

Journal of Organometallic Chemistry, 153 (1978) 239-244
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE RESISTANCE OF CYCLO-OCTA-1,5-DIENE TO
LIQUID-PHASE METAL-CENTRED AUTOXIDATION

Jeffrey Farrar, David Holland and David J. Milner*

Imperial Chemical Industries Limited
Corporate Laboratory,
The Heath,
Runcorn, Cheshire.

(Received March 3rd, 1978)

Summary

Cyclo-octa-1,5-diene is resistant to autoxidation at a Rhodium (I) centre under conditions where cyclo-octene is rapidly oxidised. This observation is consistent with the known chelating ability of the diene and with the concept that metal-centred autoxidation requires coordination of dioxygen within a square-planar intermediate. The autoxidation is compared with other metal-centred reactions in which cyclo-octa-1,5-diene reacts more readily than do monoenes.

Introduction

Rhodium (I) species promote the liquid-phase metal-centred autoxidation of styrene [1] to acetophenone and of cyclo-octene [2] to cyclo-oct-2-en-1-one and cyclo-octanone. These reactions do not involve free-radical chains or Wacker cycles. The observations are consistent with the reaction of oxygen with the co-ordinated olefin possibly within the metal's coordination sphere. Both these autoxidations are promoted by $[\{\text{RhCl}(\text{C}_2\text{H}_4)_2\}_2]$ and by the analogous complexes containing the olefins undergoing oxidation.

The complex derived from cis,cis-cyclo-octa-1,5-diene (COD), $[\{\text{RhCl}(\text{COD})\}_2]$, is not an active promoter. Moreover, addition of COD to typical autoxidising mixtures, in quantities equimolar to the Rh(I) promoter, completely suppresses further oxidation. These latter observations are surprising because COD readily undergoes other metal-centred reactions (vide infra), and autoxidation of the COD followed by its displacement from the metal might be expected. The fate of the COD in these systems, which is reported here, throws light on the mechanism of the styrene and cyclo-octene oxidations.

Results and Discussion

Non-conjugated chelating dienes, e.g. COD, readily undergo metal-centred reactions such as hydrogenation [3], hydroformylation [4], and hydrocarboxylation [5] and Wacker oxidation [6]. In these catalytic reactions, the major product is usually that formed by reaction of just one of the diene's olefinic bonds. This selectivity is attributed to the greater co-ordinating power of the chelating diene compared with monoenes. Thus, following reaction of one of the co-ordinated diene's double bonds, the product is displaced from the metal by unreacted diene. This ready reaction of and removal of the diene from the metal centre permits the use of complexes of Rh(I) with chelating dienes as catalyst precursors e.g. in the hydrogenation of monoenes [7].

It might be expected that $[\{\text{RhCl}(\text{COD})\}_2]$ would similarly yield catalytic species under conditions where the catalytic oxidation of styrene or of styrene/cyclo-octene mixtures[†] proceeds

† Cyclo-octene alone does not undergo catalytic autoxidation on Rh(I) in non-complexing solvents because of precipitation of the catalyst [2].

at centres derived from $[\{\text{RhCl}(\text{C}_2\text{H}_4)_2\}_2]$. The inactivity of $[\{\text{RhCl}(\text{COD})\}_2]$ in these systems does not result from conversion of the COD into some other tightly bound, but oxidation resistant, chelating ligand. At 74° , under conditions [2] where coordinated cyclo-octene is oxidised rapidly, $[\{\text{RhCl}(\text{COD})\text{Cl}\}_2]$ is completely unchanged by treatment with oxygen during 1 hr. and no oxygen is consumed. Furthermore, at 30° , both $[\{\text{RhCl}(\text{PhCHCH}_2)_2\}_2]$ and $[\{\text{RhCl}(\text{C}_8\text{H}_{14})_2\}_2]$ form adducts [1,8] with molecular oxygen, but $[\{\text{RhCl}(\text{COD})\}_2]$ does not adduct oxygen.

At temperatures sufficient for metal-centred autoxidation of styrene and of cyclo-octene (90° and 70° respectively), and in the presence of added olefin, solutions of their $\text{Rh}(\text{I})\text{Cl}$ complexes give N.M.R. spectra in which free and coordinated olefin are not distinguishable. Instead, broad bands (up to 50 Hz wide) result from the vinylic protons so indicating rapid exchange between free and coordinated olefin. Addition of COD to these solutions rapidly leads to the spectrum of $[\{\text{RhCl}(\text{COD})\}_2]$. The N.M.R. spectrum of this complex is not affected by added styrene, cyclo-octene or COD, so co-ordinated COD does not exchange readily with these olefins.

All these results agree with the known co-ordinating ability of COD [9] and with the suggestion that metal-centred autoxidation requires the coordination of molecular oxygen within a square-planar intermediate. Thus, oxygen can replace styrene and cyclo-octene lost from their $\text{Rh}(\text{I})\text{Cl}$ complexes, so taking up an equatorial position which can lead to autoxidation. While being coordinatively unsaturated, the COD complex is stable to autoxidation since oxygen can approach only the axial positions.

Hartley and Perie [10] have argued that other ligand combination reactions, also occurring at d^8 metal centres, involve reaction between ligands bound in the square-plane. These authors rationalise

this square-planar requirement in terms of the much stronger interaction of the metal with equatorial as opposed to axial ligands. Thus, π -back donation to antibonding orbitals of equatorial dioxygen weakens this ligands multiple bond and facilitates autoxidation of an adjacent olefin ligand.

The activity of COD and its square-planar complexes in other reactions is readily understood. The Wacker oxidation of COD is a trans-process, hydroxylation involves exo-attack on COD by non-coordinated water [11]. The hydrogenation and hydroformylation of COD catalysed by e.g. Rh(I) species involves oxidative addition of hydrogen to square planar entities so giving octahedral hydride species in which transfer of hydride to the coordinated COD occurs readily* [12, 7b]. Like hydroformylation, the hydrocarboxylation of COD probably involves metal hydride intermediates, though here hydrides result from oxidative addition of e.g. hydrogen halide to the metal [5, 13]. The metal hydride and metal-halide bonds are sufficiently strong to allow cleavage of molecular hydrogen and of hydrogen halide, but the analogous oxidative addition of dioxygen to the metal appears to be energetically unfavourable.

* It has been reported recently [14] that the hydrosilylation of non-chelating dienes is catalysed by cobalt-hydride species, but that COD is completely unreactive. The catalyst was formed in situ from $[\text{Co}_2(\text{CO})_8]$, but the nature of the Co species formed during attempts to hydrosilylate COD was not determined nor was the effect studied of adding COD to reacting mixtures.

Experimental

Stability of $[\{\text{RhCl}(\text{COD})\}_2]$. The complex (0.5 mmol) was dissolved in toluene (8.6 ml) at 74° under oxygen. After 1 hr. no precipitate had separated, no oxygen was absorbed, and no volatile products were detected by g.l.c. Removal of the solvent left a residue having I.R. and N.M.R. spectra identical to those of the original complex.

Absence of oxygen adduction. Addition of $[\{\text{RhCl}(\text{COD})\}_2]$ (0.44 mmol) to toluene (10 ml.) at 30° thoroughly equilibrated with an oxygen atmosphere did not result in the uptake of oxygen by the solution during 2 hr.

N.M.R. Spectra. Typically, samples contained the Rh(I) complex (30 mg) dissolved in 1.25 ml of the appropriate nitrogen-saturated olefin. Solutions were examined in a Varian HR220 instrument.

Acknowledgement

We thank Drs. D.J. Thompson, R. Pearce and R. Whyman and Prof. M. Lappert for valuable discussions and Mr. S. Sunley for assistance with the N.M.R. measurements.

References

1. J. Farrar, D. Holland and D.J. Milner, J. Chem. Soc., Dalton, (1975) 815.
2. D. Holland and D.J. Milner, J. Chem. Soc., Dalton, (1975) 2440.
3. (a) A. Spencer, J. Organometal. Chem., 93 (1975) 389;
A. Andretta, F. Conti and G.F. Ferrari, Aspects of Homogeneous Catalysis, (R. Ugo, Ed.) Volume 1, Carlo Manfredi, Milan, 1970, p.203,

- (b) R.R. Schrock and J.A. Osborne, *J. Amer. Chem. Soc.*, 93 (1971) 3089.
4. L. Marko, *Aspects of Homogeneous Catalysis*, (R. Ugo, Ed.), Volume 2, D. Reidel Publishing Co., Dordrecht, 1974, p.3; A. Spencer, *J. Organometal. Chem.*, 124 (1977) 85.
5. K. Bittler, N.v. Kutepow, D. Neuberger and H. Reis, *Angew. Chem., Int. Ed.*, 7 (1968) 329.
6. (a) J. Smidt, W. Hafner, R. Jira, J. Sedlmeier, R. Sieber, R. Ruttlinger and H. Kojer, *Angew. Chem.*, 71 (1959) 176;
(b) J.K. Stille and D.E. James, *J. Organometal. Chem.*, 108 (1976) 401.
7. (a) L. Horner, H. Siegel and H. Buthe, *Angew. Chem., Int. Ed.*, 7 (1968) 942.
(b) S. Montelatici, A van der Ent, J.A. Osborn, and G. Wilkinson, *J. Chem. Soc. (A)*, (1968), 1054.
8. B.R. James and E. Ochiai, *Canad. J. Chem.*, 49 (1971) 975.
9. J. Chatt and L.M. Venanzi, *J. Chem. Soc.*, (1957) 4735.
10. F.R. Hartley and J.J. Perie, *Nature*, 256 (1975) 636.
11. J.E. Backvall, B. Akermark and S.O. Ljunggren, *Chem. Commun.*, (1977) 264.
12. (a) C.A. Tolman, *Transition Metal Hydrides*, (E.L. Muetterties Ed.) Marcel Dekker, Inc., New York, 1971 p. 271;
(b) R.H. Crabtree, H. Felkin, T. Khan, and G.E. Morris, *J. Organometal. Chem.*, 144 (1978) C15.
13. R.F. Heck, *Organotransition Metal Chemistry*, Academic Press, London, 1974, p.209.
14. A.J. Cornish, M.F. Lappert, and T.A. Nile, *J. Organometal. Chem.*, 136 (1977) 73.