

Citation:

Romburgh, P. van, On the nitration of dimethylaniline dissolved in concentrated sulphuric acid, in: KNAW, Proceedings, 2, 1899-1900, Amsterdam, 1900, pp. 342-344

The following table of the E. M. F.'s of CLARK-cells containing solid $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ or $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ is given by JAEGER¹⁾ in his memoir. In the last column I have added the E. M. F.'s of our transition element.

T A B L E III.

Temperature	E.M.F. in millivolts. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	E.M.F. in millivolts $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$	E.M.F. Transition cell in millivolts
0°	1449	1434	15
10°	1439	1427	12
20°	1427	1418	9
30°	1414	1409	5
39°	1400	1400	0

From these figures the temperature coefficient is

$$\left(\frac{dE}{dT}\right)_{39^\circ} = -\frac{5}{9} = -0,55 \text{ millivolt,}$$

whilst the thermodynamic calculation gave $-0,51$ millivolt; the agreement is, thus, very satisfactory.

In a subsequent paper I shall show that the E. M. E. of our transition cell at other temperatures may be calculated by thermodynamics.

Amsterdam, University Chemical Laboratory.
December 1899.

Chemistry. — “*On the nitration of dimethylaniline dissolved in concentrated sulphuric acid*”. By Dr. P. VAN ROMBURGH.
(Communicated by Prof. A. P. N. FRANCHIMONT.)

Some years ago²⁾ I had the honour of communicating to the Academy the results of an investigation of two new dinitro-derivatives of dimethylaniline obtained by dissolving this base (1 mol.) in

¹⁾ WIEDEMANN's Annalen 63 (1897), p. 356.

²⁾ Zittingsverslag 23 Februari 1895.

twenty times its weight of concentrated sulphuric acid, and allowing 2 mols. of nitric acid, also dissolved in sulphuric acid, to act on the solution so obtained at a low temperature and pouring the mixture onto ice. Different observations made during the often repeated nitrations led me to doubt whether the dinitration really took place in the concentrated sulphuric acid solution, or whether, more probably, the reaction leading to the formation of the two nitro-products took place in the mixture of acids when diluted with ice water. Further investigation of the course of the reaction actually brought to light that the nitration in concentrated sulphuric acid solution, even in presence of excess of nitric acid, does not go further than the formation of the mononitro-compound.

If a cooled mixture of 104 gr. nitric acid of 50 pCt., or 60 gr. of 86 pCt., and 300 gr. sulphuric acid be added in small quantities to a solution of 60 gr. dimethylaniline in 1 kg. of concentrated sulphuric acid, cooled to 0°, the temperature of the mixture rises at first with each addition. When half of the nitric acid has been added, however, no further rise of temperature is observed on adding the remaining half. When all the nitric acid has been added it is clear from the smell of the mixture that it contains free nitric acid. If, after half an hour, the half of the liquid is poured into 1¼ kg. of ice water (a mixture of equal parts of water and ice) the temperature at the end of the experiment is 30° C., a yellow crystalline product (the dinitro-compound melting at 176°) is obtained and after addition of soda to the filtered acid liquid the red isomeric compound (melting point 112°). If a cooled solution of 25 grams of dimethylaniline in ½ kg. of sulphuric acid is added to the other half of the nitration liquid the rise of temperature is again clearly observable. On pouring the mass, after some time, into 2½ litres of ice water a mixture of para- and metanitrodimethylaniline with a little of Mr. MERTENS' 1. 2. 4. dinitrodimethylaniline is obtained, such as is also produced according to GROLL¹⁾ when dimethylaniline dissolved in concentrated sulphuric acid is nitrated with one molecule of nitric acid.

When the nitration mixture containing one molecule of dimethylaniline and two molecules of nitric acid is poured into a mixture of ice and soda, dinitro-compounds are formed only in very small quantity or not at all.

From these experiments it may be concluded that, in the solu-

¹⁾ Berl. Ber. 19. 198.

tion in concentrated sulphuric acid the nitration does not go further than the metamono-nitro-compound, so that the entry of the second nitro group must occur after the admixture of water.

I pointed out previously (*loc. cit.*) that the two dinitro-compounds may also be prepared by dissolving the metanitro-compound in an excess of very dilute nitric acid.

I now found that by dissolving 1 gram of metanitrodimethylaniline in a mixture of 26 grams of sulphuric acid and 50 grams of water, cooled to 30°, and adding 0.85 grams nitric acid of 50 pCt, a paste of the yellow dinitro-compound melting at 176° is obtained whilst, by means of sodium carbonate, the red isomeric is separated from the filtrate. These relative quantities are exactly those found in the liquid obtained by pouring the nitration mixture into the quantity of water prescribed.

The small quantity of the dinitrodimethylaniline of MERTENS which is produced shows that in nitrating dimethylaniline by the method of GROLL the meta-compound is formed almost exclusively in the concentrated sulphuric acid solution and that the para-compound is most probably formed in the liquid after dilution with water by the action of unused nitric acid on dimethylaniline which has escaped nitration.

When para-nitrodimethylaniline (1 mol.) is dissolved in concentrated sulphuric acid and 1 mol. of nitric acid is added to the solution, the dinitro-compound of MERTENS is found alone after pouring the mixture into water; no nitro-group has taken up the meta position with regard to the amino-group.

Chemistry — “*On the formation of Indigo from Indigoferas and from Marsdenia tinctoria*”. By Dr. P. VAN ROMBURGH. (Communicated by Prof. A. P. N. FRANCHIMONT).

The interesting communication which Prof. BEYERINCK made to the meeting of Sept. 30th last, from which it appears that the indigo yielding plants belong to two, physiologically quite distinct groups induce me to invite attention to some observations which I made some years ago during an investigation of indigo-yielding *Indigoferas* and of *Marsdenia tinctoria* which was published in the “*Verslagen van 's Lands Plantentuin*”. I would add one remark. Owing to my other affairs I was unable to devote as much time to these researches as I could have wished and they are therefore of a more or less preliminary nature. When I found, on the occasion of a meeting with Mr. HAZEWINKEL, Director of the Indigo Experimental Station