

that there are two carboxyl groups for each 4 nitrogen atoms present. Since certain compounds containing the imide group are acidic in liquid ammonia, as for example *n*-methyl acetamide, it would suggest the possibility of the imide link in the protein or the diketopiperazine rings, if they are present, as the origin of the hydrogen. An investigation of the acid properties of glycylalanine and glycylglycine has shown that the imide links of these dipeptides are not acidic. Whether or not the imide links in a longer polypeptide chain would be acidic in liquid ammonia or more readily reduced is not known and must be determined. In the case of diketopiperazine, two molecules of diketopiperazine containing 4 imide links will decolorize a solution containing 4 atoms of sodium with the liberation of 0.9 of an atom of hydrogen. Diketopiperazine is, therefore, reduced by the sodium. When an equimolecular mixture of diketopiperazine and glycylglycine is treated with sodium, there is no vigorous reaction of the sodium with the hydrogen of the carboxyl group. For each 4 atoms of nitrogen in the mixture, 4 sodiums react to give one-fourth of an atom of hydrogen or less. If proteins contain diketopiperazine rings as Abderhalden has suggested, then they would be the part of the protein molecule that is reduced by the sodium.

More experimental work must be carried out before we can state definitely what part of the protein molecule furnishes the hydrogen and what part of the molecule is reduced.

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Some Properties and Reactions of Carbohydrates in Liquid Ammonia.

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(Introduced by C. J. Farmer.)

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An accurate insight into the intermediary metabolism of carbohydrates is dependent in part upon a knowledge of the structure of glycogen and blood sugar. Water has been and still is the most frequently used medium for the study of the chemical properties of the carbohydrates, particularly of the sugars. It occurred to us that liquid ammonia might also be a solvent for the sugars and a medium for the study of the chemical properties of the polysaccharides. Schmid

and his collaborators^{1, 2, 3, 4} have studied some of the physical properties of the polysaccharides in liquid ammonia and have prepared a few of the alkali metal salts of them.

The monosaccharides, arabinose, glucose, levulose, and galactose; the disaccharides, sucrose, maltose and lactose; and the hexoside, α -methylglucoside, are readily soluble in liquid ammonia at -33.5°C . and at 25°C . Glucose is soluble to the extent of 40 gm. per cc. Maltose is the least soluble of the sugars mentioned. α -methylglucoside is soluble to the extent of 36 gm. per 100 cc. Glycogen is dispersed in liquid ammonia to give an opalescent solution. Liquid ammonia solutions of sugars that have been thoroughly dried from water and placed in sealed glass tubes show no caramelization even after standing for a year in the diffuse light of the laboratory. However, caramelization takes place readily when a small quantity of moisture is present. When the ammonia is allowed to evaporate from these solutions, the monosaccharides remain as very thick syrups, which dry in a vacuum desiccator over sulphuric acid to hard glassy substances. Even in this condition, they still contain some ammonia. They do not crystallize from their ammonia solutions. Various attempts to induce crystallization failed. The disaccharides and α -methylglucoside crystallize from their ammonia solutions during concentration. The crystalline masses contain varying quantities of ammonia which is removed with considerable difficulty. For example, a sucrose still contains $2\frac{1}{2}\%$ of ammonia after standing one week in a vacuum desiccator over sulphuric acid.

When solutions of potassium amide are combined with fairly saturated solutions of monosaccharides, disaccharides and α -methylglucosides at -33.5°C . their white potassium salts precipitate immediately. The mono-potassium salts of the monosaccharides, arabinose, glucose, and levulose, are formed; the di-potassium salts of the disaccharides, sucrose and lactose; and either the mono- or tri-potassium salt of α -methylglucoside depending upon the proportions of the potassium amide and glucoside used. There is no caramelization. The salts contain a varying amount of ammonia which is removed with difficulty. The mono-potassium salts of arabinose, glucose, and fructose when wet with ammonia turn brown and char rapidly on exposure to air, but are stable towards air when thor-

¹ Schmid and Becker, *Ber.*, 1925, **53B**, 1968.

² Schmid and Bilowitzki, *Ber.*, 1927, **47**, 785.

³ Schmid, Ludwig and Pretsch, *Ber.*, 1928, **49**, 118.

⁴ Schmid and Zacherl, *Monatsch.*, 1929, **53**, **54**, 498.

oughly dried from ammonia. The potassium salt of maltose chars in air in a few seconds even when dry. The mono-potassium salt of α -methylglucoside is stable toward air. The tri-potassium salt is stable toward air when dry but chars readily when wet with ammonia.

The sugars were recovered from all of these salts and identified by appropriate tests.

When glycogen is suspended in liquid ammonia and a solution of potassium amide is combined with it at -33.5°C ., a white precipitate separates out immediately. This precipitate chars immediately upon exposure to air, even when dry. This indicates that glycogen is precipitated as a salt and not as a result of the neutralization of the electric charge on the glycogen micelles.

When the reducing sugars, arabinose, glucose, levulose, galactose, maltose, and lactose, are sealed in glass tubes with sodamide and allowed to stand at 20°C ., caramelization takes place in less than 24 hours. This is analogous to the action of strong bases on the reducing sugars. Sucrose does not caramelize under these conditions.

Our interest in the alkali salts of the carbohydrates lies in the fact that they may be of use in the preparation of esters and ethers of these substances. Preliminary tests have justified this interest.

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Bronchial Stenosis in Suppurative Pulmonary Lesions.

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Suppurative lesions of the lungs, as well as in other parts of the body, are usually treated by securing proper drainage and rest of the part. One of the most common methods of obtaining these requisites is massive collapse of the involved region. A procedure for producing experimental massive atelectasis has recently been developed in these laboratories.¹ Briefly, this consists of the production of complete stenosis of a bronchus by cauterizing its mucous lining with a 35% solution of silver nitrate. Two weeks following the application of the cautery, the bronchial lumen is found completely occluded and is accompanied by massive atelectasis of the

¹ Adams, W. E., and Livingstone, H. M., *Ann. Surg.*, 1932, **59**, 106.