

The Preparation and Reaction of a Butadiene Cyanide Complex of Nickel(I)

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THE formation of a new butadiene complex with nickel was detected during an investigation of the possible catalysis by aqueous solutions of nickel cyanide complexes of the hydrogenation of butadiene. It has been noted previously that tetracyanonickelate(II) (TCN) ions catalyse reductions by boronates¹ and that hexacyanonickelate(I) (HCDN) ions catalyse the reduction of acetylene to ethylene by molecular hydrogen² but no work on the mechanism of these reactions has appeared, although in the latter case an unstable complex of acetylene and HCDN has been reported.³ In

the present work, it has been found that HCDN in aqueous solution reacts with butadiene and that the product further reacts so that the solution evolves a mixture of butenes, the hydrogen required being derived from the water.

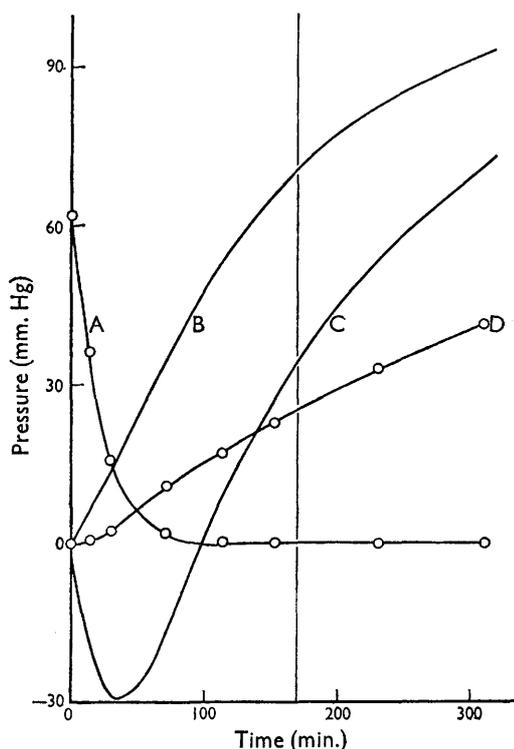
The preparation and reaction of HCDN is carried out in a vacuum system since it is readily oxidised by air. The results shown in Figure 1 were obtained when the concentration of HCDN was initially 0.035 M. The HCDN was prepared by reducing a solution containing 0.25 M-nickel sulphate and 1 M-potassium cyanide with an

¹ D. Goerrig, 1961 (to D. Goerrig), German Patent 1,099,506.

² M. S. Spencer and D. A. Dowden, 1960 (to Imperial Chemical Industries), U.S. Patent, 2,966,534.

³ W. P. Griffith and G. Wilkinson, *J. Chem. Soc.*, 1959, 1629.

excess of 0.5% sodium amalgam (approximately 1.5 atoms of sodium per atom of nickel). The extent of the reduction was calculated from the difference between the number of moles of hydrogen evolved and the number of moles which would have been evolved if the sodium had reacted with the water alone. Preliminary experiments indicated that TCN did not react chemically with either water, hydrogen, or butadiene so that incomplete reduction to HCDN was not important. A mixture of hydrogen and butadiene ($p_{H_2} = 5p_{C_4H_6}$) was shaken with the solution at room temperature ($T = 22^\circ\text{C}$). The curve A in Figure 1 shows the rapid removal of the butadiene from the gas



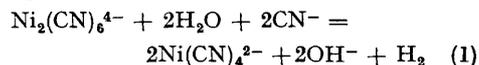
The reactions of butadiene in an aqueous solution containing hexacyanodinitrate (I) ions. $T = 22^\circ\text{C}$.; Gas volume = 218.2 ml.; Liquid volume = 98.2 ml.

phase. Although HCDN was in excess, the almost complete absorption of the available butadiene shows the complex to be reasonably stable. The curve D shows the rise in total pressure of the

butenes desorbed from solution. The isomers are evolved in the concentration ratio:

$$\text{but-1-ene} : \text{trans-but-2-ene} : \text{cis-but-2-ene} = 1 : 3.3 : 2.3,$$

the ratio remaining constant during the run within a coefficient of variation of 5%. Curve C is the change in total gas pressure during the reaction and takes the form shown by curve B when it is corrected for the change in pressure due to the solution of butadiene and evolution of the butenes. This pressure rise is probably due to the hydrogen liberated through the oxidation of HCDN to TCN by water. Bellucci⁴ used the reaction to determine the oxidation state of nickel in HCDN and Vlček⁵ has since verified that it proceeds irreversibly according to equation 1



At the time marked in the Figure by a line parallel to the pressure axis, the solution was rapidly degassed and the experiment continued. The rise in pressure and the desorption of the butenes thereafter have been displaced on the diagram to allow comparison with the results before degassing. It can be seen that the rates of both processes have not been significantly affected.

It seems likely, therefore, that in this system a butadiene cyanide complex of nickel(I) is first formed which then reacts with either water itself or with a hydride species generated as an intermediate in the reaction of HCDN with water. The n.m.r. spectrum of a solution of approximately 0.05 M-HCDN showed no trace of a hydride proton so that such a hydride, if it exists must be a minor constituent of the solution, *i.e.* less than 0.01 M. The mixture of butenes formed by the hydrogenation suggests that the butadiene-nickel bond is formed by the interaction of the π -electron cloud of butadiene with the vacant d -orbitals of nickel(I).

A further set of experiments was performed at a concentration of HCDN of about 0.005 M with similar pressures of butadiene and hydrogen to those used at the higher concentration. The decrease in the initial rate of absorption of butadiene in these experiments compared with that at the higher concentration agreed with the assumption that the rate was proportional to the concentrations of butadiene and of HCDN without any marked salt-effect. The decrease in the rate of desorption of the butenes, however, was at least

⁴ I. Bellucci and R. Correlli, *Atti R. Accad. Lincei*, 1913, **22**, 703.

⁵ A. A. Vlček, *Coll. Czech. Chem. Comm.*, 1957, **22**, 948.

ten times larger than the decrease in rate of the butadiene absorption for the same change in HCDN concentration. If the butenes were formed by the direct hydrogen abstraction from water there seems no reason why this reaction should be decreased in rate so much more than the butadiene absorption. On the other hand, if the butenes

were formed by the reaction of the butadiene cyanide complex with the unstable hydride ion mentioned previously, the difference becomes more understandable due to the possibility of a salt effect and also due to the fall in concentration of the hydride.

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