\cdot}64 \times 10^{-2}\ \mathrm{M}$.

Solution of the rate equation from the intercepts of plots of 1/Rate *vs.* $1/[\mathrm{PPh_3}]$ and 1/Rate *vs.* $1/p(\mathrm{O_2})$ (the slope of this latter plot having been converted from units of $\mathrm{l\ mol^{-1}\ s\ cmHg}$ to units s by use of a conversion factor involving the approximate value of $[\mathrm{O_2}]$) gave values of $k_1 = 0{\cdot}50 \pm 0{\cdot}02 \times 10^{-2}\ \mathrm{s^{-1}}$ and $K_2 = 2{\cdot}53 \pm 0{\cdot}01\ \mathrm{l\ mol^{-1}}$. It is not possible to evaluate K_1 because the value of [CO] is small and unknown.

In view of the approximations made in evaluating $[\mathrm{O_2}]$, and the fact that there is only an 80% conversion of carbonyl compound into oxygen adduct when the latter catalyst is formed *in situ*, there is reasonable agreement between the constants found for the two sets of experimental data.

[1/2081 *Received, 8th November,* 1971]

[21] W. F. Linke, ' Solubilities of Inorganic and Metal-Organic Compounds,' 4th edn., Amer. Chem. Soc., 1965.