

# Platinum Metals in Homogeneous and Heterogeneous Catalysis

## A REVIEW OF PAPERS PRESENTED AT THE AMERICAN CHEMICAL SOCIETY MEETING

The catalytic properties of the platinum group metals and their salts featured significantly in two symposia held as part of the one hundred and fifty-second meeting of the American Chemical Society held in New York in September. The first symposium, on the subject of "Mechanisms of Heterogeneous Catalysis", was arranged by the Division of Petroleum Chemistry and occupied two days. Most of the papers relating to metal catalysis were concerned with the use of deuterium as a tracer in understanding mechanisms of hydrogenation.

### Isotopic Tracer Studies

F. Hartog (Dutch State Mines) reported results on the reaction of benzene with deuterium on all the Group VIII metals. All catalysed multiple exchange of the benzene, giving  $C_6D_6$  as a primary product, this process being most favoured by ruthenium and least by platinum. Additional exchange occurred in the hydrogenation step, and completely deuterated cyclohexanes were observed.

A paper by A. W. Weitkamp (American Oil Company) described a study of the interaction of naphthalene with deuterium using charcoal-supported noble metal catalysts. This system is complex by reason of the large number of possible products: in addition to exchanged naphthalene and tetralin, there are four possible octalin isomers and two decalin isomers. Palladium in particular gives high yields of tetralin, with little exchange of naphthalene, suggesting that the latter molecule behaves more like a diolefin and a benzene ring than two fused benzene rings.

Four papers described the interaction of

olefins with deuterium. G. C. Bond and J. M. Winterbottom showed that when deuterium interacted with the *n*-butenes over alumina-supported palladium in the region of room temperature, the isomerised butenes contained much less than one deuterium atom per molecule: the results strongly suggested that dissolved hydrogen and deuterium atoms play an important role in reactions catalysed by palladium. J. J. Phillipson and R. L. Burwell (Northwestern University) described their attempts to simplify the study of the olefin-deuterium reaction by assisting the removal of adsorbed hydrogen atoms, which would otherwise have gone into the alkane, by means of deuterated solvents. They used cyclopentene as the olefin and a platinum-alumina catalyst: using  $CH_3OD$  containing some deuterated ethanolamine they obtained over 60 per cent cyclopentane- $d_2$  and only 3 to 4 per cent cyclopentane- $d_0$ .

G. V. Smith and J. A. Roth (Illinois Institute of Technology) reported that a phenyl substituent at an olefinic double bond leads to preponderant 1, 2-*cis* addition relative to other processes such as exchange and double-bond migration which normally occur with facility over palladium catalysts: the effect was attributed to  $\pi$ -bonding of the aromatic ring to the catalyst surface. E. Selke, W. K. Rohwedder, C. R. Scholfield and H. J. Dutton (U.S. Department of Agriculture, Peoria) reported a detailed study of exchange and isomerisation of methyl oleate catalysed by palladium: this is another complex system, for double-bond migration leads to a large number of olefinic products, but by careful use of several different analytical techniques

the authors were able to form a satisfactory picture of the principal reaction mechanisms.

### Homogeneous Catalysis

The symposium arranged by the Division of Industrial and Engineering Chemistry entitled "Homogeneous Catalysis—Industrial Applications and Implications" also occupied two days and aroused wide interest. J. Halpern (University of Chicago) and G. C. Bond both gave general reviews of the field, the latter emphasising the correlations between homogeneous and heterogeneous catalysis: G. Szonyi (CIBA) reviewed the present commercial status of homogeneously catalysed reactions, and A. W. Gessner (Lummus Company) discussed some aspects of mass and heat transfer pertaining to such reactions. K. A. Taylor (ICI, Runcorn Heath) associated the activity of  $d^8$ -complexes with their ability to exist in either four- or five fold co-ordination, and reported on the catalytic hydrogenation properties of diphosphine complexes of  $\text{Ir}^I$  and  $\text{Rh}^I$ .

Olefin oxidation by palladous chloride commanded much attention. P. M. Henry (Hercules Powder Company) discussed the kinetics of ethylene oxidation and contrasted  $\text{Pd}^{II}$ , which yields acetaldehyde, with  $\text{Tl}^{II}$  which yields ethylene glycol in addition. R. G. Schultz and D. E. Gross (Monsanto) had studied the vinylation of acetic acid by hexenes and reported that product distributions were sensitive to the concentration of acetate ion: some new reaction mechanisms were suggested. The same subject arose in a small symposium on "New Chemistry of Ethylene": D. Clark and P. Hayden (ICI, Heavy Organic Chemicals Division) described how the products of vinylation of acetic acid by ethylene could be controlled by variation of the solvent chosen: in acetic acid acetaldehyde and ethylidene diacetate predominated, whereas in dimethylacetamide, vinyl acetate was the major product. In the same symposium, J. Tsuji and K. Ohno (Toyo Rayon Company) showed that palladous chloride catalyses the carbonylation of olefins and

decarbonylation of aldehydes and acyl halides: the latter reactions are also catalysed by tris (triphenylphosphine) rhodium chloride.

It is now well known that rhodium chloride catalyses the polymerisation of butadiene to trans-1, 4-polybutadiene: two papers presented at the Division of Polymer Chemistry, one by M. Morton and B. Das (Institute of Polymer Science, Akron) and the other by V. A. Kormer and colleagues (U.S.S.R.), reported studies of the reaction, the mechanism of which shows signs of being complex. R. E. Rinehart (U.S. Rubber Company) showed that noble metal-olefin complexes were also polymerisation catalysts.

### Werner Centenary Symposium

In the Werner Centenary symposium, under the auspices of the Division of Inorganic Chemistry, several papers were presented which related to noble metal complexes of actual or potential interest as homogeneous catalysts. Thus J. C. Bailar (University of Illinois) described complexes of palladium and platinum possessing the ability to catalyse the reduction of all but one olefinic double bond in a polyolefin: such complexes are of great interest in the fat-hardening process. L. Vaska (Clarkson College of Technology) summarised his spectroscopic examination of iridium carbonyl hydride and deuteride complexes.

Homogeneously-catalysed processes are clearly in a period of rapid development. Two such processes are already operating commercially and more are likely to follow soon. Homogeneous catalysts have the potential advantages over heterogeneous catalysts of greater specificity and more economic use of the noble metals. The size of the current research effort in this field was amply demonstrated at this meeting and is a testimony to the great promise which this field holds out. It has particular relevance to the rapidly-growing petrochemicals industry, where conversion of cheap olefin feedstock to more valuable products is urgently being sought. G. C. B.