

Citation:

A.F. Holleman & Potter van Loon, J., The transformation of benzidine, in:
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131° and 38 % KNO_3 to 134°.5 and 45 % KNO_3 ,

Consequently, there exists no pure melting point but D is transformed on heating to 134°.5 into KNO_3 solid + solution of 45 %.

All mixtures of 0—50 KNO_3 solidify at 131° to $\text{Ag}_2 + \text{D}$, all mixtures of 50—100 KNO_3 at 134°.5 to conglomerates of $\text{D} + \text{K}_1$. The first named remain unchanged on further cooling. The last named ought to change at 126° into $\text{D} + \text{K}_2$ but this takes place with great difficulty.

The double salt is also not readily formed. If it does not make its appearance, the melting-point-line for K_1 runs through to 126°, and below this K_1 is converted into K_2 much more readily than in the solid conglomerates. The melting-line of K_2 runs through to 120° at 42 % KNO_3 where it meets the prolongation of the melting line of Ag_2 . If D does not appear, all liquid mixtures solidify at 120° to a conglomerate of $\text{Ag}_2 + \text{K}_2$.

The following zones comprised between the full lines represent stable conditions

1 $\text{Ag}_1 + \text{L}$	4 $\text{L} + \text{K}_1$
2 $\text{Ag}_2 + \text{L}$	5 $\text{L} + \text{D}$
3 $\text{Ag}_2 + \text{D}$	6 $\text{D} + \text{K}_1$
	7 $\text{D} + \text{K}_2$

All metastable boundaries are indicated by dotted lines. The regions concerned may be easily deduced from the figure.

From the above it follows that at the ordinary temperature, only the simple salts in the forms which are stable at that temperature and also the double salts 1 : 1 can occur as stable conditions; this agrees with what RETGERS has previously found for the products of crystallisation from aqueous solutions at 15°.

Chemistry. — “*The transformation of benzidine*”. By Prof. A. F. HOLLEMAN and J. POTTER VAN LOON.

(Communicated in the meeting of September 26, 1903).

In the report of the meeting of this section of Nov. 29, '02 there will be found a preliminary communication as to the experiments conducted in my laboratory by Dr. J. POTTER VAN LOON, who has since brought his research to a close. His results are briefly described below.

The method by which he succeeded in obtaining benzidine and hydrazobenzene in a perfectly pure condition has already been given in the preliminary communication. In connection with this it may be mentioned that hydrazobenzene was separated as a snow-white

substance, but after a few days exposure to the air it again turns faint yellow.

An improvement was also desirable in the quantitative determination of benzidine. At first VAN LOON collected the precipitated benzidine sulphate on a weighed filter, which was then dried at 100° in a steam oven and reweighed. Here we met with the unpleasant fact that the filter often turned blackish probably owing to a decomposition of the sulphate, which may unfavourably affect the determinations. The improved process now consisted in removing the washed sulphate from the filter and boiling it with excess of standard alkali. If now the excess of alkali is titrated at the boiling heat with standard acid, the benzidine sulphate behaves like free sulphuric acid when litmus is used as indicator. In this way the determination becomes more rapid and accurate. The usual correction for the solubility of benzidine sulphate had, of course, to be made.

The determinations made by Dr. VAN LOON of the ratio between the quantities of benzidine and diphenylene formed during the transformation of hydrazobenzene by acids have demonstrated the influence of various circumstances on that relation and may be best represented in a tabular and graphical form.

I. INFLUENCE OF THE CONCENTRATION OF THE ACID (HYDROCHLORIC ACID).

a) Solvent: Water.

Temp. 18°—25°.

Concentration of the acid.	Amount of acid in mgr. mol.	Mgr. mol. hydrazobenzol.	% benzidine.	Weight of diphenylene on 100 parts of benzidine.
25% = 7.8 n.	77.8	1 —	84.5	18.3
25% = 7.8 n.	77.8	2.011	80.0	25
3.90 n.	77.8	2 —	90.0	11.1
1/1 n.	50	2.—	90.5—89.5	10.5—12.4

b) Solvent: Alcohol of 50%¹⁾.

Temp. 25°.

Concentration of the acid.	Amount of acid in mgr. mol.	Mgr. mol. hydrazobenzol.	% benzidine.	Weight of diphenylene on 100 parts of benzidine.
3.1 n.	77.8	2.—	80.0	25
1/1 n.	50 —	2.—	84.8	17.9
0.6 n.	30 —	1.440	83.6	19.6
0.1 n.	5 —	2.—	83.0	20.5

¹⁾ Always percents of weight are meant.

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II. INFLUENCE OF THE SOLVENT. Temp. 18°—25°. HYDROCHLORIC ACID.

Nature of the solvent.	Concentr. of the acid	Amount of acid in mgr. mol	Mgr. mol hydrazo.	% benzidine.	Weight of diphenyline on 100 parts of benzidine.
Alcohol of 97%	0.12 n.	12	1.533	80.5	24.2
» » 50%	0.1 n.	10 and 5	1.6304 and 2	84.1 and 83.1	18.9—20.3
» » 50%	1/1 n.	50	2	84.8	17.9
» » 15%	0.1 n.	5	2	87.5	14.3
Water	1/1 n.	50	1.6304 and 2	90.5 and 89.0	10.5—12.4
Methyl alcohol	0.1 n.	5	2	74 %	35.1

Alcohol and methyl alcohol alter the relation of the transformation to the disadvantage of the benzidine and the effect becomes greater when the amount of water becomes less. This may be caused by the circumstance that in another medium the reaction may take a different course (for instance, the velocity of the formation of diphenyline may increase) but it is also possible that the deviation must simply be attributed to the increased solvent action which dilute alcohol exerts on hydrazobenzene or an intermediary product of the reaction. It is *not* due to an increased solubility of benzidine sulphate in dilute alcohol as has been proved by a purposely made direct experiment.

III. INFLUENCE OF THE KIND OF ACID.

a) Temp. 100°. Water.

Acid.	Concentration	Amount of acid in mgr. mol.	Mgr. mol. hydrazobenzene	% benzidine.
HCl	0.03 n.	4	1.6304	66.4—70.6
HNO ₃	0.05 n.	6.4	1.6304	67.3—71.7
H ₂ SO ₄	0.03 n.	4.4	1.6304	63.1
HBr	0.03 n.	4	1.6304	65.8

As at 100° a small quantity of azobenzene or aniline may be formed (the formation of the latter has not been investigated for the weak hydrochloric acid concentration) the figures for the formation of diphenyline would be valueless and they have, therefore, been omitted in table III. Those for benzidine are probably a little too low as the formation of azobenzene could not be entirely avoided.

b) Temp. 25°. 50 % Alcohol. Columns as under I and II.

HCl.	1/1 n.	50	2	84.8	17.9
HNO ₃ .	1/1 n.	50	2	82.2	21.7
H ₂ SO ₄ .	1/1 n.	50	2	89.8	11.4
CHCl ₂ .COOH.	1/1 n.	50	2	83.5	19.8

Except for sulphuric acid which yields a higher value, the relation of the transformation does not differ much in the case of the other acids.

IV. INFLUENCE OF THE TEMPERATURE.

a) Alcohol of 50%. Hydrochloric acid.

Temp.	Conc. of the acid.	Amount of acid in mgr. mol.	Mgr. mol. hydrazo.	% benzidine.	Weight of diphenyline on 100 parts of benzidine.
0°	0.1 n.	5	1	87.8	13.9
25°	1/1 n.	50	2	84.8	17.9
50°	1/1 n.	50	2	79.0	26.6
75°	1/1 n.	50	2	67.4	48.4
b) Water. Hydrochloric acid.					
18°	1/1 n.	50	1 6304	90 5	10 5
25°	1/1 n.	50	2	89 0	12 4
50°	1/1 n.	50	2	86 6	15.5
75°	1/1 n.	50	2	80.8	23 8
100°	1/1 n.	50	2	74.9	33 51
100°	0 03 n.	4	1 6304	66.4-70 6	50 6-41.6

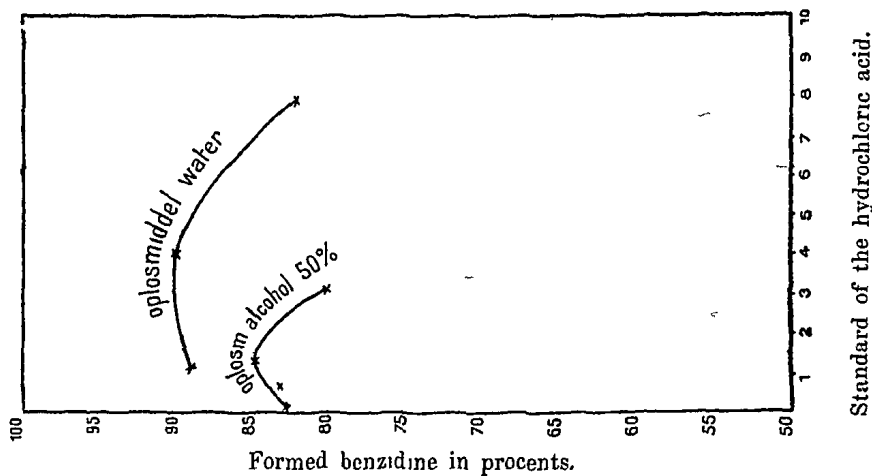
The figures given in the tables are in most cases the average of several fairly concordant determinations.

The influence of the temperature as shown by this table is again the same for both solvents and is shown by a fall in the ratio of the transformation with a rise in the temperature.

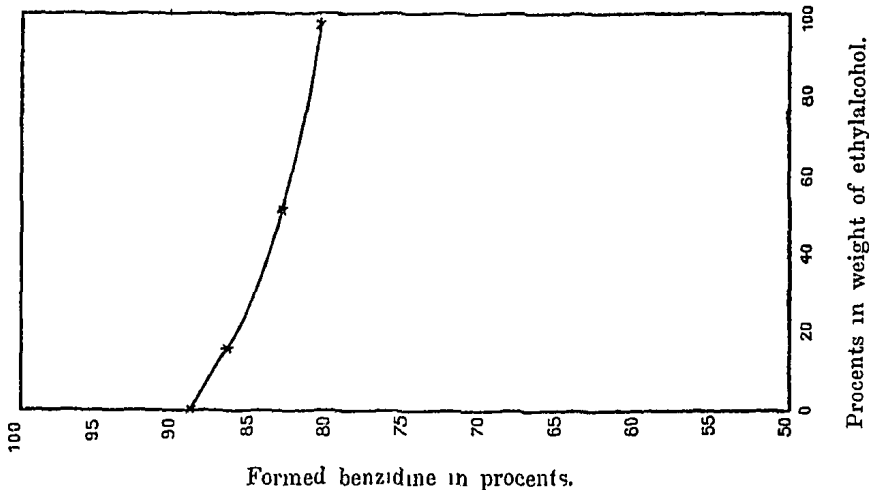
The following observation should be made as to the last column contained in these tables; the substance which was not precipitated as benzidine sulphate is supposed to have been converted into diphenyline. This, however, has only been once isolated as such, so that it is not impossible that other bases besides diphenyline may have been formed, the sulphates of which are soluble in water. As other investigators have already taken up this subject, Dr. VAN LOON has not extended his research in that direction.

The graphic representations, following here, are those of the above mentioned tables.

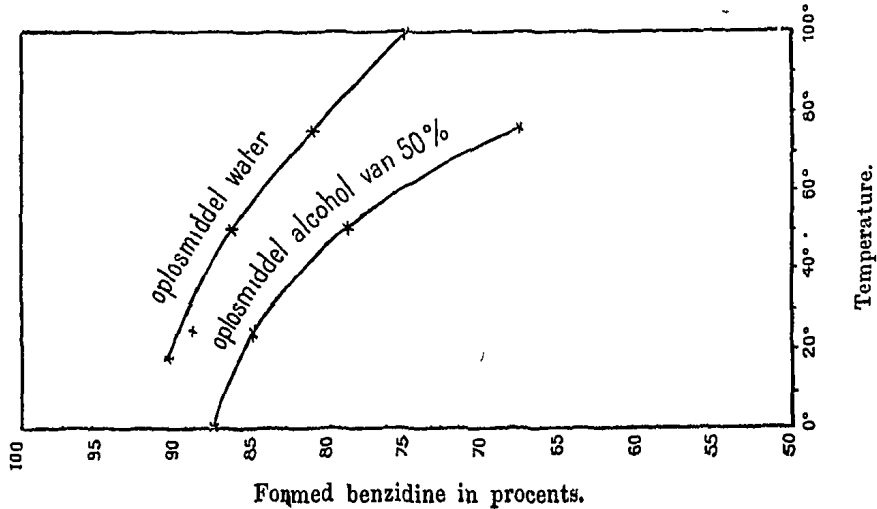
Fig. I. Influence of the concentration of the acid on the ratio of transformation.
Temp. 25°.



Figuur II. Influence of the amount of alcohol on the ratio of transformation.
0.1 n. hydrochloric acid, $t = 25^\circ$.



Figuur III. Influence of the temperature on the ratio of transformation.
1.- n. hydrochloric acid



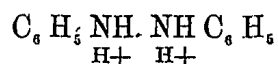
Dr. VAN LOON has also been engaged in determining the velocity of the transformation. An excess of finely powdered hydrazobenzene was introduced into dilute alcohol, to which had been added acid of a definite concentration, the mixture being vigorously stirred. At stated times certain quantities of liquid were withdrawn from the mixture and the amount of benzidine was quantitatively determined.

If C_b is called the concentration of the benzidine formed, C_{HCl} that of the hydrochloric acid at any moment, the equation

$$\frac{d C_b}{dt} = K C_{HCl}^2$$

was found to represent the transformation; in this t is the time (in minutes) and K the reaction constant. No special figure is given for the concentration of the hydrazobenzene as this may be taken as constant in the modus operandi followed.

The transformation is due to the hydrogen ions of the acid, for on comparing the action of hydrochloric acid and dichloroacetic acid the reaction constant was shown to be proportional to the degree of ionisation of the acids employed. This caused Dr. VAN LOON to suggest that during the transformation two H-ions are first linked to hydrazobenzene forming



and that then the repulsion of the two positive charges causes the molecule to break up between the two nitrogen atoms, whereupon the two portions again unite in such a manner that the positive charges are at a greater distance from each other. This representation accounts for the presence of C_{HCl}^2 in the equation of velocity, as according to this equation one mol. of hydrazobenzene reacts with two H-ions.

Chem. Lab. Univ. Groningen, July 1903.

Chemistry. — “*The transformation of diphenylnitrosamine into p-nitroso-diphenylamine and its velocity.*” By H. RAKEN. (Communicated by Prof. C. A. LOBRY DE BRUYN as communication N^o. 6 on intramolecular rearrangements).

(Communicated in the meeting of September 26, 1903).

In 1886 OTTO FISCHER discovered the interesting fact that under the influence of alcoholic hydrochloric acid the nitrogen-combined nitrosogroup of methylphenylnitrosamine changes place with the para-hydrogen atom of the benzene nucleus and is thus converted into the isomeric nitrosobase.