Tetrahedron Letters No. 52, pp 5273 - 5276, 1972. Pergamon Press. Printed in Great Britain.

RHODIUM(I) PROMOTED OXYGENATION OF TERMINAL OLEFINS TO METHYL KETONES BY MOLECULAR OXYGEN

C. Dudley and G. Read

Department of Chemistry, University of Exeter, Exeter, Devon, U.K.

(Received in UK 9 November 1972; accepted for publication 23 November 1972)

Activation of molecular oxygen at ambient temperatures by metal ions in homogeneous systems has been the subject of much speculation, particularly in respect to the interplay of oxygen and metal ions in biological hydroxylations.[1] However there are very few *in vitro* examples of such reactions where direct oxygenation of the substrate by molecular oxygen has been demonstrated.[2]

In an initial attempt to find a good model for the biochemical process we have examined the air sensitive rhodium(I) complexes $Rh(Ph_3P)_3H(CO)$[3] and $Rh(Ph_3P)_3Cl$[4] and have established that these react with 1.92 ± 0.02 and 1.59 ± 0.1 equivalents of molecular oxygen in anhydrous benzene at ambient temperatures. Significantly, when solutions of these complexes (6×10^{-3} M) in benzene hex-1-ene mixtures were oxidised an additional oxygen uptake was detected which was proportional to the concentration of hex-1-ene. Markedly higher oxygen uptakes were also found when $Rh(Ph_3P)_3Cl$ was oxidised in the presence of hept-1-ene (0.75 M) and oct-1-ene (0.65 M) but precipitation of a rhodium complex at higher concentrations prevented an examination of the concentration dependence. Cyclohexene (2.0 M) appeared to cause only a small increase in the oxygen uptake. Attempts to account quantitatively for the additional oxygen uptake have met with only partial success but hexan-2-one* (20-25%), heptan-2-one (20-25%) and octan-2-one (35-50%) have been isolated from reactions involving the corresponding olefins; several runs being carried out on each system.

---

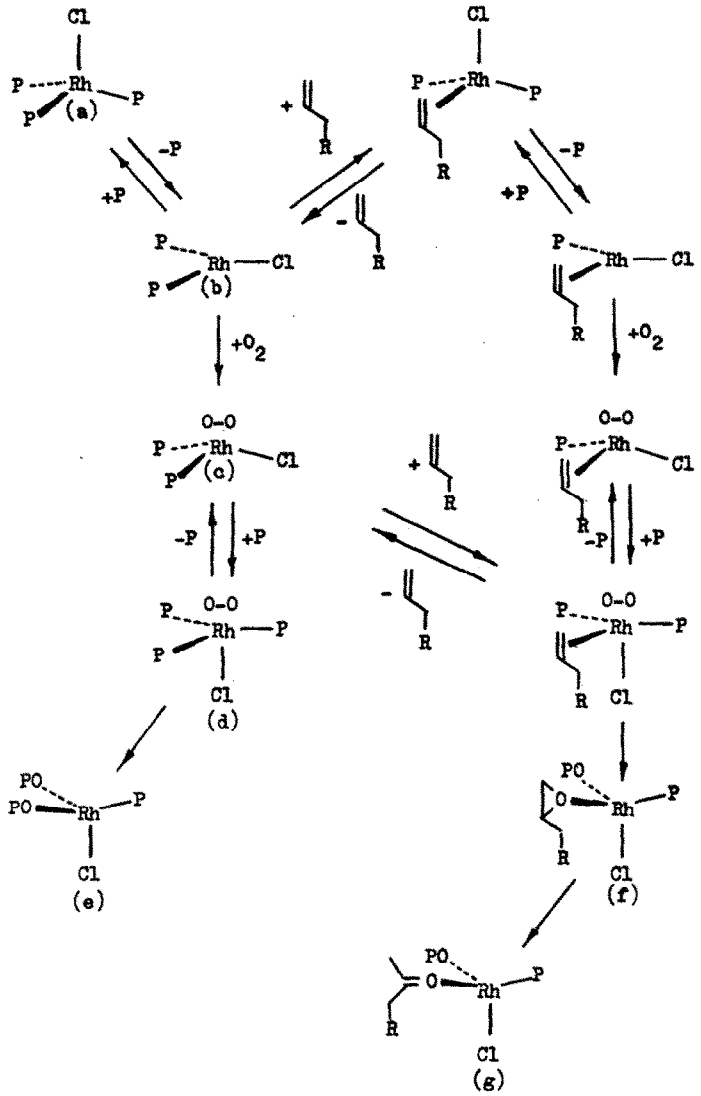
*The methyl ketones were identified by g.l.c. and mass spec., and by t.l.c. of their 2,4-D.N.P. derivatives and were estimated as their 2,4-D.N.P. derivatives by colourimetric methods.

Since $Rh(Ph_3P)_3Cl$ has been shown to catalyse the break down of intermediate hydroperoxides in free radical chain reactions[5] we have sought evidence for such a chain reaction in the cases reported here. However we have been unable to detect hydroperoxide, allylic alcohol or epoxide in the reaction products when hex-1-ene was oxidised, and we have been unable to induce, by the addition of hydroperoxide, a sustained radical oxidation in this system. Furthermore terminal olefins are not normally converted to methyl ketones in such a reaction. We conclude therefore that metal ion activation of oxygen is involved in this oxygenation process.

Augustine found that $Rh(Ph_3P)_3Cl$ in benzene reacts with 1.5 equivalents of molecular oxygen and proposed a dimeric peroxide, in which the $Rh:Ph_3P$ ratio was 1:1, for the final product of this reaction.[6] We have confirmed that only two molecules of triphenylphosphine are converted to the oxide by following the changes in the i.r. spectrum of the solution during oxidation and since a peroxy complex can be isolated when methylene dichloride is the solvent[7] we suggest that a likely sequence for the initial steps in the simple oxidation of the complex is (a) to (e) in the Scheme, c.f. the oxygenation of Ph_3P by Pt(0).[8] When a terminal olefin is present it may be expected to compete for the co-ordination sites both in the complex and in the transient intermediate species and become oxygenated in an analogous manner (Scheme). The final complex appears to be the same in both cases. Whilst the immediate oxygenated product at the complex might be formally represented by an epoxide this would be expected to be unstable and be further modified by a hydride migration, (f) to (g). Metal ion catalysed rearrangements of epoxides under anhydrous conditions have been noted by several workers[9] and Rickborn was able to isolate moderate yields of a methyl ketone from such a reaction but not the isomeric aldehyde which was the other anticipated product.[9a]

The proposed mechanism for the competing oxygenation of the alkenes parallels in three important respects that generally thought to operate in the hydroxylation of aromatic compounds by mixed functional hydroxylases.[10] These are (i) the participation of a transition metal ion, (ii) the participation of an acceptor for one oxygen atom and (iii) the migration of the hydrogen attached to the oxygenated position.[11] Studies to test these mechanistic proposals are in progress.

Scheme



P = triphenylphosphine

PO = triphenylphosphine oxide

References

1. L. Vaska, Science, 1963, 140, 809; L.L. Ingraham, "Biochemical Mechanism". Wiley, New York, 1962, p. 68; R.W. Estabrook, A. Hilbebrandt, H. Remmer, J.B. Schenkman, O. Rosenthal, and D.Y. Cooper, "Biochem. des Saurstoffs", Springer Verlag, Berlin, 1968, p. 229; O. Hayaishi, Y. Ishimura, T. Nakazawa, and M. Nozaki, ibid. p. 196.
2. V. Ullrich and H. Standinger, "Biochem. des Saurstoffs", Springer Verlag, Berlin, 1968, p. 229; M. Viscontini, Angew. Chem. Int. Ed., 1968, 6, 477; B.R. James and E. Ochai, Can. J. of Chem., 1971, 49, 975.
3. C. O'Conner and G. Wilkinson, J. Chem. Soc. (A), 1968, 2665.
4. J.A. Osborn, F.H. Jardine, J.F. Young, and G. Wilkinson, J. Chem. Soc. (A), 1966, 1711.
5. V.P. Kurkov, J.Z. Pasky, and J.B. Lavigne, J. Amer. Chem. Soc., 1968, 90, 4743; J.E. Baldwin and J.C. Swallow, Angew. Chem. Int. Ed., 1968, 8, 601.
6. R.L. Augustine and J. Van Peppen, Chem. Comms., 1970, 497.
7. M.J. Bennett and P.B. Donaldson, J. Amer. Chem. Soc., 1971, 93, 3307.
8. J.P. Birk, J. Halpern, and A.L. Pickard, J. Amer. Chem. Soc., 1968, 90, 4491.
9. (a) B. Rickborn and R.M. Gerkin, J. Amer. Chem. Soc., 1971, 93, 1693; (b) J. Staroscik and B. Rickborn, ibid., 3046; (c) G. Adames, C. Bibby, and R. Grigg, Chem. Comms., 1972, 491.
10. I.C. Gunsalus, H.E. Conrad, and P.W. Trudgill, "Oxidases and Related Redox Systems, Vol. 1," Wiley, New York, 1965, p. 417.
11. G. Guroff, J.W. Daly, D.M. Jerina, J. Renson, B. Witkop, and S. Udenfriend, Science, 1967, 157, 1524.