Catalytic Oxidation of Triphenylphosphine using a Ruthenium–Oxygen Complex

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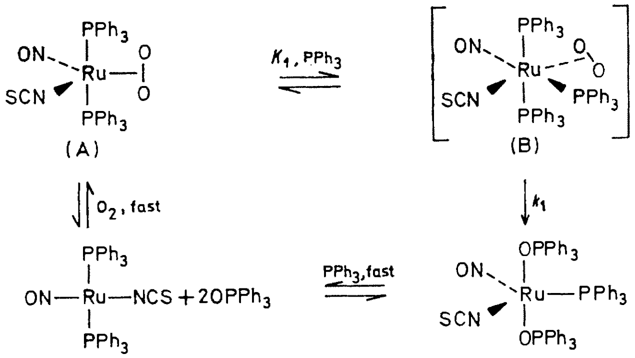
Summary $Ru(O_2)(NCS)(NO)(PPh_3)_2$ is an efficient homogeneous catalyst for the oxidation, by molecular oxygen, of triphenylphosphine to triphenylphosphine oxide; the mechanism of this process has been studied.

THE preparation and some reactions of the oxygen complex $Ru(O_2)Cl(NO)(PPh_3)_2$ have been described.[1] We have since found that a series of complexes $Ru(O_2)X(NO)(PPh_3)_2$ (X = OH, Br, I, NCO, NCS, N_3, CN) may be prepared and discovered that the complexes with X = NCS and CN are efficient catalysts for the oxidation of triphenylphosphine at or near room temperature. Other members of the series behave similarly at higher temperatures. The efficiency of the process is revealed by the following typical experiment, at 80° in xylene using $Ru(O_2)(NCS)(NO)(PPh_3)_2$ (75 mg, 2 mM), PPh_3 (6·55 g, 0·5 M) is 60% converted into $OPPh_3$ in 1 h using sub-atmospheric pressures of oxygen. Using this catalyst we have investigated the rate of formation of triphenylphosphine oxide (by oxygen uptake) over a catalyst concentration range 0·2—2·0 mM, triphenylphosphine concentration range 0·0—1·0 M, oxygen partial pressures 10—60 cm Hg, and temperatures 50—80°. The rate law has been found to be

$$\text{Rate} = k_1K_1[\text{P}][\text{A}]/(1 + K_1[\text{P}])$$

where [P] and [A] are the concentrations of triphenylphosphine and catalyst, respectively.



The following mechanism is consistent with the above rate law where K_1 is the formation constant of the phosphine intermediate complex B, and k_1 is the rate constant for the rate-determining oxygen-transfer step.

At 80° in xylene, $k_1 = 1{\cdot}10 \times 10^{-2}\ \text{s}^{-1}$, $K_1 = 1{\cdot}62\ \text{M}^{-1}$, and from the data we obtain $\Delta H^{\ddagger} = 21{\cdot}8$ kcal.mole^{-1} and $\Delta S^{\ddagger} = -7{\cdot}1$ e.u.

In contrast to Halpern's results[2] for the related $Pt(O_2)(PPh_3)_2$ catalysis of phosphine oxidation we find that the rate does not show first-order dependence upon PPh_3, but instead $1/\text{Rate} \propto 1/[PPh_3]$, necessitating an initial equilibrium step leading to the intermediate B. Also in contrast to these results, we find that the rate is quite independent of oxygen concentration as required by the Scheme above. The intermediate B is reasonably formulated as a six-co-ordinate derivative of Ru^{II}, the nitrosyl group being bound as NO^-. This implies that the Ru-N-O linkage will be bent, 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. The corresponding iridium oxygen complex $Ir(O_2)X(CO)(PPh_3)_2$ 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 mechanism outlined above suggests that other substrates, in particular unsaturated organic molecules might be oxidised using this catalyst, and we are investigating this possibility.

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[1] K. R. Laing and W. R. Roper, *Chem. Comm.*, 1968, 1556, 1568.

[2] J. P. Birk, J. Halpern, and A. L. Pickard, *J. Amer. Chem. Soc.*, 1969, **90**, 4491.

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