

interface between the two phases and as a result promotes an enhancement in the reaction rate of between 10 and 50 times (5, 6).

Polymer-Supported Catalyst Systems

Ever since the 1970s polymer-supported metal complex catalysts have been investigated, as their use would facilitate the separation of catalysts from products at the end of the reaction. Such materials were hailed as a third generation of catalysts (3), after heterogeneous and homogeneous systems. Polymer-supported metal complex catalyst systems combine reasonable activity with selectivity, specificity and the easy separation of the catalyst. Although activities are usually reduced compared with homogeneous systems, every metal atom is used in the catalysis, and this gives a potential advantage over heterogeneous systems where only a small percentage of the metal atoms (those at the surface) are exposed to the reactants. This last factor can be significant when selecting the platinum metals catalyst systems. As the structures of homogeneous and polymer-supported systems are well defined, their activities can be modified systematically by changing the chemical environment of the active site much more easily than in heterogeneous systems.

Work on polymer-supported catalyst systems is continuing and there are recent reports of interesting selectivities. One such report describes the remarkable synergistic effect of polymer-anchored bimetallic palladium-ruthenium catalysts in the selective hydrogenation of *p*-chloronitrobenzene, see Scheme I (7).

When PVP-PdCl₂-RuCl₃ (I) (PVP = poly(*N*-vinyl-2-pyrrolidone)) is used as the catalyst for the hydrogenation of *p*-chloronitrobenzene in the presence of 0.01 per cent of sodium acetate, and with a palladium:ruthenium ratio of 1:1 or 1:2, selectivities of 94.1 and 94.9 of *p*-chloroaniline are obtained, respectively. When PVP-PdCl₂ (II) was used as the catalyst in the presence of sodium acetate, the normal dehydrohalogenation to aniline took place, giving selectivities of up to 97.8 aniline. Although ruthenium species are not active both for the hydrodechlorination and the reduction of the nitro group of the nitrochloroaniline, the ruthenium species that are formed *in situ* may inhibit the oxidative addition of the carbon-chlorine bond to the active palladium centres.

Use of Glass Micro-Beads with a Chiral Ruthenium Catalyst

Stimulated by the demands of the regulatory agencies, there is an increasing market for enantiomerically pure pharmaceuticals and for

insecticides (1, 8, 9). Recent work by Wan and Davis (10, 11) indicates the use of glass microbeads, with controlled pore size for the absorption of a polar liquid (ethylene glycol), together with a chiral ruthenium complex to form a catalyst phase. This catalyst system has been used in synthesis to give a high enantiomeric excess of the important anti-inflammatory agent (S)-naproxen (IV) from 2-(6'-methoxy-2'-naphthyl)acrylic acid (III), using hydrogen reduction at a pressure of 94 to 101 MPa and a temperature of 276 to 297 K and a 1:1 mixture of chloroform and cyclohexane as solvent, see Scheme II.

The ruthenium complex used was [Ru(BINAP)-4SO₃Na(C₆H₅)Cl]Cl and the controlled-pore glass (CPG-240) had an average pore size of 242 Å and 120/200 mesh size. At 276 K the enantiomeric excess at 100 per cent conversion of (III) was 96 per cent, and the initial turnover frequency for this system at 297 K was 41/hour compared with 131/hour for the homogeneous system in neat methanol. The high reaction rate and enantiomeric excess for this new homogeneous catalyst are accomplished without loss of ruthenium to the organic phase at a detection limit of 32 ppb.

The success of this new catalyst system is attributed to the fact that the phase containing the organometallic complex and ethylene glycol is physically immobilised onto the support, rather than joined to the support via a chemical bond (which considerably reduces the activity). The new heterogeneous system

is basically the same as the homogeneous system from which it derives, leading to only a small reduction in activity while retaining high enantioselectivity.

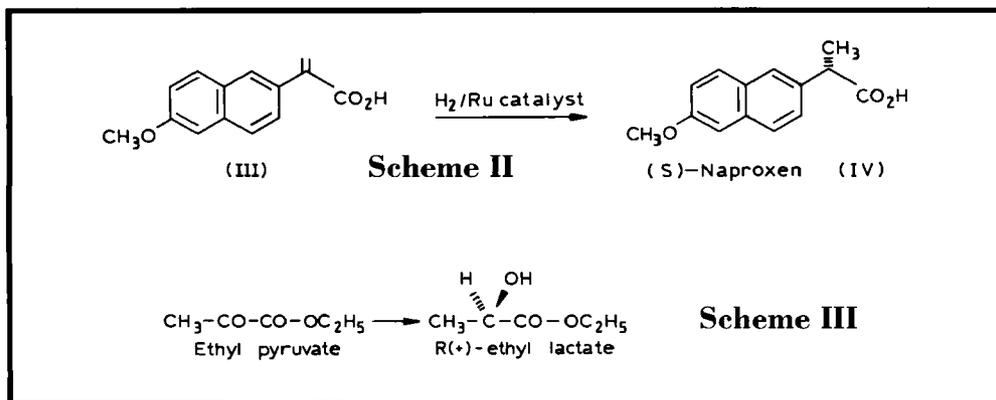
Greater Optical Yield with Platinum Modified by Dihydrocinchonidine

There have been reports of useful optical yields resulting from the reduction of methyl pyruvate with platinum in the presence of the alkaloid, cinchonidine (9). Recent work, in which the hydrogenation of ethyl pyruvate over dihydrocinchonidine-modified platinum was studied, has indicated a distinct trend of increasing optical yield with increasing conversion, ultimately reaching a plateau of 54 to 58 per cent enantiomeric excess at conversions over 50 per cent (12), see Scheme III.

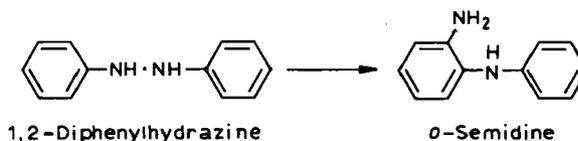
This trend occurred over a wide range of reaction temperatures where the reaction time to reach the conversion varied from 2 minutes to 2 hours.

It has been concluded that the dynamic adsorption/desorption processes which occur early on in the reaction ultimately establish an equilibrated surface environment, thus allowing the full potential of this system for chiral hydrogenation to be realised.

A second conclusion drawn from this work was a suppression of optical yield for reactions carried out under diffusion limitations. This suggests that the formation of the R(+)-ethyl lactate has a strong positive dependence on the hydrogen concentration. Development of



Scheme IV



an overall kinetic model of this reaction is helping to contribute to a greater understanding of chiral heterogeneous catalysis.

Rhodium Catalysed Rearrangement of 1,2-Diphenylhydrazine

The complexation behaviour of 1,2-diphenylhydrazine to metals has not been widely studied, but its reactions with samarium and tungsten complexes have resulted in either the formation of hydrazido complexes or cleavage of the N-N bond; no rearrangement of the aromatic hydrazine has been observed. It has been reported recently that 1,2-diphenylhydrazine rearranges exclusively to *o*-semidine in the presence of square planar rhodium(I) complexes and this reaction is catalytic when there are two *cis*-sites in the square plane which are occupied

by labile ligands (13), see Scheme IV.

Treatment of a dichloromethane solution of $[\text{Rh}(\text{PPh}_3)_2(\text{nbd})]\text{ClO}_4$ (nbd = norbornadiene = bicyclo[2,2,1]hepta-2,5-diene) containing an equimolar amount of 1,2-diphenylhydrazine with hydrogen gas (with caution, bearing in mind the possible explosion hazard) gives a deep red solution of $[\text{Rh}(\text{o-semidine})(\text{PPh}_3)_2]\text{ClO}_4$ which contains a bidentate ligand bonded to rhodium.

It is proposed that the rearrangement involves the initial co-ordination of the 1,2-diphenylhydrazine as a bidentate ligand to rhodium(I). Steric constraints then place the phenyl rings of the co-ordinated ligand in a perfect position to allow the exclusive formation of *o*-semidine via a similar mechanism to that which occurs in the acid-catalysed benzidine rearrangement.

References

- 1 A. W. Parkins in "Insights into Speciality Inorganic Chemicals", ed. D. T. Thompson, Royal Society of Chemistry, Cambridge, 1995, p. 105
- 2 P. J. Davidson, R. R. Hignett and D. T. Thompson, in "Catalysis", Spec. Per. Report, Royal Society of Chemistry, London, 1977, 1, 369
- 3 F. R. Hartley, "Supported Metal Catalysts", Reidel, Dordrecht, Holland, 1985
- 4 Y. Iwasawa, "Tailored Metal Catalysts", Reidel, Dordrecht, Holland, 1986
- 5 D. T. Thompson, *Platinum Metals Rev.*, 1995, 39, (2), 62
- 6 R. V. Chaudhari, B. M. Bhanage, R. M. Deshpande and H. Delmas, *Nature*, 1995, 373, (6514), 501
- 7 Z. Yu, S. Liao, Y. Xu, B. Yang and D. Yu, *J. Chem. Soc., Chem. Commun.*, 1995, 1155
- 8 J. M. Brown in "Insights into Speciality Inorganic Chemicals", ed. D. T. Thompson, Royal Society of Chemistry, Cambridge, 1995, p. 123
- 9 G. C. Bond in "Insights into Speciality Inorganic Chemicals", ed. D. T. Thompson, Royal Society of Chemistry, Cambridge, 1995, p. 63
- 10 K. T. Wan and M. E. Davis, *Nature*, 1994, 370, (6489), 449
- 11 J. M. Brown and S. G. Davies, *Nature*, 1994, 370, (6489), 418
- 12 U. K. Singh, R. N. Landau, Y. Sun, C. LeBond, D. G. Blackmond, S. K. Tanielyan and R. L. Augustine, *J. Catal.*, 1995, 154, 91
- 13 C. J. Davies, B. T. Heaton and C. Jacob, *J. Chem. Soc., Chem. Commun.*, 1995, 1177

Conference on Chemistry of the Platinum Group Metals

The Sixth International Conference on the Chemistry of the Platinum Group Metals will be held at York University, England, from 21st to 26th July 1996. The conference, organised by the Dalton Division of the Royal Society of Chemistry, is convened by Professor R. N. Perutz.

Keynote speakers are H. Takaya, M. Brookhart, P. Sadler, M. Grätzel, O. Eisenstein and G. Ertl.

Both oral and poster contributions will be welcome. For further information contact Dr John F. Gibson, R.S.C., Burlington House, Piccadilly, London W1V 0BN, UK; Fax: 0171-734-1227.