

The "normal" oxygen valence angle has been determined from these measurements as $90 \pm 5^\circ$. This value is the first experimental confirmation, by electric moment measurements, of the same angle suggested by the quantum mechanical considerations of Pauling. From these results it can be definitely shown that the pyranose ring of carbohydrates and related polysaccharides represents a "strainless" puckered ring system in which the carbon valence linkages are tetrahedral while the oxygen valence angle is approximately 90° . The pyranose ring has therefore a di-planar structure with all the carbon atoms in one plane and the oxygen atom in a different plane from the carbon atoms. On the other hand, the furanose ring structure of similar compounds represents a strained flat ring in which both the carbon and oxygen valence angles are distorted. The relative instability of furanose as compared with pyranose rings thus finds a satisfactory explanation. A full account of this work will be published in the near future.

DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY
MCGILL UNIVERSITY
MONTREAL, CANADA

HAROLD HIBBERT
J. STANLEY ALLEN

RECEIVED SEPTEMBER 22, 1932
PUBLISHED OCTOBER 5, 1932

NICKEL BY THE RANEY PROCESS AS A CATALYST OF HYDROGENATION

Sir:

There is now available (Murray Raney, Chattanooga, Tennessee, U. S. Patent 1,628,190, May 19, 1927) a pure nickel catalyst which under some circumstances is preferable to the "nickel on kieselguhr" type of catalyst [Covert, Connor and Adkins, *THIS JOURNAL*, **54**, 1651 (1932)]. The Raney catalyst is prepared by alloying equal parts of nickel and aluminum and then dissolving out the latter with aqueous sodium hydroxide. Both the alloy and the metallic nickel suspended in water are commercially available. The latter is satisfactory for many hydrogenations but a more active catalyst may be prepared from the alloy by the following procedure. Three hundred grams of the finely ground nickel-aluminum alloy was added slowly (two or three hours) to a solution of 300 g. of sodium hydroxide (80%) in 1200 ml. of distilled water, contained in a 4-liter beaker surrounded by ice. The mixture was then heated on a hot-plate for four hours with occasional stirring at $115-120^\circ$. A further 400 ml. of a 19% solution of sodium hydroxide was added and the mixture kept at $115-120^\circ$ for about three hours or until bubbles of hydrogen were no longer evolved, after which it was diluted to a volume of three liters. The clear solution of sodium aluminate was decanted, and the nickel washed by decantation six times, and then alternately by suspension and by washing on a Buchner filter with distilled water until the filtrate was neutral to litmus. The nickel was then washed three times with 95% ethanol and kept under

ethanol in glass-stoppered bottles. (Nickel prepared by this process is so reactive that it deoxygenated nitrobenzene, *o*- and *p*-nitrobenzene and *p*-nitrophenol with 38 to 50% yields of azo- and azoxybenzenes, when mixed with the nitro compounds in an open beaker.)

The outstanding characteristic of the Raney catalyst is its activity at low temperatures and pressures. For example, with a supported nickel catalyst, acetone did not undergo hydrogenation in any considerable amount much below 100°, while with the Raney catalyst, complete hydrogenation was obtained after 11.2 hours at 23° and 2 to 3 atmospheres' pressure. Similar hydrogenations were obtained with mesityl oxide and acetoacetic ester. Complete hydrogenations at room temperature but at 110 atmospheres' pressure were obtained with benzaldehyde, acetaldehyde, cinnamaldehyde, azobenzene and benzyl cyanide. In the case of all of these compounds hydrogenation proceeded to completion at pressures and (or) temperatures below those at which the supported catalyst was sufficiently active for the satisfactory hydrogenation of these compounds. Both catalysts are active against certain alkenes such as styrene at 23° and 2-5 atmospheres. The hydrogenation of aldol, furfural and the diethyl furfural acetal also proceeded at temperatures somewhat lower than have been observed with the supported catalyst. In the case of benzene, toluene, acetophenone, benzyl alcohol, ethyl benzoate, diethyl phthalate and pyridine the Raney catalyst was not active at markedly lower temperatures and pressures than was the supported catalyst. (The ratio of nickel to organic compound in the experiments referred to in this paragraph was in most instances approximately 1 to 15.)

A precise comparison of the activity of the Raney catalyst with the supported catalyst is impossible not only because they may show their optimum activity for a given compound in quite different temperature ranges but because there is no ratio of catalyst to hydrogen acceptor which would be fair to both catalysts. For example, 8 g. (occupying a volume of 4 ml.) of Raney catalyst was required for the hydrogenation at 23° of 74 ml. of acetone within 11.2 hours. An equivalent amount of nickel on the supported catalyst would have necessitated using 80 g. or 300 ml. of the supported catalyst with 74 ml. of acetone! If the Raney catalyst had been used in the same proportion as was nickel on kieselguhr (0.2 g. for 74 ml. of acetone), it would have been quite ineffective. The ratio of surface to weight of nickel is of course much higher for the supported than for the Raney catalyst so that comparisons of activities on the basis of weight of nickel in the catalyst are unduly unfavorable to the Raney catalyst.

LABORATORY OF ORGANIC CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

LLOYD W. COVERT
HOMER ADKINS

RECEIVED SEPTEMBER 22, 1932
PUBLISHED OCTOBER 5, 1932