FARADAY SOCIETY

Homogeneous Catalysis

from a Correspondent

THE "discussion" meeting of the Faraday Society held at the University of Liverpool on September 17-19, on the subject of homogeneous catalysis, was attended by 210 people, of whom seventy-eight were from overseas. The growth of catalytic studies in recent years has been so rapid that it was necessary to confine the discussion to hydrogenation and oxidation. Many of the topics which were discussed were of recent origin. The impetus for these new developments has been provided by an increased understanding of the bonding and electronic structures of coordination compounds and the discovery of whole new classes of compounds (for example, hydrido, organo and π -bonded complexes of the transition metals) with unusual catalytic properties or bearing a significant relation to intermediates in catalytic reactions.

A range of transition metal complexes has been found to effect homogeneous hydrogenation of olefins, and in common with the corresponding heterogeneous reactions these complexes also induce olefinic bond migration. Among the most interesting active catalysts in this group are the (triphenyl phosphine) rhodium halides. The first group of five papers was concerned with the kinetics and mechanism of the hydroisomerization of olefins, especially oct-1-ene, pent-1-ene and *cis*-2-pentene using this catalyst and the corresponding ruthenium, platinum, palladium and nickel complexes, and also cobaltocyanide complexes. Many examples of selective hydrogenation of alkynes and dienes to the intermediate alkenes were discussed. Although it was generally accepted that both olefin coordination and hydride metal complexes are reaction intermediates, there was no agreement as to whether both reactants need to be simultaneously coordinated and activated. Neither was the sensitivity of the reaction to the nature of the solvent fully understood.

The oxidation of olefins to partially oxidized products represented one of the outstanding triumphs of homogeneous catalysis. The oxidation of ethylene to acetaldehyde by PdCl_2 was the first homogeneous process to be commercially utilized and this discovery caused an intense research effort in the oxidation of the higher olefins and on the catalysed reaction of olefins with acetic acid. Whereas the mechanism of the simple oxidation of olefin to aldehyde is fairly well understood that of the other olefins (or ethylene) to other products is not nearly so clear; at the meeting much discussion centred on the effects of acetate ion and solvent in the palladium acetate catalysed oxidation of ethylene and propylene.

The oxidation of alkyl and aryl hydrocarbons has received considerable attention in recent years and the general mechanism of these reactions through hydroperoxide intermediates is now fairly clear. It is generally accepted that in the presence of heavy metal salts the reaction sequence is modified principally by catalysed decomposition of the hydroperoxide. There is, however, considerable evidence that metal ions take part in other specific reactions and that these are largely responsible for the wide variety of products prepared by catalytic oxidation processes. Papers presented on the Co and Mn-catalysed oxidation of saturated and unsaturated aldehydes and the inhibition

of oxidation were particularly relevant to this problem. Other contributions dealt with the very specific effects of cobalt bromide in acetic acid. This is an extraordinarily active catalyst of the oxidation of hydrocarbons to the organic acids and one of the most important examples discussed was the CoBr_2 -catalysed oxidation of *p*-xylene to terephthalic acid, which is a prime intermediate in the industrial manufacture of terylene.

The discussion as a whole was of interest in regard to both the theory and mechanism of the basic reactions involved in catalysis by transition metal ions and complexes and also in relation to the reactions of immediate or future practical importance to the chemical industry.

POLYMER CHEMISTRY

Studying Long Polymer Molecules

from a Correspondent

A SYMPOSIUM on the application of structural analysis to polymers was held by the plastics and polymer group of the Society of Chemical Industry at Cambridge from September 11-13. Three papers on highly cross-linked polymers showed that the symposium did not wish to shrink from difficult subjects. All three of them, from the Ciba company, dealt with the use of chromatograph, electron microscopy and visco-elasticity studies of gel permeation as a means of relating morphological and physical properties. Professor M. Gordon of the University of Essex explained how topological statistics (concerned with gel point and the molecular weight distribution, for example) can be used instead of more familiar parameters (such as bond lengths and angles) to indicate molecular structure and configuration. This theoretical treatment was complemented by Mr J. Mills of Bradford University, who described experiments intended to identify parameters which can characterize the degree of branching in polyethylene.

On polymers in the solid state, both Professor Schoon of Würzburg University and Dr Qvale of Derby College of Technology outlined methods of sample preparation for electron microscope studies. The former advocated the use of silica replicas and of gelatine layers to transfer thin films from polymer surfaces to the microscope grids. Dr Qvale indicated that dilute polymer solutions could be dispersed in solvent-precipitant mixtures and atomized directly onto any thin substrate. Dr Richardson of the National Physical Laboratory, who pointed out that large discrepancies existed when the degree of crystallinity of a polymer was determined by established techniques.

The nature and significance of molecular motions and relaxation effects were considered during the final session. Dielectric, viscoelastic, electro-optic and mechanical measurements were all reported and discussed. For flexible polymers, Dr North of Strathclyde University pointed out the necessity of comparing the results of relaxation studies from more than one technique before assigning any particular molecular motion to an observed relaxation. One welcome aspect of the meeting was the presentation of papers describing the development and application of somewhat novel experimental techniques. Dr Reynolds of Vinyl Products Ltd described the integration of solid pyrolysis with gas chromatography, and its use in indicating