

# Platinum Metal Complexes in Homogeneous Catalysis

PAPERS AT THE FARADAY SOCIETY GENERAL DISCUSSION

By G. C. Bond, D.Sc., F.R.I.C.

Research Laboratories, Johnson Matthey and Co Limited

*A General Discussion of the Faraday Society was held at the University of Liverpool last September on the subject of "Homogeneous Catalysis with Special Reference to Hydrogenation and Oxidation". Of the eighteen papers presented for discussion, six related particularly to platinum metal salts and complexes, five being concerned with hydrogenation or hydrogen transfer and one with oxidation. These papers are reviewed here.*

The General Discussions of the Faraday Society are internationally noted as occasions for leisurely and penetrating consideration of limited fields of research at the borderline between chemistry and physics. They are usually held at a time when the selected field is ripe for such consideration, that is, when sufficient work has been done to show that much more work is needed; and for this reason they frequently act as important milestones along the scientific way, to be looked back on in future years with affectionate regard.

Although the catalytic action of base metal ions (especially cobalt ions) in oxidation has been known for many years, and still features prominently in current research, the ability of palladium salts to catalyse the partial oxidation of olefins has been recognised for only a little more than a decade. Our knowledge of the catalytic properties of salts and complexes of the platinum metals in general

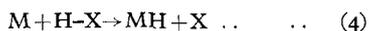
for hydrogenation and hydrogen transfer (as in olefin isomerisation) results from work published only during the last five years; and so rapid has been the progress in this period, and so many the unsolved problems which have arisen, that a discussion of the field in depth was most timely.

## Hydrogenation and Hydrogen Transfer

The homogeneous hydrogenation of olefins catalysed by complexes of the platinum metals has attracted enormous attention in recent years, but many aspects of the mechanism remain unresolved. It is well established that there are three basic processes whereby a metal atom in a complex can activate molecular hydrogen: these may be represented as:



where M is the complexed metal atom. The first certainly operates in the case of  $d^8$  complexes such as  $(Ph_3P)_3Rh^I Cl$  and Vaska's complex  $(Ph_3P)_2 Ir^I(CO)Cl$ . The heterolytic process (2) operates with uncomplexed ions such as  $Cu^{++}$  and  $Ag^+$  and probably also with  $d^6$  compounds (e.g.  $Ru^{II}Cl_2$ ). The third process has not been observed with platinum metal complexes although it holds where M is the pentacyanocobaltate ion  $[Co(CN)_5]^{3-}$ . It is also well known that metal hydrides may be formed by the complex abstracting a hydrogen atom from the solvent, e.g. when this is an alcohol:



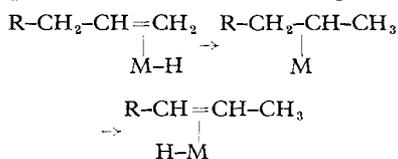
Olefins are well-known to co-ordinate to

metal atoms, especially those having a  $d^6$  or  $d^8$  configuration:

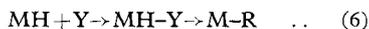


where Y represents an olefin.

It is now possible to set down a number of formal mechanisms to account for hydrogenation and hydrogen transfer catalysed by metal complexes. For olefin isomerisation it is now generally agreed that a metal-alkyl must be formed: then by loss of a hydrogen atom from a carbon atom other than that to which the first hydrogen atom added, an isomerised olefin is formed and may appear as a product after disoordination, e.g.:



This represents the metal-alkyl M-R as having been formed from co-ordinated olefin and metal hydride, viz.



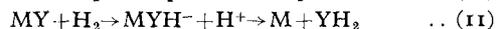
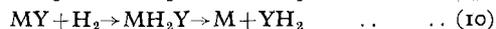
However this requires a vacant co-ordination site for the olefin, and an alternative formulation involves 'olefin insertion' in the MH bond, as:



The paper by D. E. Webster and P. B. Wells and their associates (University of Hull) reported an extensive study of the formation of hydride species by process (4), using the complex  $(Ph_3P)_3Rh^{III}Cl_3$  as the starting material. It appears that at least one of the chlorine atoms is replaced by hydrogen in forming the active species, and that the vacant site required for olefin co-ordination is provided by solvolysis of one of the phosphines. In confirmation of this hypothesis they showed that more rapid catalysis of olefin isomerisation results if a hydrogen atom is present in the original complex (e.g. as in  $(Ph_3P)_3Rh^{III}HCl_2$ ). They also demonstrated that a vacant co-ordination site (as in  $(Ph_3P)_3Ru^{II}Cl_2$ ) is not alone sufficient to give efficient catalysis, but that much faster rates result when both a vacant site and a hydrogen

atom are present (as in  $(Ph_3P)_3Ru^{II}HCl$ ). P. Abley and F. J. McQuillin (University of Newcastle upon Tyne) reported that  $d^8$  complexes such as  $(Ph_3P)_3Rh^I Cl$ , and Vaska's complex and its rhodium analogue, catalyse olefin isomerisation in the absence of hydrogen at 60 to 80°C, but how the hydride intermediates were formed was not investigated.

Turning now to hydrogenation mechanisms, a number of formal possibilities need to be considered: these are represented as:



All of these mechanisms have been proposed at some time or other, (8) and latterly (9) by Wilkinson and his colleagues, who rejected (10) from consideration on various grounds. J. P. Candlin and A. R. Oldham (I.C.I. Petrochemical and Polymer Laboratory) stated that *both*  $(Ph_3P)_3Rh^I Cl$  and the ethylene complex  $(Ph_3P)_2Rh^I(C_2H_4)Cl$  are active catalysts for the reduction of alkynes and olefins, and they queried whether the so-called "unsaturate route" (10) should be dismissed from consideration. B. R. James and G. L. Rempel (University of British Columbia) reported a careful kinetic study of the hydrogenation of maleic acid catalysed by  $RhCl_3$  in dimethylformamide, and also decided in favour of mechanism (10); mechanism (11) was originally suggested by Halpern for hydrogenation catalysis by  $Ru^{II}Cl_2$ .

A subsidiary question of general interest is the extent to which alkyl intermediates are formed from the hydrido-olefin complexes  $MH_2Y$  and  $MYH^-$  before the saturated hydrocarbon  $YH_2$  is formed. The paper by G. C. Bond and R. A. Hillyard (Johnson Matthey) reported the formation of considerable quantities of isomerised olefins during hydrogenation of 1-pentene catalysed by  $(Ph_3P)_3Rh^I Cl$ : similar but less detailed observations were reported by Abley and McQuillin (although not by the I.C.I. group), suggesting that alkyl complexes are indeed formed. The mechanism proposed by James

and Rempel for maleic acid hydrogenation also involved an alkyl intermediate. At the moment it cannot be firmly stated that isomerisation is associated with hydrogenation, and it may proceed quite independently; but several observations suggest that it requires (or at least is facilitated by) molecular hydrogen.

### Oxidation

The partial oxidation of olefins catalysed by Pd<sup>II</sup> salts received surprisingly little attention at this meeting, only the paper by D. Clark, P. Hayden and R. D. Smith (I.C.I. Heavy Organic Chemicals Division) treating this area. It is now well appreciated that oxidation of olefins in the presence of acetic acid and Pd<sup>II</sup> gives rise to a variety of products whose concentration can be varied over

a wide range by altering reaction conditions. The authors reported for example that, when oxidising ethylene with Pd(OAc)<sub>2</sub> as catalyst in the presence of acetic acid, increasing the chloride ion concentration from zero to 2M decreased the yield of vinyl acetate from 85 to 1 per cent, and increased the yield of diacetoxyethane from zero to 80 per cent (based on total products). Much further work is required before we can hope to understand this extremely complex system.

### Conclusion

Both the areas of hydrogenation and oxidation continue to receive the keen attention of academic and industrial scientists alike. Much new and fascinating chemistry is appearing, although the day of its industrial exploitation may not be yet at hand.

## Electrochemistry and Heterogeneous Catalysis

A symposium on "Electrocatalysis" was held at the Technological University, Eindhoven, on November 21st and 22nd, and was attended by some 120 people, mainly from continental Europe. The purpose of the meeting was to bring together workers from the fields of electrochemistry and of heterogeneous catalysis for, although both are intimately concerned with the behaviour of surfaces and of adsorbed intermediates, there are all too few opportunities for the exchange of ideas and information in this area. Work performed in recent years on surface morphology at the atomic scale using techniques such as field-emission microscopy and low-energy electron diffraction has greatly influenced thinking about catalysis but seems not to have much influenced electrochemists. Conversely recent work on the mechanism of electrode processes and the influence of electrode structure on efficiency has not yet been received into the canon of heterogeneous catalysis.

Each author designed his paper to instruct persons not of his discipline concerning some aspect of his subject: some were inevitably more comprehensible and helpful than others. The one theme which ran through many of the papers and much of the discussion was that of the relation between bulk properties

and surface reactivity. Professor W. M. H. Sachtler (Leiden) argued on the basis of his own work on the behaviour of Group VIII<sub>3</sub> - IB alloys that each atom in the surface acts independently and that therefore the collective electron model is not the right one to use. Dr J. N. Butler (Tyco Laboratories, Waltham, Mass.) produced results which showed some of the limits of the "chemical" approach to alloy properties. He with his associates had studied the hydrogen evolution reaction on dilute amalgams of palladium and platinum, and had found they behaved just as mercury. A platinum amalgam containing 0.03 per cent platinum should have increased the exchange current density by more than 10<sup>6</sup> fold, and Dr Butler concluded that the absence of surface structure might have been responsible for the lack of effect. Reporting on an extensive study of platinum black as a fuel cell catalyst, Dr Butler said their results indicated particle size to be the most important factor, and that stored energy had no effect on electrocatalytic efficiency.

The symposium served a useful purpose, but more frequent meetings of this kind are essential if the trend towards the compartmentalisation of science is to be arrested.

G. C. B.