The Polymerisation of Acetylenes

A NEW CATALYTIC SYSTEM

It has been known for some years that compounds of metals such as titanium and vanadium play an essential role in the stereospecific polymerisation of α-olefins. Recently it has been recognised that salts of the noble Group VIII metals have related properties; thus for example palladous chloride can trimerise diphenylacetylene to hexaphenylbenzene, and further examples of "co-ordination catalysis" are constantly appearing. A recent paper by L. B. Luttinger and E. C. Colthup of the Central Research Division of the American Cyanamid Company (*J. Org. Chem.*, 1962, **27**, 3752–3756) describes a novel method for polymerising mono-substituted acetylenes such as 1-heptyne. The essential ingredients of the catalytic system are (i) a salt of a metal of the platinum group ($PdCl_2$, $PdCl_2(n\text{-}Bu_3P)_2$, $RuCl_3$, $PtCl_4$, $OsCl_3$), (ii) an hydridic reducing agent ($NaBH_4$ or $LiAlH_4$ for preference) and (iii) a suitable solvent to bring these into solution (ethanol, acetonitrile or even in certain cases water). Under favourable conditions the polymerisation proceeds smoothly at room temperature to yield a mixture consisting predominantly of dimers and trimers; total polymer yields range between about 8 and 35 per cent. Palladous chloride di(n-butyl phosphine) gives a much larger yield of polymer than does uncomplexed palladous chloride. Dilute solutions of the metal salts were used, the concentrations ranging between 0.01 and 0.05 M.

A number of other metal salts were investigated, but catalytic activity was found to be confined to the salts of the Group VIII metals. Salts and complexes of nickel and cobalt were particularly active; cobaltous nitrate gave 60 per cent polymer, mainly trimer.

No detailed formulation of the reaction mechanism was presented. The reaction was thought to proceed homogeneously, and to be initiated by reduction of the Group VIII metal ion to a metal hydride. This is consistent with the observation that only *hydridic* reducing agents were effective. The acetylene is then thought to form a π-complex with the metal hydride, and subsequent steps may resemble those proposed for stereospecific polymerisation. This reaction lengthens the already rapidly growing list of examples of homogeneous co-ordination catalysis.

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High Temperature Strain Gauges

TUNGSTEN-PLATINUM ALLOY WIRES

Nickel-chromium alloy wires are invariably used for strain gauges operated at temperatures above 250°C. Above 340°C, however, order-disorder reactions affect the electrical resistivity and make gauge readings unreliable. The demand for reliable strain measurements extending for long periods on such parts as turbine blades or on heated structures such as steam piping has thus encouraged search for a more stable wire material.

In reporting the results of experiments at the Central Electricity Research Laboratories, Leatherhead, K. E. Easterling points out (*Brit. J. Appl. Phys.*, 1963, **14**, 79–84) that the need is for a strong oxidation resistant alloy of high electrical resistivity which, since it must not undergo structural changes, should be of the solid-solution type. It should also have a low temperature coefficient of resistance.

By far the most satisfactory materials tested were the tungsten-platinum alloys with 5 to 9 per cent of tungsten, the 8 per cent alloy being preferred. Gauges made from this had a gauge factor of 4.45, appeared unaffected by cold work, and showed outstanding stability up to 800°C.