

Citation:

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A second conclusion of general interest is the one which relates to the constitution of anorganic polysulphides.

From the fact that sodium disulfide causes the formation of organic disulfides one mol. of which on oxidation with nitric acid splits up into two mol. of a sulphonic acid, it follows that in sodium disulfide one sodium atom is linked to each of the sulphur atoms; its constitution is, therefore, NaS-SNa and those of the organic disulfides $\text{RS-SR}'$. As, moreover, tetrasulfides are quantitatively formed from RS-SNa and iodine they may be assumed to have the constitution $\text{RS-S-S-SR}'$ which supposes the existence in the molecule of a series of four atoms of sulphur linked to each other, comparable to those of carbon atoms. For the trisulfides the formula $\text{R-S-S-S-R}'$ is then arrived at.

Finally, attention may be called to the fact that sodium disulphide acts as a deoxidiser on those nitro-compounds on which it does not act with double decomposition. The reaction takes place without formation of bye-products; so for instance m.m. dinitroazoxybenzene is formed from m. dinitrobenzene and p. p. dinitro-azobenzene from p. dinitrobenzene. The Na_2S_2 itself becomes $\text{Na}_2\text{S}_2\text{O}_3$ ¹⁾.

For further particulars the dissertation should be consulted; its contents with a few additional observations will appear later on in the "Recueil".

Amsterdam, Dec. 1900.

Chemistry. — Mr. N. SCHOORL: "*On urea derivatives of sugars*".
(Communicated by Prof. C. A. LOBRY DE BRUYN).

The investigation as to the existence of these compounds originated in the vain efforts to readily detect lactose in urine in a short time and to distinguish it from glucose. LOBRY DE BRUYN and ALBERDA VAN EKENSTEIN have attempted this by inverting the sugars and then reducing the same with sodium amalgam, the dulcitol formed from the galactose may be identified by its benzal-compound which is very adapted for this purpose. The negative result given by these experiments made it seem possible to me that on treating urine with a dilute acid the sugar combines with the urea and got removed as such.

¹⁾ See Proc. Royal Acad. of Amsterdam Oct. 27, 1900.

From the following experiments it appears that under the influence of dilute acids glucose reacts with urea even at the ordinary temperature and more rapidly at an elevated one.

At 25°: 10 grams glucose, 2½ gram of urea, dissolved in 5 pCt. sulphuric acid up to 50 c. c.

| | |
|-------------------------------|---------|
| rotation at the commencement: | 20° 20' |
| » after 7- hours | 20° 10' |
| » » 24 » | 19° 5' |
| » » 48 » | 17° 40' |
| » » 101 » | 15° 15' |
| » » 580 » | 7° 0' |

At 50°: 5 grams of glucose, 1,6 gram of urea, dissolved in 5 pCt. sulphuric acid up to 50 c. c.

| | |
|-------------------------------|---------|
| rotation at the commencement: | 10° 10' |
| » after 42 hours | 6° 10' |
| » » 96 » | 5° 10' |

I did not succeed in isolating from the so obtained reaction products a compound of glucose with urea, chiefly because the change seemed to be a limited reaction and because the excess of sugar formed a syrup and prevented a separation by solvents.

Therefore, another way was tried which led to a favourable result. Glucose (1 mol.) and urea (2 mols.) were warmed with 5 percent sulphuric acid for 20 days at 50°; the liquid was then freed from sulphuric acid by neutralisation with barium carbonate and filtered. By fermenting during 5 days the excess of glucose was removed and the now laevo-rotatory liquid evaporated to a syrup. After some days, a crystallisation took place, the crystals containing besides the excess of urea also a laevo-rotatory substance which was obtained pure by recrystallisation from alcohol and possessed the following properties.

Melting point: 206°. Rotation: $[\alpha]_D^{15} = -23^\circ$ (1 percent solution).

Easily soluble in water, difficult in absolute alcohol, not or very little in ether, petroleumether, benzene, chloroform and acetone.

Analysis:

Substance: 0,1705 gram, CO_2 : 0,237 gram, H_2O : 0,0976 gram.

Nitrogen estimation (according to KJELDAHL):

Substance: 0,121 gram = 10.65 cc. $N_{/10}$ acid.

Found: C: 37,9 percent, H: 6,4 percent, N: 12,2 percent.

Calculated for $\text{C}_6 \text{H}_{12} \text{O}_5 \cdot \text{N} \cdot \text{CO} \cdot \text{NH}_2$:

C: 37,8 percent, H: 6,3 percent, N: 12,6 percent.

On boiling the aqueous solution the rotation remained about constant; on warming with dilute acid it rapidly became positive.

FEHLING'S liquid was reduced although less rapidly than by glucose. 0,040 gram of glucose-ureid reduced a quantity corresponding with the following amounts of $N_{/10}$ thiosulfate:

| | | | | | |
|-------|----|--------|----------|------|-----|
| after | 1 | minute | boiling: | 8,7 | cc. |
| > | 2 | > | > | 9,4 | > |
| > | 5 | > | > | 10,1 | > |
| > | 10 | > | > | 10,3 | > |

while the quantity of glucose (0,0324 gram) corresponding with 0,040 gram of glucose-ureid reduced copper to the extent of 10 cc. after boiling for two minutes.

Neutral copperacetate is not reduced by glucose-ureid. With a solution of phenylhydrazine in acetic acid it yields no osazone at first, but only on prolonged boiling.

An analogous compound of glucose with phenyl-urea [melting point 223° , $[\alpha]_D = -55^\circ$ in 1 percent solution] was prepared in practically the same manner. The analysis gave:

Substance: 0,1596 gram, CO_2 : 0,3014 gram, H_2O : 0,0875 gram.

Nitrogen estimation (KJELDAHL). Substance: 0,151 gram = 9,9 $N_{/10}$ acid.

Found: C: 51,7 percent, H: 6.1 percent, N: 9,2 percent.

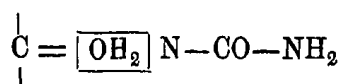
Calculated for: $\text{C}_6 \text{H}_{12} \text{O}_5 \cdot \text{N} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6 \text{H}_5$:

C: 52,4 percent, H: 6,0 percent, N: 9,4 percent.

The chemical properties proved to be analogous to those of the urea derivative.

Besides by heating in acid solution, it was found that the reaction of glucose with urea and phenyl-urea also takes place by melting these together at 100°—150° and also by heating under pressure in methyl- or ethylalcoholic solution.

It was further noticed that lactose, galactose, mannose, arabinose and xylose also react with urea. On the other side the following derivatives of urea were tested as to their behaviour towards glucose: methyl-, phenyl-, benzyl-, symm. dimethyl, symm. diethyl- and symm. diphenyl-urea and it was noticed that the first three did react with sugar but the last three did not. On account of this and of the properties of the obtained glucose-ureids cited above, it may be assumed that at the condensation the carbonyl group of the sugar combines with one of the amido groups of urea with liberation of water:



and that these derivatives are, therefore, comparable with oximes and hydrazones.

It was also ascertained that thiourea and phenyl-thiourea react with glucose, although slower.

The study of these substances, which may also be important to physiology both by their possible occurrence in diabetic urine and with a view of a future synthesis of albuminous substances, will be continued.

Amsterdam, December 1900.

Chemistry. — Dr. A. F. HOLLEMAN: "*On the nitration of ortho-chloro- and orthobromobenzoic acid*" (Communicated by Prof. C. A. LOBRY DE BRUIJN).

MONTAGNE has shown in his dissertation¹⁾ that in the nitration of orthochlorobenzoic acid with nitric acid, there is formed besides the already known chloronitroacid (CO₂H : Cl : NO₂ = 1 : 2 : 5) a second mononitroacid which, however, he could not isolate in a pure condition. In this, I have succeeded by fractional crystallisation

¹⁾ Compare also Rec. 19, 54.