UPON THE ACTION OF TETRAZODI-*o*-TOLYLMETHANE CHLORIDE UPON NAPHTHOL AND NAPHTHYLAMINE SULFO ACIDS

[FIRST PAPER]

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Prior to 1885, cotton fiber had to be put through a preparatory treatment before it could be dyed with artificial coloring matters. In 1884, P. Böttiger¹ discovered and patented a new dyestuff, which a year later was introduced into commerce by the "Actien-gesellschaft für Anilinfabrikation" under the name of Congo. This new product was the first of a series which had the property of dyeing the cotton fiber direct, without prior mordanting.

Congo is produced by the action of 1 molecule of tetrazobenzidine chloride (tetrazodiphenyl chloride) upon 2 molecules of sodium naphthionate.¹

G. Schultz² has shown that benzidine is a dipara-aminodiphenyl, NH_2 - - - NH_2 , hence the constitution of Congo is:

When *o*-nitrotoluene is subjected to alkaline reduction it forms hydrazotoluene, which, on treatment with acids, is transformed into di-*p*-aminoditolyl, or toluidine having the constitution:³

This product like benzidine is capable of forming a tetrazo compound on treatment with nitrous acid, which in turn may be coupled with two molecules of sodium naphthionate to form the red substantive dye known as Benzopurpurin 4B. The property of Congo of fixing itself directly to the cotton fiber is evidently due to the presence of the diphenyl residue in its molecule, since other coloring matters derived from benzidine and its homologues possess the same characteristics.

The homologous bases of the aniline series may be divided into two classes, according to their behavior with formaldehyde:⁴

1—Those in which an unsubstituted carbon atom (*i. e.*, hydrogen-bearing carbon atom) stands in the para position to the amino group. Among the technically most important bases of this class are aniline,

2—Those which contain a substituted carbon atom in the para position to the amino group.

The technically most important bases of this class are *p*-toluidine, CH_3 - - NH_2 , and asymmetrical

The bases of this second class unite with formaldehyde with much greater difficulty, under the same conditions, than those of Class 1. Furthermore, bases of Class 2 in admixture with bases of Class 1 will not unite at all with formaldehyde as long as bases of Class 1 are present. This peculiarity permits a complete quantitative separation of such bases.

Availing myself of this reaction, 200 g. technical *o*-toluidine (about 2 moles) were dissolved in the calculated amount of HCl of sp. gr. 1.19 or 71.9 cc., diluted with 400 cc. H_2O , and 75 g. of 40 per cent formaldehyde added. The mixture was now heated on the water bath to 70–76° C. for 4 hrs. and then made alkaline with NaOH solution. A copious, whitish, crystalline precipitate is thus thrown down and the latter steam-distilled until no more toluidine passed over. The crystalline mass thus obtained was collected upon a filter, dried and then recrystallized from alcohol, from which, on rapid cooling, it is obtained in the shape of small octahedra, among which are many twin crystals. On slow cooling, it crystallizes in rhombic prisms, also showing much twinning. Melting point, 149° C.

The product is, therefore, diparaaminodi-*o*-tolylmethane,

obtained by the condensation of 2 molecules of *o*-toluidine with 1 molecule of formaldehyde.

As this product partakes somewhat of the structure of benzidine and toluidine, but differing from the latter compounds in having the two benzene rings coupled to a methane rest, it was of interest to ascertain whether diaminodi-*o*-tolylmethane, like benzidine and toluidine, may be tetrazotized and coupled with phenols, amines and their sulfo acids to form substantive dyes, or whether its difference in structure would materially affect the nature of the dyestuffs derived therefrom. To answer these questions, the following experiments were made.

¹ D. R. P. No. 28,753, Feb. 27, 1884.

² Ann., 174 (1874), 227.

³ Ber., 17 (1884), 467.

⁴ D. R. P. No. 87,615, Sept. 1895; Friedländer, 4, 65.

EXPERIMENTAL

TETRAZODI-*o*-TOLYLMETHANE CHLORIDE—A few qualitative tests showed that nitrous acid combines with diaminodi-*o*-tolylmethane in HCl solution to form a diazo compound, but the question which naturally arose was whether only one, or both of the amino groups in the above-named product were diazotized. This question was easily settled by titrating a known quantity of the diamino base with sodium nitrite solution, using iodide of starch paper as an indicator.

Base taken.....	1.00 g.
Dissolved in 3 cc. HCl (sp. gr. 1.2) diluted with 200 cc. H ₂ O. Cooled with ice and titrated with NaNO ₂ solution.	
1 cc. NaNO ₂ soln. =	0.0047 HNO ₂
Required for titration.....	85.4 cc. NaNO ₂ soln.
HNO ₂ used.....	0.4003 g.
Calculated.....	0.4159 g.

It will be seen that the above figures agree very closely with the theory for di-para-aminodi-*o*-tolylmethane and consequently the product formed on treating the above compound in hydrochloric acid solution with nitrous acid must be a tetrazo-di-*o*-tolylmethane chloride,

DI-*o*-TOLYLMETHANE - 4 - HYDROXYAZO-1-NAPHTHOL-4-SULFO ACID—According to the usual manner of coupling tetrazo compounds with amines, phenols and their sulfo acids,¹ it was expected that 1 molecule of tetrazo-di-*o*-tolylmethane chloride and 2 molecules of 1,4-naphtholsulfo acid would interact to form

However, subsequent examination of the product obtained showed this not to be the case.

0.01 mole diaminodi-*o*-tolylmethane, or 2.26 g., were dissolved in 0.04 mole HCl, or 3.11 cc. HCl of sp. gr. 1.2, diluted with 200 cc. water. This solution was now cooled with ice and tetrazotized by slowly stirring in 0.02 mole NaNO₂, or 1.38 g. dissolved in 50 cc. H₂O. The above solution was now allowed to stand until the complete absorption of the HNO₂ had taken place as shown by iodide of starch paper, and then slowly stirred into a solution of 0.01 mole of 1,4-naphtholsulfo acid, or 2.24 g., made alkaline with 0.02 mole Na₂CO₃, or 2.12 g. My motive in using only one-half the theoretical quantity of 1,4-naphtholsulfo acid was to note whether as in the case of tetrazodi-phenylchloride² an intermediary compound of the following formula would be formed:

¹ Böttiger, D. R. P. No. 28,753; Witt, *Ber.*, 19, 1719; G. Schultz, 2d Edition, p. 302; *Ibid.*, 257.

² Bucherer, p. 362.

On mixing the tetrazo solution with the 1,4-naphtholsulfo acid solution a copious blood-red precipitate is formed. The latter was allowed to stand over night and the next morning was collected upon a filter and washed. The filtrate, on being tested with an alkaline solution of β -naphthol, was found to be free from tetrazo compound. The red precipitate formed is insoluble in water and when boiled with the latter gives off nitrogen, which would suggest the presence of an intermediary compound of the foregoing composition. It was then rinsed into a beaker and treated with an additional 0.01 mole 1,4-naphtholsulfo acid, or 2.24 g., and made alkaline with 0.01 mole of Na₂CO₃, or 1.06 g., and the mixture allowed to stand, with occasional stirring, for 24 hrs.

No apparent change having taken place, the red precipitate was collected upon a filter, thoroughly washed and dried.

The product thus obtained is but little soluble in hot or cold water, but is soluble in dilute caustic soda solution. The filtrate from the above red precipitate on being tested with diazosulfanilic acid showed the presence of considerable uncombined 1,4-naphtholmonosulfo acid, showing that the second molecule of sulfo acid had not combined with the red product.

Thinking that possibly better results might be obtained by treating the tetrazo compound at once with the two moles of 1,4-naphtholsulfo acid, the experiment was twice more repeated, using 4.48 g. sulfo acid instead of 2.24. The final result, however, was the same.

Believing prolonged digestion of the red product (which was considered to be an intermediary product) with an extra molecule of naphtholsulfo acid might bring about a union of the two, a mixture of the two was digested at 37.5° for 24 hrs. A more soluble product was obtained, but the additional molecule of sulfo acid remained uncombined. Therefore, we must infer that an intermediate compound of the formula

has been formed, which on standing or upon heating loses nitrogen and is gradually transformed into a product of the following composition:

This reasoning has been fully borne out in the course of our experiments. In further evidence of the foregoing, a nitrogen estimation of the free dyestuff acid, prepared as follows, was made:

The acid soda salt of di-*o*-tolylmethane-4-hydroxy-azo-1-naphthol-4-sulfo acid, obtained by boiling the insoluble red precipitate with the calculated amount of sodium hydroxide, was filtered and the filtrate treated with an excess of concentrated HCl. The red precipitate of the free acid thrown down was collected upon a filter, washed with cold water till free from HCl and NaCl, air-dried upon a porous plate and then finally dried at 130–135° C.

All attempts to obtain the free acid in a crystalline form failed and, therefore, the product obtained as just described had to be used for analysis.

The nitrogen was estimated by the Kjeldahl method and gave the following result:

Free acid taken.....	0.1018 gram
N found.....	5.92 per cent
Theory for $\text{C}_6\text{H}_5(\text{CH}_3)\text{N}=\text{N}-\text{C}_{10}\text{H}_7 \begin{array}{l} \text{OH}(1) \\ \text{SO}_3\text{H}(4) \end{array}$	6.04 per cent
$\begin{array}{c} \\ \text{CH}_2 \\ \\ \text{C}_6\text{H}_5(\text{CH}_3)\text{OH} \end{array}$	

Barium in the barium salt was estimated as follows:

The salt was prepared by dissolving the acid soda salt in boiling water and treating with an excess of barium chloride. This threw down the barium salt as a red precipitate. The latter was collected upon a filter, washed with boiling water till free from BaCl₂, air-dried, and then finally dried at 100° C. The product thus obtained is by no means pure, but is the best that could be obtained under the circumstances.

Barium salt taken.....	0.1592 gram
BaSO ₄ weighed.....	0.0366 gram
Equivalent to barium.....	13.19 per cent
Theory for $\left[\text{C}_6\text{H}_5(\text{CH}_3)\text{N}=\text{N}-\text{C}_{10}\text{H}_7 \begin{array}{l} \text{OH}(1) \\ \text{SO}_3(4) \end{array} \right]_2$	13.013 per cent
$\begin{array}{c} \\ \text{CH}_2 \\ \\ \text{C}_6\text{H}_5(\text{CH}_3)\text{OH} \end{array}$	

Hence the free acid must be constituted as previously stated and consequently the acid soda salt must have the following constitution:

It is further shown that in following the technique previously described, one molecule of tetrazodi-*o*-

tolylmethane chloride unites with only one molecule of 1,4-naphtholsulfo acid to form the intermediate product,

which latter compound is gradually transformed by substitution of OH for N into

Up to very recently it was found to be impossible to combine 1 molecule of tetrazodi-*o*-tolylmethane chloride with more than 1 molecule of 1,4-naphtholsulfo acid, but lately upon taking the subject up again and slightly modifying the technique, I have been able to combine 1 molecule of the tetrazo compound with two molecules of 1,4-naphtholsulfo acid with the greatest ease. Briefly described, the new technique is as follows:

2.26 g. diaminodi-*o*-tolylmethane are dissolved in 4.5 cc. HCl of 1.19 sp. gr. diluted with 100 cc. H₂O. The solution is then cooled with ice and tetrazotized by gradually stirring in 1.38 g. NaNQ₂ dissolved in 25 cc. H₂O.

The tetrazo solution is then gradually stirred into a solution of 4.48 g. 1,4-naphtholsulfo acid (0.02 mole) dissolved in 50 cc. water and 50 cc. alcohol (denatured will do). A heavy carmine precipitate with bluish tinge is at once formed. This is allowed to stand over night and the next morning is filtered under suction and dried. The product thus obtained is the acid soda salt of¹

It appears as a dark red powder, is easily soluble in water, and dyes wool, in a bath containing sulfuric acid and sodium sulfate, a fine, scarlet color, which is fairly fast to light (4 weeks' exposure) and to washing and fulling. Contrary to expectations, however, it has but little affinity for cotton. Why the mere addition of a little alcohol to the reaction mixture should bring about a union of 1 molecule of tetrazo compound with 2 molecules of sulfo acid is hard to explain.

DI-*o*-TOLYLMETHANE-AZO-2-NAPHTHOL-3,6-DISULFO ACID, AZO-2-NAPHTHOL-3,6-DISULFO ACID—On mixing an

¹ That the 2 molecules of 1,4-naphtholsulfo acid had combined with the 1 molecule of tetrazo compound was easily proved by treating a drop of the reaction mixture upon filter paper with a drop of diazosulfanilic acid. As no coloration was observed, it is evident that all the sulfo acid had combined with the tetrazo solution.

aqueous solution of 1 mole tetrazodi-*o*-tolylmethane chloride with an aqueous Na_2CO_3 solution of 2 moles 2,3,6-naphtholdisulfo acid, an intense scarlet-red precipitate is obtained, and on testing the outer watery edge of a drop of this solution upon filter paper with a drop of diazosulfanilic acid, no red coloration is obtained. From this it is evident that the 2 moles of 2,3,6-naphtholdisulfo acid have combined with the 1 mole of tetrazo compound.

On heating the solution to boiling, all the red precipitate dissolves, and separates again, on cooling, in a semi-crystalline form. It was collected upon a filter at the pump and finally dried upon a porous plate. When dry, the acid soda salt of the new product appears in the shape of a dark red powder with beetle-green luster. It is easily soluble in hot or cold water with a scarlet color and has the following constitution:

It likewise is a strong wool dye and dyes the latter, in a bath acidulated with sulfuric acid, a bright scarlet shade, somewhat resembling that obtained with the previous product.

It will, therefore, be seen that we here have a certain deviation from the results obtained with 1,4-naphtholmonosulfo acid, for, whereas only 1 molecule of the latter will unite with 1 molecule of tetrazodi-*o*-tolylmethane chloride when operating under normal conditions, *i. e.*, in aqueous solution, in the present case the tetrazo compound unites easily in an all-aqueous solution with 2 molecules of the disulfo acid.

Why these two naphtholsulfo acids should act so differently I am hardly prepared to say, but if I may venture an opinion, I would attribute it to the different positions of the sulfo groups in the naphthalene rings.

In coupling diazo salts with phenols or amines of the naphthalene series, if a hydroxyl group or amino group is in the alpha-position, combination takes place in the 4-position. If this is occupied, or if the positions 3 or 5 are occupied by sulfonic groups, union takes place in the 2-position.

Now in the case of the product from 1 molecule of tetrazo compound and 1 molecule of 1,4-naphtholsulfo acid the 4-position of the naphtholsulfo acid is occupied by a sulfo group, thereby forcing the tetrazo compound to couple in the 2-position and it has been shown that it took quite a little coaxing to cause the tetrazo compound to unite with an extra molecule of 1,4-naphtholsulfo acid under these conditions. On the other hand, in the case of the last-named dye from 1 molecule of tetrazodi-*o*-tolylmethane chloride and 2 molecules of 2,3,6-naphtholdisulfo acid, the 4-position, of the disulfo acid being unoccupied, the tetrazo compound was enabled to couple directly in the 4-position, and as we may infer that the 4-position is the one of least resistance, this may possibly account for the greater ease of union between the 1 molecule of tetrazodi-*o*-

tolylmethane chloride and 2 molecules of 2,3,6-naphtholdisulfo acid.

If, as is supposed, the presence of the diphenyl residue in the molecule is necessary for the production of substantive cotton dyes, then it is possible that the presence of the methane rest uniting the two benzene rings in tetrazodi-*o*-tolylmethane may be the reason why the dyes obtained from this product are wool dyes and have practically no affinity for cotton.

This is only a surmise on my part which at present I am unable to back up by further proof.

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METHOD OF CALCULATING COMPARATIVE STRENGTH AND EFFICIENCY OF HIGH EXPLOSIVES FROM THEIR COMPOSITION AND APPARENT DENSITIES

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INTRODUCTION

A number of laboratory tests have been devised for obtaining comparative or definite values as to "strength" of explosives, of which may be mentioned the Trauzl test, ballistic pendulum, mortar tests, pressure gauges, etc., in each of which it is the practice to note the effect of a certain *unit weight* of an explosive and compare some with results of an equal of another explosive.

These results, however, do not always conform with those obtained in the field, for the reason that "strength" of explosives is there often judged by the effect of a certain *bulk* of explosive, *i. e.*, the volume of the charge chamber, in which explosives are compared in the field, is practically a constant, whether it is a bore hole or a war head. The importance of loading density of explosives for military purpose has been considered by the U. S. Ordnance Department, which even includes the same in their specifications.

It would therefore seem more rational to compare explosives in the laboratory by *volume*; for instance, instead of using the customary charge of 10 g. in the Trauzl test, a charge equivalent to the weight of 10 cc. at its apparent (or loading) density should be used.

All ballistic tests in the laboratory require careful and elaborate execution, and the method of calculating "strength" and efficiency as outlined in this paper is suggested as a means of obtaining values which have been proved to conform with carefully made laboratory tests.

The word efficiency, as applied to explosives, is generally used to express the amount of useful work that is done with a certain weight or "bulk" of an explosive; in coal-mining, for instance, it means the amount of lump coal that is obtained from a certain amount of explosive, while in tunnel work it means the progress that can be made, etc. In this article, however, the word efficiency denotes *the maximum available energy stored up in a unit "bulk" of an explosive*, and which, according to definition below, is proportional to the volume which the gaseous products of explosion of a unit "bulk"—say 1 cc.—would occupy at t° and atmospheric pressure.