

Homogeneous Catalysis by Some Ruthenium and Rhodium Complexes

A CONSIDERATION OF THE CATALYTICALLY ACTIVE SPECIES

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One of the most important applications for organometallic compounds is likely to be their use as homogeneous catalysts in the industrial production of organic chemicals. The majority of these catalysts will undoubtedly be complexes of the platinum metals. This article focuses attention on the problems associated with the production and characterisation of catalytically active species formed in solutions of a number of rhodium and ruthenium complexes. Factors determining activity are described and a suggested formulation for an active species is presented.

It has been suggested in a recent report from the Science Research Council (1) that in twelve to twenty years' time possibly half of the catalyst systems in use in the heavy organic chemical industry will be homogeneous. If it is conservatively assumed that the turnover of these chemicals in the United Kingdom will double in this time, the turnover derived from homogeneous catalysts will then equal the present total of £650 million per annum. Possible royalty payments on this amount have been estimated at £10 to £15 million per annum. These are rich rewards indeed, and are reason enough for the rapidly growing interest in homogeneous catalysis. The present indications are that the bulk of these catalysts will be complexes of the platinum metals, just as

the majority of heterogeneous catalysts at present in use are these metals in their elementary state.

But progress in our understanding of heterogeneous catalysis has been, still is, and is likely to remain, very slow. It is severely hampered by the experimental difficulties encountered when any direct method such as nuclear magnetic resonance or infra-red spectroscopy is used to examine the nature of the intermediates participating in the catalysed reaction, and by the theoretical complexities that arise when considering a metal surface.

It is partly against this background that we must view the possibilities of catalysing chemical reactions homogeneously in solution by complexes of the platinum metals. The rapid advances in organometallic chemistry over the past fifteen years have brought about a situation in which much is known about the methods of preparation of a wide variety of platinum metal complexes, and about the mechanisms of ligand displacement reactions. Many examples of homogeneous catalysis have been reported, but in very few has there been a determined effort to investigate the nature of the catalytically active species. However, the problems facing the investigator of homogeneous systems may be less formidable than those facing the investigator of heterogeneous systems. First, it is reasonable to assume that the catalytic species themselves are metal complexes, describable in normal chemical terms, and capable of being examined by direct spectroscopic and other

methods. One of the major breakthroughs in this field will be the development of techniques that monitor the changes that occur during the conversion of the complex, in solution, into the catalytic species. The next step will then be to prepare complexes that approximate more closely to the catalytic species. Like others (1) we believe that guarded optimism is well founded and that once mechanisms have been clarified, catalysts for such familiar processes as hydrogenation and isomerisation may be devised which are more selective or specific than their heterogeneous counterparts and indeed, we may hope that entirely new processes will be discovered.

Furthermore, homogeneous catalysis is potentially more efficient than heterogeneous catalysis in its utilisation of the metal because, under optimum conditions, each molecule of complex would be a catalyst, and hence every platinum metal atom would be "working". This contrasts strongly with catalysis by polycrystalline metal where a fair proportion of the atoms are present in the bulk of the crystallites and are "idle".

Before discussing some aspects of homogeneous catalysis in detail it is worth while to compare briefly the elementary processes that occur in the two types of catalysis. The materials that are sold as heterogeneous metal catalysts are often no such thing! The metal surface, on exposure to air, becomes covered by chemisorbed oxygen and a process of activation (frequently heat treatment in a hydrogen atmosphere) has to be carried out before the metal becomes catalytically active. This activation removes the adsorbed gases from the surface metal and renders the surface atoms coordinatively unsaturated so that they become sites for chemisorption of reactants. Conversion to products can then occur. In homogeneous catalysis the situation is not very different. A solution of $\text{Cl}_2(\text{Ph}_3\text{P})_2\text{Rh(III)}$ in chloroform, for example, exhibits catalytic activity for the isomerisation of pent-1-ene to pent-2-ene; but a substance of this formula (like oxidised metal) cannot

strictly be termed a catalyst, because it is coordinatively saturated. An activation process is necessary whereby some ligands are displaced and sites are made available for the coordination of reactant molecules. This activation may be achieved, as will be shown below, by processes that occur when the solid complex is dissolved in a solvent.

In either type of system, interaction between reactant and catalyst has to occur. In homogeneous catalysis we may expect the situation to be comparatively simple since the number of types of coordination site in the catalytically active metal complexes is necessarily limited. In the heterogeneous case the site of chemisorption may be a single surface metal atom, or a special combination of metal atoms, and there may be an exceedingly large number of types of site available on a polycrystalline metal surface. If the profusion of types of sites is accompanied by an equivalent profusion in the types of reaction that can occur, then it is reasonable to suppose that homogeneous catalysts may be potentially more selective in their mode of action than their heterogeneous counterparts.

In either system, reaction has to be followed by displacement of the products from the site of reaction and, by definition, the catalytic species must be regenerated when the products have become free chemical species.

Thus, it is clear that there are conceptual similarities between the two types of catalysis, and it is to be expected that there will be cross-fertilisation of ideas between the two fields.

Let us now consider some particular examples of homogeneous catalysis, especially from the standpoint of the catalytic species itself. The reactions that we have chosen to study in our laboratory over the last five years are isomerisations of olefins, and in particular the conversion of pent-1-ene to *cis*- and *trans*-pent-2-ene. Catalysis has been achieved using solutions of various rhodium and ruthenium complexes. These systems were chosen for several reasons. First, the double-

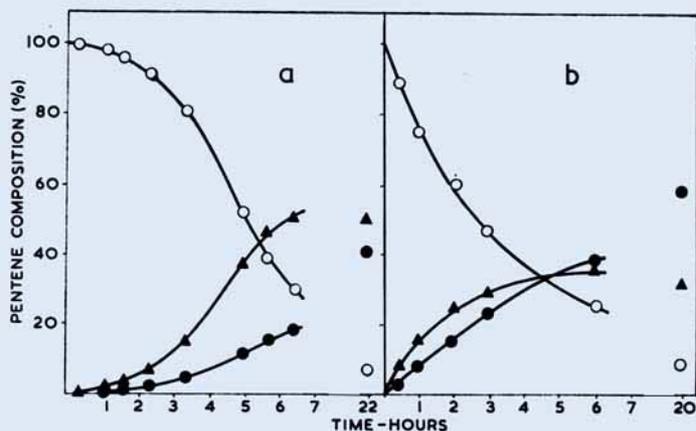


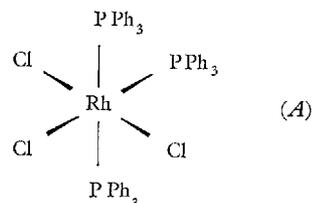
Fig. 1 Variation of pentene composition with time for reactions at 50°C catalysed by $(7 \times 10^{-3})M$ solutions of $\text{Cl}_3(\text{Ph}_3\text{P})_3\text{Rh(III)}$ in chloroform. Initial concentration of pentene = 2.30M. Solutions of complex were allowed to stand at 20°C before addition of pent-1-ene for periods of 0.17 h (reaction (a)) or 41.2 h (reaction (b)).
 ○ pent-1-ene ▲ cis-pent-2-ene ● trans-pent-2-ene
 Equilibrium composition at 50°C is trans-pent-2-ene = 77 per cent; cis-pent-2-ene = 21 per cent; pent-1-ene = 2 per cent.

bond migration reaction involves only one reactant. This is a liquid, and hence complications that arise when gaseous reactants are used (such as diffusion) are avoided. Secondly, it is reasonable to suppose that a detailed knowledge of the chemistry of hydrogen atom transfer will be valuable in the future in wider contexts such as hydrogenation and polymerisation. Thirdly, we have in the past studied olefin isomerisation catalysed heterogeneously by both ruthenium and rhodium, and hence we have been interested in comparing and contrasting the two types of catalysis at first hand.

The work described here has been reported in greater detail in a paper read at a recent Faraday Society General Discussion (2) and elsewhere (3, 4, 5).

Solvolysis in the Formation of Catalytically Active Species

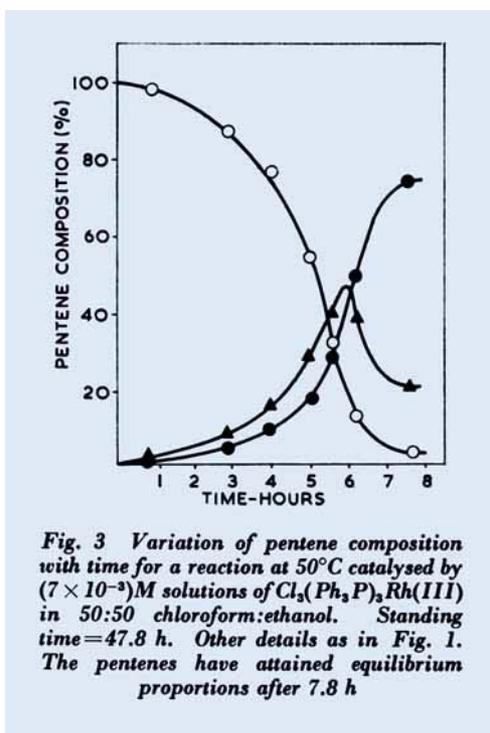
A useful starting point is to consider what happens when the coordinatively saturated complex trichlorotrakis(triphenylphosphine)rhodium(III) (A) is dissolved in chloroform or benzene.



Reactions exhibit composition versus time curves as shown in Fig. 1 (a); first, an induction period is observed after which the rate of double bond migration becomes easily measurable (~ 25 per cent h^{-1} under our conditions). In contrast, the rate of *cis-trans* isomerisation in the product is very slow indeed.

The induction period is associated with processes in which molecules of chloroform and of pent-1-ene displace a proportion of the triphenylphosphine ligands from the original complex, thus providing conditions for the generation of the catalytic species.

This interpretation of the induction period is supported by three pieces of evidence. First, the initial rate increases markedly,



high a degree of solvolysis. For example, in the system that we have been discussing, solvolysis appears to go too far, or to be of the wrong sort, when $Cl_3(Ph_3P)_3Rh(III)$ is dissolved in chloroform-ethanol mixtures containing from 30 to 66 per cent ethanol. Conversion versus time plots using such a solution are shown in Fig. 3 from which it appears, from the low initial rate, that the concentration of catalytically active species formed by interaction of the complex with the solvent is relatively low. However, the rate accelerates as the reaction progresses, and this we attribute to the production of further catalytic species by the reaction of pent-1-ene with the solvolysed rhodium complexes. This sequence of reactions gives catalytic species which must be substantially different from those formed in chloroform containing little or no alcohol, because they not only catalyse double bond migration, but also rapid *cis-trans* isomerisation of the product pent-2-ene. This is interpreted to mean that the alcohol may have displaced all three

triphenylphosphine ligands, and hence co-ordination of pent-2-ene to rhodium is no longer sterically prohibited.

Lastly, if, as we contend, the degree and type of solvolysis is of prime importance, then conditions should exist in which solvolysis in mixed chloroform-ethanol solvent just exceeds the optimum; here the addition of triphenylphosphine to the reaction should *increase* the rate of isomerisation because its effect would be to restore the equilibrium towards the optimum position. Such activating effects of triphenylphosphine have been found in our work.

A Nearer Approach to the Catalytic Species

"Is it possible to prepare the catalytically active species as isolated chemical substances, and to dissolve them unchanged to give catalytically active solutions?" If the answer to this question is in the affirmative then maximum efficiency in the use of noble metal would be achieved, and the number of unknowns in the system would be significantly reduced. Intuitively, we may expect the answer "no", because catalytic species are necessarily highly reactive substances whereas materials that can be isolated have, by their nature, a fair stability. Time will provide the answer to the question. However, as an optimistic first step we have found that a certain amount of tailoring of the original complex does provide more active catalytic solutions. In view of the discussion in the previous section it is reasonable to suppose that formation of the catalyst would be facilitated if the original complex contained a hydrogen atom as a ligand, or if it contained a nominally vacant ligand site, or both. We have examined the activities for pent-1-ene isomerisation at 50°C of solutions ($\sim 5 \times 10^{-3}M$) of the complexes listed in the table in benzene: the characteristics of reaction are as stated.

Clearly, the complexes that have both a vacant ligand site and a hydride ligand are the most active, and we conclude that these com-

| Complex | Number of Hydrogen Ligands | Number of vacant Ligand Sites | Induction Period | Maximum rate (Per cent h ⁻¹) |
|---|----------------------------|-------------------------------|------------------|--|
| Cl ₃ (Ph ₃ P) ₃ Rh(III) | 0 | 0 | present | 20 per cent h ⁻¹ after 4 h |
| α-HCl ₂ (Ph ₃ P) ₃ Rh(III) | 1 | 0 | present | 28 per cent h ⁻¹ after 2.5 h |
| β-HCl ₂ (Ph ₃ P) ₃ Rh(III) | 1 | 0 | absent | 36 per cent h ⁻¹ (initial) |
| H(CO)(Ph ₃ P) ₃ Rh(I) | 1 | 1 | absent | 50 per cent h ⁻¹ (initial) |
| Cl ₂ (Ph ₃ P) ₃ Ru(II) | 0 | 1 | | very slow reaction |
| HCl(Ph ₃ P) ₃ Ru(II) | 1 | 1 | absent | 43 per cent h ⁻¹ (initial) |

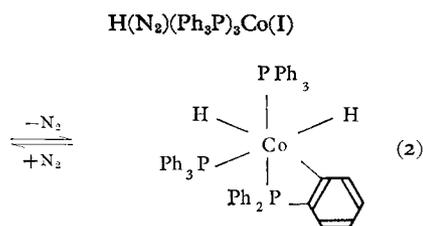
plexes need the least modification by solvolysis in order to convert them to catalytically active species. The differences in activity between α- and β-HCl₂(Ph₃P)₃Rh(III) are particularly interesting. In the α-isomer the hydride ligand is *trans* to chlorine, whereas in the β-isomer it is *trans* to the triphenylphosphine group (7). The so-called *trans*-effect would predict that a group *trans* to a triphenylphosphine ligand will be more readily substituted than a group *trans* to a chlorine ligand. Consequently it is no great surprise that the β- gives more active solutions than the α-isomer.

Much more work needs to be done with other series of complexes to see whether similar effects can be observed. However, these results demonstrate that we are able to go some way towards making complexes that resemble the catalytic species more closely than the complex Cl₃(Ph₃P)₃Rh(III) that we considered first. In our work we are examining ruthenium complexes more closely. Such complexes can be prepared pure, and hence these systems appear to be better defined than many rhodium systems, besides being among the most active.

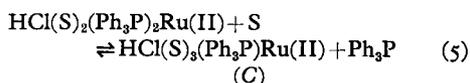
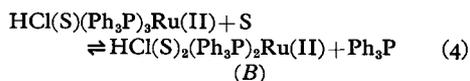
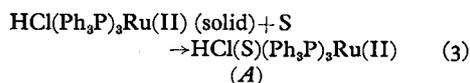
Tentative Formulation of the Catalytic Species

We have recently obtained information that may eventually lead us to precise formulations of the catalytically active species in our systems. When a deuterated olefin such as 1,2-dideutero-pent-1-ene or *trans*-C₂H₂D₂

reacts with solutions of the ruthenium complex, HCl(Ph₃P)₃Ru(II), in benzene at 50°C, redistribution of the deuterium occurs. The surprising observation is that hydrogen isotope exchange takes place between the labelled olefin and the two *ortho*-hydrogen atoms of each phenyl group of the triphenylphosphine molecules. This demonstrates clearly that Ph₃P ligands are not as inert as is sometimes supposed. The exchange takes place, almost certainly, through hydride intermediates of the type recently reported by Parshall (8) for a cobalt complex:

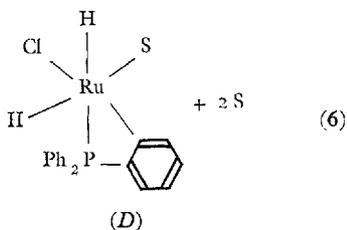
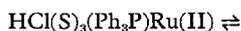


If we now assume that the triphenylphosphines are the groups displaced by the solvent, then solvolysis (3, 4, and 5) leads to species *B* and *C*:



(S = solvent).

Either *B* or *C* can now undergo ligand-hydrogen exchange through a ruthenium (IV) complex such as *D*.



The Ru(IV) complex (*D*) has all the features required of a catalyst – it is a hydrido-metal complex with a vacant ligand site (displacement of S by olefin is facile).

The interconversion of the species involved in these equilibria is very rapid because all triphenylphosphine molecules originally present in the complex, and any added to the system, exchange up to six hydrogen atoms. Further work will examine whether catalytic isomerisation and ligand exchange are closely linked, and if so whether they proceed via a common intermediate. Some recent experiments have shown a decrease in the reactivity of the complex with a decrease in the number of phenyl groups on the phosphine. For

example, the complex $\text{Cl}_3(\text{Et}_2\text{PhP})_3\text{Rh}(\text{III})$ is much less active as an isomerisation catalyst than $\text{Cl}_3(\text{Ph}_3\text{P})_3\text{Rh}(\text{III})$. This indicates that the two reactions discussed above are closely related, and we are hoping that a detailed formulation of the catalyst will be one outcome of this work.

Acknowledgements

Experimental work was carried out by Dr P. C. Taylor, Mr B. Hudson, and Mr C. Anspack who have been supported financially by Johnson, Matthey & Co Limited, The Science Research Council, and B.P. Limited respectively. We are also grateful to Johnson Matthey for the loan of salts of the platinum metals.

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Glass Sheathed Rhodium and Iridium Filaments

Molten metals and alloys can, when contained within a viscous glass tube, be drawn directly to exceedingly fine wires. For several years this technique has been largely confined to copper and copper base alloys which are conveniently handled in borosilicate glass, this remaining as an integral glass skin in place of the conventional organic enamel insulation.

Few attempts have been made to draw fine refractory metals in this way because of the shortage of suitable glasses. A recent report from the Frankfurt branch of Battelle, (K. H. Grunthaler, J. Nixdorf and H. Rochow, *Metall*, 1969, **23**, (4), 310–314) indicates, however, that this problem may now have

been solved. Rhodium wire drawn direct from the melt had a blemish-free surface and at diameters of the order of 15 microns retained sufficient ductility for subsequent deformation. The higher temperatures needed for iridium production necessitated improved induction heating equipment.

The technical problems associated with the selection and/or development of a glass capable of behaving viscously and yet containing molten rhodium at temperatures above 2000°C are not discussed in this paper which, surprisingly enough, does not mention whether the residual glass skin adhered to or spalled off the solidified rhodium wire.

A. S. D.