

Homogeneous Catalysis with the Platinum Metals

A REVIEW OF THE FIRST INTERNATIONAL SYMPOSIUM

By Professor F. R. Hartley

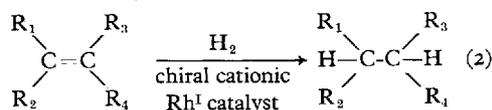
The Royal Military College of Science, Shrivenham, England

The First International Symposium on Homogeneous Catalysis was held in December last in Corpus Christi, Texas, one of the petrochemical centres of the United States of America. This review presents only a brief account of the conference and concentrates on the contributions that particularly concerned the platinum metals.

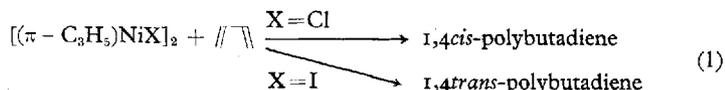
Perhaps the most surprising thing about the first International Symposium on Homogeneous Catalysis organised by Professor Minoru Tsutsui was that the first such symposium should have taken place in 1978 and not twenty years earlier. The conference clearly demonstrated that homogeneous catalysis is a steadily growing subject and the large number of industrial chemists present demonstrated that it has much wider appeal than a purely academic subject.

The meeting got off to a good start with a keynote address from Professor G. Wilke from the Max Plank Institut für Kohlenforschung in which he emphasised how far man had still to go in order to approach the type of turnover numbers that nature had developed for its enzymes. Wilke summarised the steering factors available to modify catalytic reactions as: (i) metal, illustrated by the effect of changing cobalt for rhodium on the n:iso aldehyde (or alcohol) ratio resulting from terminal alkene hydroformylation, (ii) neutral ligand in which both the steric and electronic nature of the ligand can be altered, (iii) anionic ligand where a change of electronegativity can significantly alter the product of a reaction, for example reaction (1), shown on the right, and (iv) temperature.

Professor Jack Halpern from Chicago demonstrated that free radicals may play a greater role in organometallic catalytic reactions than has hitherto been appreciated. Akira Nakamura from Osaka introduced the subject of selectivity control concentrating particularly on ways of achieving both enantioselectivity and diastereoselectivity in products by using complexes with asymmetric ligands. Asymmetric hydrogenation was taken up in subsequent short papers, in particular one by K. Achiwa of the University of Tokyo which described a simple, novel method for the synthesis of molecules with two adjacent chiral centres using a cationic chiral pyrrolidinephosphine-rhodium complex as shown in reaction (2).

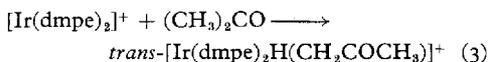


Later lectures by both W. S. Knowles of Monsanto and P. Pino of Zürich demonstrated that, while a number of successful asymmetric catalysts have been developed, progress has been slow largely because in the absence of any fundamental understanding of how



chirality in the catalyst is passed on to the products such asymmetric catalysts as have been discovered have been found empirically. One of the barriers to the systematic study of the intimate mechanism of asymmetric catalysis is the lack of detailed knowledge of the structure of the actual catalytic species.

G. W. Parshall of du Pont, in a lecture on the activation of aliphatic C-H and C-C bonds, emphasised that chemists developing homogeneous catalysts can learn a great deal by studying heterogeneous systems because rearrangement of carbon skeletons catalysed heterogeneously has been known and used for many years in the catalytic reforming of hydrocarbons. By contrast skeletal rearrangements catalysed homogeneously are unknown. Parshall demonstrated that before a C-C bond is broken a C-H bond has to be broken. C-H bond cleavage by cationic iridium(I) complexes was surprising because aryl C-H bonds are inert whereas CH_3X ($\text{X} = \text{CN}, \text{Ac}, \text{NO}_2$) undergo oxidative-addition, reaction (3).



Particularly unexpected was the discovery that while benzonitrile and acetonitrile do not react on their own with $[\text{Ir}(\text{dmpe})_2]^+$, acetonitrile in the presence of carbon dioxide yields *trans*- $[\text{Ir}(\text{dmpe})_2\text{H}(\text{OCOCH}_2\text{CN})]$, a reaction which does not appear to take place by the expected insertion of carbon dioxide into an Ir-C bond.

A. E. Shilov, of the Institute of Chemical Physics, Moscow, reviewed attempts to activate alkanes. The major problem is a thermodynamic one, but by comparing the properties of a number of alkanes with hydrogen, which is readily activated by transition metal complexes Shilov showed that the relatively high reactivity of hydrogen is due to its low pK_a which enables it to be activated through oxidative-addition to basic metal ions. This reasoning also accounts for the relative ease of acetylene activation. By plotting the known metal-carbon and metal-hydrogen bond energies of transition metals

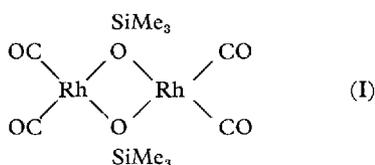
against the number of d-electrons Shilov showed: (i) both form double-humped curves with maxima at $d^2 - d^3$ and $d^8 - d^9$, (ii) $E_{\text{M-H}}$ is always greater than $E_{\text{M-C}}$ and (iii) in a given group, $E_{\text{M-C}}$ increases from first to second to third transition series. As a result we may expect metals of value in alkane activation to include the d^8 systems Os^0 , Ir^{I} and Pt^{II} and perhaps the d^{10} Pt^0 . In reporting recent studies on the H/D exchanges in hydrocarbons catalysed by platinum(II), Shilov reported ^1H and ^{13}C evidence for the presence of Pt^{IV} -aryl compounds during H/D exchange on aromatic hydrocarbons. As yet he has not obtained comparable NMR evidence for the formation of Pt^{IV} -alkyl compounds during H/D exchange on aliphatic hydrocarbons, possible due to too low a concentration of these intermediates. Recent work by Sestakov and Shilov (1978) has looked at the $d_{x^2-y^2}/d_{z^2}$ orbital mixing in $[\text{PtX}_n(\text{H}_2\text{O})_{4-n}]$ complexes because an ability by the complex to allow such mixing is an important factor in promoting the oxidative-addition of C-H to the metal. These authors found that *trans*- $[\text{PtX}_2(\text{H}_2\text{O})_2]$ gives rise to the greatest $d_{x^2-y^2}/d_{z^2}$ orbital mixing, which is consistent with their earlier evidence that this species is highly active in promoting H/D exchange.

A stimulating lecture by Professor J. Chatt of Sussex University on both the biological and chemical fixation of nitrogen demonstrated that while no chemical system to rival the Haber process has yet been devised, nevertheless a great deal of progress has been made both in understanding how nature fixes nitrogen and in attempting to imitate her.

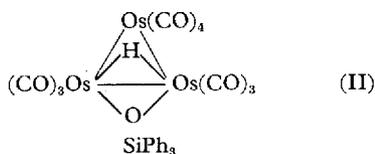
A plenary lecture by Earl Muetterties of the University of California provided an introduction to a number of papers on clusters. The systematic study of clusters is often based on the idea that they provide a better model for a surface than a mononuclear coordination compound. Muetterties emphasised that there were important differences between clusters and surfaces, in that (i) the metal-metal co-ordination numbers are very much less in clusters, (ii) the metal-ligand

co-ordination number is 1 for a surface, but generally greater than 1 for a cluster and (iii) the chemical reactivities of clusters are generally much less than of surfaces. Muetterties then described two rhodium(I)-hydride complexes $[\text{HRh}\{\text{P}(\text{OMe})_3\}_2]_3$ and $[\text{HRh}\{\text{P}(\text{O}^i\text{Pr})_3\}_2]_2$ both of which are active hydrogenation catalysts for olefins, arenes and acetylenes. Acetylenes are reduced to olefins at a slower rate than olefins are reduced to alkanes, an unexpected result that arises because acetylenes compete very favourably with olefins for co-ordination to the rhodium.

The theme of clusters was continued by Renato Ugo of Milan University who reported some very elegant studies of osmium and rhodium carbonyl clusters that had been dispersed on inorganic oxide supports which provide a valuable means of preventing aggregation of the cluster. When rhodium carbonyl is supported on dehydrated silica and treated with oxygen a rhodium(I) species with a similar infra-red spectrum to I is obtained.



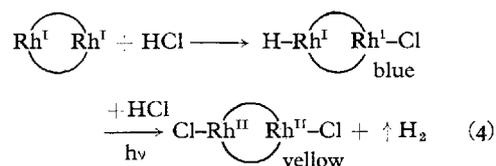
When supported osmium carbonyl is treated similarly, infra-red spectroscopy indicates that the product is similar to II.



When rhodium carbonyl supported on alumina, silica or magnesium oxide is heated under argon, carbon monoxide, carbon dioxide, hydrocarbons, particularly methane, and hydrogen are evolved. A similar reaction occurs when heating is carried out under an atmosphere of carbon monoxide except that far greater quantities of hydrocarbons are

formed. In fact carbon monoxide is "catalytically" converted to hydrocarbons, the source of hydrogen being bound water molecules which react with carbon monoxide to undergo the water shift reaction. Ugo's final conclusion was that the reactivity and stability of supported carbonyl clusters is much greater than their reactivity in solution, a point that was also emphasised in a separate paper presented by Anthony K. Smith and his colleagues at the French Institut de Recherches sur la Catalyse on silica-supported rhodium carbonyl clusters in which $\equiv\text{Si}-\text{O}-\text{Si}(\text{OEt})_{3-n}(\text{CH}_2\text{CH}_2\text{PPh}_2)_n$ ($n=1-3$) groups are used to form the link between silica and rhodium.

H. Gray both entertained and informed the Symposium with a description of $[\text{Rh}_2\{\text{CN}(\text{CH}_2)_3\text{NC}\}_4]^{2+}$ which on photolysis in hydrochloric acid solution evolves hydrogen in a reaction which can be written schematically as in (4).



Photolysis of the blue species does not yield the yellow species directly, but reaction involves an as yet unidentified, photochemically produced, transient species which subsequently decomposes to yield hydrogen. The subtlety of the reaction mechanism is demonstrated by the fact that replacing the $\text{CN}(\text{CH}_2)_3\text{NC}$ ligands by $\text{CN}(\text{CH}_2)_4\text{NC}$ produces a similar dimeric rhodium cationic species with an identical Rh-Rh bond length of 3.2 Å although the two rhodium planes are staggered rather than eclipsed. This latter complex does not liberate hydrogen on photolysis in hydrochloric acid solution.

In summary this First Symposium provided ample evidence that the subject of homogeneous catalysis is alive and growing one. It is to be hoped that the second Symposium, to be held in Düsseldorf in 1980, will be as fruitful.