

Metal-Ligand Reactivity and Homogeneous Catalysis

The Oxford Inorganic Discussion, an annual meeting sponsored by the Chemical Society and designed to afford an opportunity for inorganic chemists to meet and discuss topics of common interest, was held this year on September 30th. The subject under consideration, metal-ligand reactivity and homogeneous catalysis, was one of obvious interest to those concerned with the chemistry of the platinum group metals.

The meeting was opened by Professor Geoffrey Wilkinson (Imperial College) with a lecture entitled "Homogeneous Hydrogenation of Olefins using Rhodium Catalysts". The preparation and structure of the rhodium (I) complex tris(triphenylphosphine)rhodium (I) chloride was described. Its dissociation in solution and the take-up of hydrogen and solvent molecules was discussed with reference to its catalytic activity. The mechanism of its function as a remarkably active catalyst for the hydrogenation of olefins was considered in detail and its reactions with hydrogen, deuterium and hydrogen-deuterium mixtures both alone and in presence of olefins were described and discussed.

"A Comparison of Homogeneous and Heterogeneous Catalysts" was the subject introduced by Dr G. C. Bond, of Johnson Matthey. The function of metals of Group VIII in heterogeneous catalytic reactions such as hydrogenation, oxidation and hydrogenolysis was outlined, stressing the importance of electronic and geometric structure of the metal. Important factors governing the behaviour of salts and complexes in homogeneous catalytic reactions of olefins such as the oxidation state of the metal, electronic configuration, and ligands surrounding the metal atom were discussed and illustrated with reference to the use of the carbonyls of cobalt and iron, rhodium chloride, palladium chloride, phosphines and platinum-tin complexes in isomerisation, the pentacyanocobalt (III) anion, iron carbonyl, platinum-tin com-

plexes, tris(triphenylphosphine)rhodium (I) chloride and Vaska's iridium compound in hydrogenation, palladous chloride in the Wacker process for oxidation of ethylene to acetaldehyde and rhodium trichloride in the polymerisation of butadienes.

Dr D. N. Clark, of Imperial Chemical Industries, considered "Palladium-catalysed Oxidation in Nonaqueous Solvents" with particular reference to the oxidation of ethylene by oxygen in solutions of palladous chloride in such solvents as methanol and acetic acid. The distribution of the products of the reaction such as vinyl ether, vinyl acetate, acetal and vinylidene chloride when the oxidation was carried out in acetic acid was described and the marked effect on this distribution of the addition to the system of dimethyl acetamide was stressed. The yield of vinyl acetate increased with increasing additions of this compound so that finally 100 per cent yield could be obtained. Mechanisms to explain the reactions were postulated and the effects of other solvents considered.

"The Activation of Small Inert Molecules" was the subject of Professor J. Chatt (University of Sussex) with particular reference to the nitrogen molecule in the context of atmospheric nitrogen fixation. The difficulty of breaking the $N\equiv N$ bond was stressed and explained from energy considerations. This emphasised the problems involved in devising methods for nitrogen fixation, a problem inexplicably solved by the bacterium, azobacter.

F. M. L.