

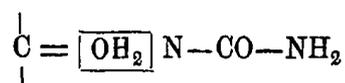
Citation:

A.F. Holleman, On the nitration of orthochloro and orthobromobenzoic acid, in:
KNAW, Proceedings, 3, 1900-1901, Amsterdam, 1901, pp. 462-463

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.

of the potassium salts. The K-salt of the main product crystallises first in thin long needles; in the very last motherliquors the bye-product has accumulated. This is liberated by hydrochloric acid and further purified by repeated crystallisation from dilute alcohol. It then has a melting point of 185° ; in dilute alcohol it is a little less soluble than the main product.

In the nitration of orthobromobenzoic acid only a single mononitroacid has, as yet, been noticed, namely the acid $(\text{CO}_2\text{H}:\text{Br}:\text{NO}_2 = 1:2:5)$. Here, however, is also formed a second mononitroacid which may be also obtained by fractional crystallisation of the K-salts. After repeated crystallisation from dilute alcohol, it melts at 191° . Its solubility in this liquid is about equally great as that of the main product of the nitration.

The nitrogroup enters the place 3 both in the o-Cl- and the o-Br-acid, so that the structure of two bye-products is $\text{CO}_2\text{H}:\text{Cl}(\text{Br}):\text{NO}_2 = 1:2:3$. This was proved by heating the acids with ammonia to 150° when from both the same nitroamidoacid is obtained $(\text{CO}_2\text{H}:\text{NH}_2:\text{NO}_2 = 1:2:3)$ which was identified by its melting point (204°), its solubility in water, benzene and chloroform and by the melting point of its ethyl ether (104°).

The quantity which is formed of both bye-products will be determined accurately.

Chemistry. — Dr. J. H. ADRIANI: "*Eutectic curves in systems of three substances of which two are optical antipodes*". (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

In my dissertation "Systems consisting of optical antipodes" (Amsterdam, 1900) I mentioned briefly (p. 53) a paper by BRUNI (Rendic. Accad. dei Lincei, 9 April 1899, pg. 332) in which he describes a method of deciding whether an externally-compensated inactive substance is a conglomerate, a racemic substance or a pseudo-racemic mixed crystal. BRUNI-proposes to determine the eutectic point of a solution of one of the antipodes, to afterwards dissolve mixtures of the antipodes in known proportion in the same solvent and again find the eutectic points. If all mixtures from 100 percent *d*- to 100 percent *l*- are tested in this way such a point will be found for each mixture. These temperatures may be considered, for the solvent under consideration, as functions of the composition of the mixture of antipodes and a figure may